Two-site model analysis of ^{13}C n.m.r. of polypropylene polymerized by Ziegler–Natta catalyst with external alkoxysilane donors

Riichirô Chûjô* and Yoshiaki Kogure
Department of Materials Engineering, The Nishi-Tokyo University, Uenohara-cho, Kitatsuru-gun, Yamanashi 409-01, Japan

and Taito Väänänen
Neste Oy, Technology Centre, PO Box 310, Porvoo SF-06101, Finland

(Received 26 February 1993; revised 30 April 1993)

Two-site model analysis was carried out for ^{13}C n.m.r. of polypropylene polymerized by Ziegler–Natta catalyst with external alkoxysilane donors. Four effects of the external donors were found: selective poisoning of symmetric site; transformation of a symmetric to an asymmetric (but fluctuating) site; increase of whole isotacticity due to that of polymers obtained by the fluctuating site; and increase of isotacticity of the polymers obtained by the fluctuating site when the concentration of external donor is high enough.

(Keywords: two-site model; polypropylene; external donor)

INTRODUCTION

In polypropylene manufacturing one of the most important strategies is the increase of isotacticity, i.e. the increase of *meso* (*m*) diad fraction according to the terminology of n.m.r. This enables improvement of physical properties such as stiffness and modulus of elasticity via an increase in the degree of crystallinity. This strategy has been performed by the use of Ziegler–Natta catalysts. Isotacticity is much enhanced by the addition of alkoxysilane as external donor (e.g. refs 1–6).

N.m.r. of polypropylene has been widely accepted as the most powerful method for the analysis of microstructure and the polymerization mechanism since Chûjô and co-workers applied high resolution ^{1}H n.m.r. to polypropylene[7]. Even today, the number of parameters for the description of the propagation reaction mechanism is limited to three, based on the n.m.r. peak intensities with sufficient accuracy. Amont three-parameter models, the two-site model is the most reasonable. A preliminary analysis was done in 1973[8]. The adjective 'preliminary' indicates that the analysis was carried out under the assumption of a mixture of completely isotactic and symmetric Bernoullian parts (according to ref. 9 this is equivalent to the case $\alpha = 1$). This was due to insufficient resolution of ^{13}C n.m.r. at that time. The first complete analysis based on a two-site model was done in 1983[10], making use of the results of stochastic theory[9].

Väänänen and co-workers[11] have already observed ^{13}C n.m.r. spectra of polypropylene obtained with the system $MgCl_2/TiCl_4/DIBP\text{-}AlEt_3$/external donor (DIBP = diisobutyl phthalate). Compounds used as external donors in this work are tabulated in *Table 1* with codes and suppliers.

If our interest is limited to the evaluation of catalyst activity, two-site model analysis is less important, because progress in catalyst development has brought about the situation that the majority of the polymer is produced by the asymmetric site (according to the notation in ref. 9, ω is approaching to unity). This means that the two-site model reduces to a one-parameter (α) model. On the other hand, if our interest is extended to the effect of the external donors, the two-site model is exclusively powerful; only this model enables us to consider separately the contribution from asymmetric and symmetric sites.

In this paper we will analyse the ^{13}C n.m.r. peak intensities of methyl regions referred to in ref. 11 with the aid of the procedure described in ref. 9. From the results of analysis we will quantitatively discuss the effect of alkoxysilane in the polymerization of propene.

PROCEDURE

Analyses were done for the relative intensities of pentad peaks in the ^{13}C n.m.r. methyl region referred to in ref. 11.

The analytical procedure of the two-site model has been established in ref. 9; if three stochastic parameters, α, σ and ω, are introduced, the probabilities of the appearance of 10 pentads are given in *Table 2*. The parameter α is the probability of the selection of *d* monad in the asymmetric Bernoullian site, while σ is that of *m* diad in the symmetric Bernoullian site. The remaining parameter ω is the mole fraction of the monomer units

---

* To whom correspondence should be addressed

0032-3861/94/020339-04

Table 1 Compounds used as external donors with codes and suppliers[11]

Alkoxysilane	Code	Supplier
Diethoxydimethylsilane	1a	Petrarch
Diethoxymethylphenylsilane	1b	Petrarch
Diisopropenyloxydimethylsilane	7	Petrarch
Dimethoxydiphenylsilane	2	Petrarch
Dodecyldiethoxymethylsilane	1c	Petrarch
Dodecyltriethoxysilane	4a	Petrarch
Ethoxytrimethylsilane	5	Alfa
Isobutyltrimethoxysilane	3a	Hüls
Triethoxymethylsilane	4c	Alfa
Triethoxyphenylsilane	4b	Alfa
Trimethoxymethylsilane	3b	Fluka
Trimethoxyphenylsilane	3c	Petrarch
Trimethoxypropylsilane	3d	Fluka
Tripropoxymethylsilane	6	Petrarch

Table 2 Probabilities of the appearance of pentads[9] (α, probability of the selection of *d* monad in the asymmetric Bernoullian site; σ, probability of the selection of *m* diad in the symmetric Bernoullian site; ω, mole fraction of the monomer units produced by the α process; $\beta=\alpha(1-\alpha)$)

$mmmm=\omega(1-5\beta+5\beta^2)+(1-\omega)\sigma^4$
$mmmr=\omega(2\beta-6\beta^2)+2(1-\omega)\sigma^3(1-\sigma)$
$rmmr=\omega\beta^2+(1-\omega)\sigma^2(1-\sigma)^2$
$mmrr=\omega(2\beta-6\beta^2)+2(1-\omega)\sigma^2(1-\sigma)^2$
$mmrm=2\omega\beta^2+2(1-\omega)\sigma^3(1-\sigma)$
$rmrr=2\omega\beta^2+2(1-\omega)\sigma(1-\sigma)^3$
$rmrm=2\omega\beta^2+2(1-\omega)\sigma^2(1-\sigma)^2$
$rrrr=\omega\beta^2+2(1-\omega)(1-\sigma)^4$
$mrrr=2\omega\beta^2+2(1-\omega)\sigma(1-\sigma)^3$
$mrrm=\omega(\beta-3\beta^2)+(1-\omega)\sigma^2(1-\sigma)^2$

produced by the former process (α process). In *Table 2* a parameter β is used instead of α ($\beta=\alpha(1-\alpha)$). Three parameters, α, σ and ω, will be determined to minimize the standard deviation of the calculated values of pentads from corresponding experimental values.

RESULTS AND DISCUSSION

The most important matter is the increase of isotacticity via the increase of ω, because the following three effects of external donors were suggested[12]: (1) selective poisoning of symmetric site; (2) transformation of symmetric to asymmetric site; (3) increase in the propagation rate constant of asymmetric site. These three effects are also described in refs 13–20. (Strictly speaking, four effects are described in ref. 12; the fourth one will be considered later in *Figure 2*.) As seen in *Figure 1*, the addition of any alkoxysilane actually enhances the value of ω in unfractionated samples except for diethoxydimethylsilane. The enhancement of ω is consistent with the above three effects; any one of the three factors brings about the enhancement of isotacticity via the increase of ω. The above three effects do not ensure the increase of α, but nevertheless, α values are always enhanced by the addition of alkoxysilane. Whether this is real evidence or only apparent, owing to the insufficient number of parameters, will be discussed later in the analysis of heptane-insoluble fractions. The behaviour of σ will be discussed later in *Figure 2*. However, the addition enhances the isotacticity via the increase of ω in most cases.

Enhancement of the value of ω is greatest in isobutyltrimethoxysilane. In order to study more quantitatively the effect of this donor, the values of the three parameters are plotted against the molar ratio, donor/AlEt$_3$ (*Figure 2*). An increase in the value of ω is observed with an increase of the ratio. This finding implies the quantitative validity of the above three effects. Compared with the monotonic increase of ω as well as α, the behaviour of σ is complicated: an increase in the value follows a decrease. Soga *et al.*[21] reported direct evidence that ethyl benzoate does not only deactivate the symmetric site but also induces the transformation from symmetric to asymmetric site. If isobutyltrimethoxysilane induces a similar situation, and the newly converted site is not so rigid as the original asymmetric site, the polymers obtained by this converted fluctuating site may become mixtures of α- and σ-type polymers. The order of fractions of pentads in α-type polymers, if α is close to unity, is:

mmmm ≫ *mmmr*, *mmrr* > *mrrm* ≫ *mmrm*, *rmrr*, *rmrm*,
mrrr > *rmmr*, *rrrr*

while in σ-type polymers, if σ is smaller than 1/2, it is:

rrrr ≫ *rmrr*, *mrrr* ≫ *mmrr*, *rmrm* > *rmmr*, *mrrm* ≫ *mmmr*,
mmrm ≫ *mmmm*

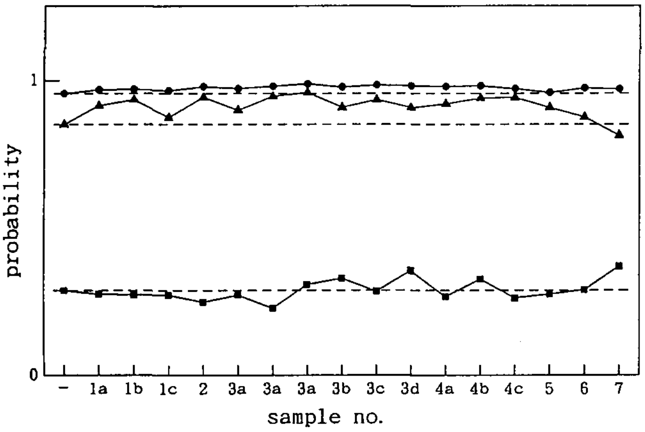

Figure 1 Calculated values of three parameters for unfractionated samples: ▲, ω; ●, α; ■, σ. Broken lines indicate the values for the sample prepared without alkoxysilane

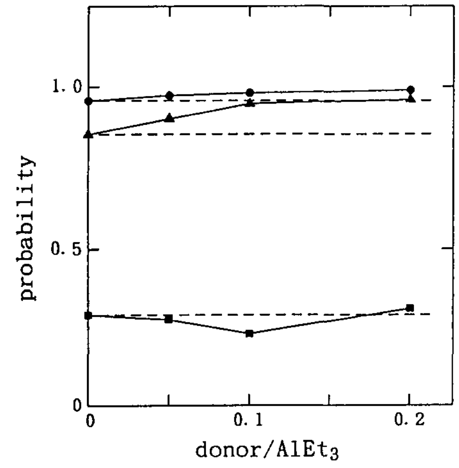

Figure 2 Dependence of three parameters on the ratio, isobutyltrimethoxysilane/AlEt$_3$, for unfractionated samples: ▲, ω; ●, α; ■, σ. Broken lines indicate the values for the sample prepared without alkoxysilane

These orders imply that some pentads (e.g. *rmrr* and *mrrr*) are produced by the fluctuation between asymmetric and symmetric sites in catalysis, and this fluctuation leads to the apparent increase of σ-type polymers. This is due to the greater influence on the analysis by the minor component. The behaviour of σ (an increase following a decrease) may be due to the fluctuating character of the newly converted site. This finding is somewhat inconsistent with the fourth effect in ref. 12, i.e. deactivation of the asymmetric site when the concentration of external donor is high enough. Instead of this, we can describe the effect as an increase of isotacticity of the polymers obtained by the fluctuating site when the concentration of external donor is high enough. This effect will be checked further for fractionated samples.

For heptane-insoluble fractions the analysis was carried out in a similar way as for the unfractionated samples. The results are shown in *Figure 3*. Compared with the corresponding values for unfractionated samples, the values of ω and α increase. Compared with the corresponding values of ω and α for the sample without external donor, the increases of ω and α are not so significant. From the latter finding, we can say that the effect of the external donors is not so significant for ω and α in heptane-insoluble fractions. On the other hand, the values of σ increase considerably compared with σ values both in corresponding unfractionated samples and in heptane-insoluble fraction without external donor. If the two-site model is sufficient for the description of the propagation state, the values of ω should be different before and after fractionation, while those of α and σ should be kept constant. The difference of α and σ values shows the insufficiency of the two-site model for the description. Nevertheless, this model is the best among three-parameter models. On the other hand, from the change of the parameter values we can find some evidence both in asymmetric and symmetric sites. The small change in the values of α implies that the model is almost sufficient for the description of the asymmetric site, while the considerable change in values of σ suggests that there are two kinds of symmetric sites: one is truly symmetric and the other is actually asymmetric but apparently symmetric due to the fluctuation in transformed site. We, therefore, conclude that the increase of whole isotacticity is due to that of polymers obtained by the fluctuating site.

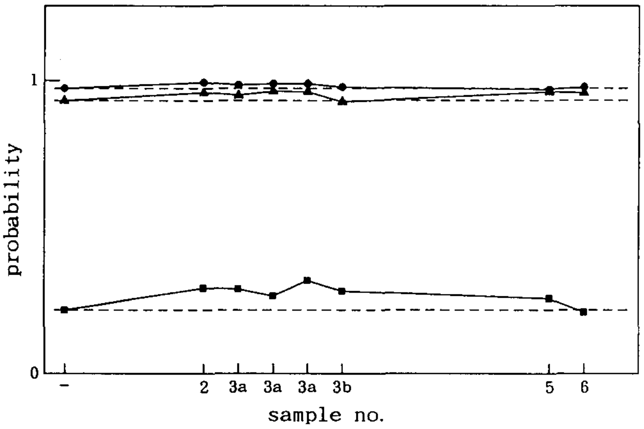

Figure 3 Calculated values of three parameters for (selected) heptane-insoluble fractions: ▲, ω; ●, α; ■, σ. Broken lines indicate the values for the sample prepared without alkoxysilane

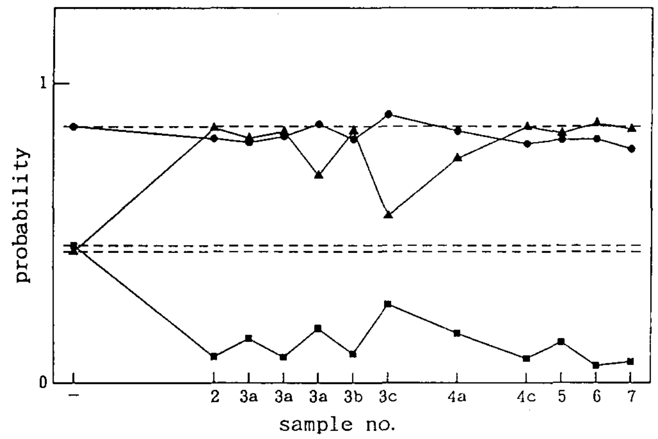

Figure 4 Calculated values of three parameters for (selected) heptane-soluble fractions: ▲, ω; ●, α; ■, σ. Broken lines indicate the values for the sample prepared without alkoxysilane

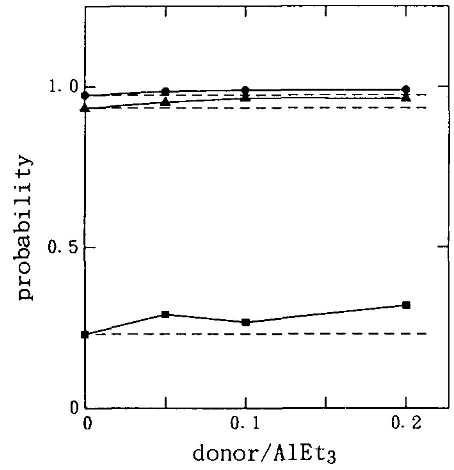

Figure 5 Dependence of three parameters on the ratio, isobutyltrimethoxysilane/$AlEt_3$ for heptane-insoluble fractions: ▲, ω; ●, α; ■, σ. Broken lines indicate the values for the sample prepared without alkoxysilane

Figure 4 shows the results for heptane-soluble fractions. Compared with the corresponding values for unfractionated samples, a decrease in the values of ω and an increase in values of σ are observed. Compared with the values of ω and σ for the sample without external donor, a significant increase of the former and a significant decrease of the latter are observed. For α-type polymers, fractionation is performed by the difference of molecular weight as well difference in tacticity[22]. The heptane-soluble fractions are therefore still mixtures of σ-type polymers with any molecular weight and α-type polymers with low molecular weight. The significant changes may arise from this fact. The resolution of the n.m.r. instrument is still insufficient for further analysis. Among the external donors, the effect of trimethoxyphenylsilane is exceptional; there is some possibility of the formation of stereoblock polymers[23] by the fluctuating site.

Figures 5 and *6* are plots for heptane-insoluble and heptane-soluble fractions, respectively, similar to *Figure 2*. All findings from these figures are the same as those from *Figures 3* and *4*.

In summary, we conclude that the four effects of external donors are as follows:

1. selective poisoning of symmetric site;

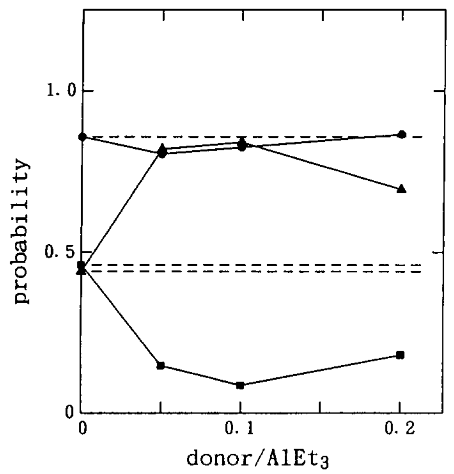

Figure 6 Dependence of three parameters on the ratio, isobutyltrimethoxysilane/AlEt$_3$ for heptane-soluble fractions: ▲, *ω*; ●, *α*; ■, *σ*. Broken lines indicate the values for the sample prepared without alkoxysilane

2. transformation of symmetric site to asymmetric (but fluctuating) site;
3. increase of whole isotacticity due to that of polymers obtained by the fluctuating site;
4. increase of isotacticity of the polymers obtained by the fluctuating site when the concentration of external donor is high enough.

ACKNOWLEDGEMENT

R. C. expresses sincere thanks to Professor Kazuo Soga (Tokyo Institute of Technology) for valuable discussions.

REFERENCES

1 Barbé, P. C., Albizzati, E., Giannini, U., Baruzzi, G. and Noristi, L. European Patent Application 267576 (Himont Inc.); *Chem. Abstr.* 1988, **109**, 150246t
2 Hoppin, C. R. and Tovrog, B. S. European Patent Application 250229 (Amoco Corp.); *Chem. Abstr.* 1988, **109**, 7118x
3 Job, R. C. US Patent 4710482 (Shell Oil Co.); *Chem. Abstr.* 1987, **108**, 113153u
4 Kioka, M., Toyoda, A. and Kashiwa, N. Japan Patent Kokai 88/37104 (Mitsui Petrochemical Industries Ltd); *Chem. Abstr.* 1988, **109**, 74105d
5 Terano, M., Soga, H. and Inoue, M. Japan Patent Kokai 88/182306 (Toho Titanium Co.); 1988, **109**, 23173z
6 Werner, R. A., Zolk, R. and Schweier, G. Ger. Offen. 3644368 (BASF A-G); *Chem. Abstr.* 1988, **109**, 191061x
7 Satoh, S., Chûjô, R., Ozeki, T. and Nagai, E. *J. Polym. Sci.* 1962, **62**, S101
8 Inoue, Y., Nishioka, A. and Chûjô, R. *Makromol. Chem.* 1973, **168**, 163
9 Chûjô, R. *Kagaku* 1981, **38**, 420
10 Zhu, S. N., Yang, X. Z. and Chûjô, R. *Polym. J.* 1983, **15**, 859
11 Härkönen, M., Seppälä, J. V. and Väänänen, T. *Makromol. Chem.* 1991, **192**, 721
12 Härkönen, M., Seppälä, J. V. and Väänänen, T. in 'Catalytic Olefin Polymerization' (Eds T. Keii and K. Soga), Kodansha, Tokyo, 1990, p. 87
13 Barbé, P. C., Noristi, M. A. and Schexnayder, M. A. in 'Advances in Polyolefins' (Eds B. Seymour and T. Cheng), Plenum Press, New York, 1987, p. 295
14 Chien, J. C. W. and Hu, Y. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 2847
15 Guyot, A., Bobichon, R., Spitz, R., Duranel, L. and Lacombe, J. L. in 'Transition Metals and Organometallics as Catalyst for Olefin Polymerization' (Eds W. Kaminsky and H. Sinn), Springer-Verlag, Berlin, 1988, p. 13
16 Kashiwa, N., Yoshitake, J. and Toyota, A. *Polym. Bull.* 1988, **19**, 333
17 Sacchi, M. C., Tritto, I. and Locatelli, P. *Eur. Polym. J.* 1988, **24**, 137
18 Soga, K., Shiono, T. and Doi, Y. *Makromol. Chem.* 1988, **189**, 1531
19 Keii, T., Suzuki, E., Tamura, M. and Doi, Y. in 'Transition Metal Catalyzed Polymerization: Alkenes and Dienes, Part A' (Ed. R. P. Quirk), Harwood Academic, New York, 1983, p. 97
20 Seppälä, J. V. and Härkönen, M. *Makromol. Chem.* 1989, **190**, 2535
21 Soga, K., Park, J. R., Shiono, T. and Kashiwa, N. *Makromol. Chem., Rapid Commun.* 1990, **11**, 117
22 Kawamura, H., Hayashi, T., Inoue, Y. and Chûjô, R. *Macromolecules* 1989, **22**, 2181
23 Antberg, M., Dolle, V., Klein, R., Rohrmann, J., Spaleck, W. and Winter, A. in 'Catalytic Olefin Polymerization' (Eds T. Keii and K. Soga), Kodansha, Tokyo, 1990, p. 501