

Studies of the stereospecific polymerization mechanism of propylene by a modified Ziegler–Natta catalyst based on 125 MHz ^{13}C n.m.r. spectra

Yoshio Inoue, Yûichi Itabashi and Riichirô Chûjô

Department of Polymer Chemistry, Tokyo Institute of Technology, 12-1 O-okayama 2-chome, Meguro-ku, Tokyo 152, Japan

and Yoshiharu Doi

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4529 Nagatsuda-cho, Midori-ku, Yokohama 227, Japan

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The mechanism of stereospecific polymerization of propylene (catalysed by a modified Ziegler–Natta system, $\text{TiCl}_4/\text{MgCl}_2/\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5/\text{Al}(\text{C}_2\text{H}_5)_3$), has been analysed using the values of triad and pentad tacticity determined using 125 MHz ^{13}C n.m.r. spectroscopy. The well-known single active-site models, such as the Bernoullian, first- and second-Markovian, and enantiomorphic models, were found to be inadequate to describe the observed tacticity. A two-sites model, in which at one site the stereospecific polymerization proceeds in obedience to the Bernoullian model and at the other proceeds under the control of enantiomorphic-site model, is proposed. It was found that the pentad tacticities of both soluble and insoluble (in boiling heptane) fractions of polypropylene agreed well with the two-sites model.

(Keywords: polypropylene; Ziegler–Natta catalyst; polymerization; carbon-13 n.m.r.; tacticity; configuration; stereoregularity)

INTRODUCTION

The two-component catalytic systems (Ziegler–Natta catalysts) and their modifications are normally used for olefin polymerization¹. Up till now, the conditions (such as the combination and the contents of catalyst components) for obtaining polypropylenes with various steric configurations have become well known. However, some ambiguities regarding the mechanism of stereospecific polymerization of propylene with these catalysts still remains to be solved.

After a well-resolved stereochemical pentad splitting (of the methyl resonance in the continuous-wave mode, proton-decoupled ^{13}C n.m.r. spectra) of polypropylene had been observed at 25 MHz^{2,3}, a lot of attention was devoted to the ^{13}C spectra and the analysis of the microstructures of polypropylenes⁴. Improvement of sensitivity and spectrometer resolution by the introduction of high-field superconducting magnets and instrumentation with the Fourier-transform system, has increased the importance of ^{13}C n.m.r. We are now in a position to examine more precisely a mechanism for the stereospecific polymerization of propylene catalysed by a Ziegler–Natta system.

In this paper, several statistical models of stereospecific polymerization will be examined for polypropylenes prepared with a titanium-based modified Ziegler–Natta catalyst based on the triad and pentad tacticities determined by means of 125 MHz ^{13}C n.m.r. spectroscopy.

EXPERIMENTAL

Materials

The polypropylene was prepared with a titanium-based catalyst supported on MgCl_2 , i.e. $\text{TiCl}_4/\text{MgCl}_2/\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5/\text{Al}(\text{C}_2\text{H}_5)_3$.⁵ Two polymers S7 and 17 are the boiling heptane soluble and insoluble fractions, respectively, of the original polymer. These samples are exceedingly suitable for out study, because they do not contain any detectable amounts of regioirregularity of propylene units^{5,6}, the absence of which was confirmed by ^{13}C n.m.r. spectra^{7,8}.

Methods

^{13}C n.m.r. (proton-decoupled natural abundance Fourier-transformed) spectra were recorded on a JEOL JNM GX-500 spectrometer operated at 125.6 MHz and 130°C. The sample solutions, in 10 mm o.d. glass tubes, were prepared in 1,2,4-trichlorobenzene (90 vol%)/dioxane- d_8 (10 vol%) to give 0.25 g (polymer)/1 cm³ (solvent). Dioxane- d_8 provided the signal for the n.m.r. internal ^2H lock. The details of the instrumental conditions were: 90°-pulse width, 26 μs ; pulse repetition time, 10 s; data points, 32 K; sweep width, 20 kHz (160 p.p.m.).

The ^{13}C n.m.r. spectra of methyl region of the samples S7 and I7 are shown in Figures 1 and 2, respectively. Chemical shifts were measured with respect to the central peak of dioxane- d_8 resonance, which was

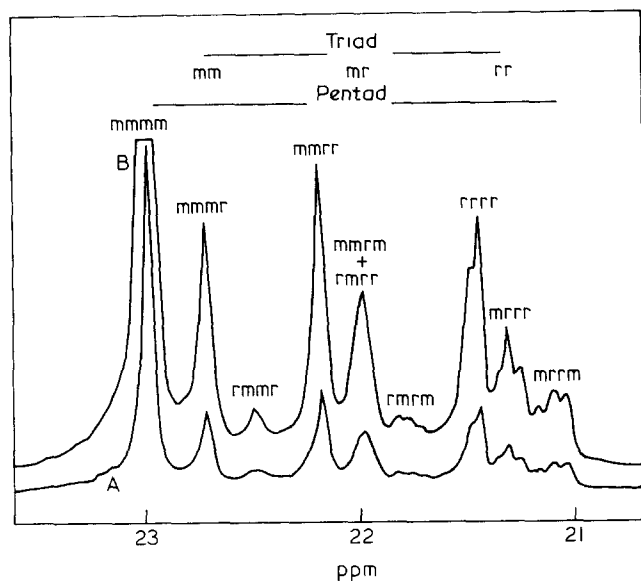


Figure 1 (a) Proton-decoupled ^{13}C n.m.r. spectrum (at 125.6 MHz) of the methyl carbon region in the (boiling-heptane) soluble fraction (S7) of polypropylene, prepared with a $\text{TiCl}_4/\text{MgCl}_2/\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5/\text{Al}(\text{C}_2\text{H}_5)_3$ system, in 25% w/v 1,2,4-trichlorobenzene (90 vol%)/dioxane- d_8 (10 vol%) solution at 130°C . The spectrum is the result of 6000 accumulations of time-domain signals. (b) Expanded spectrum of (a) and triad and pentad assignments

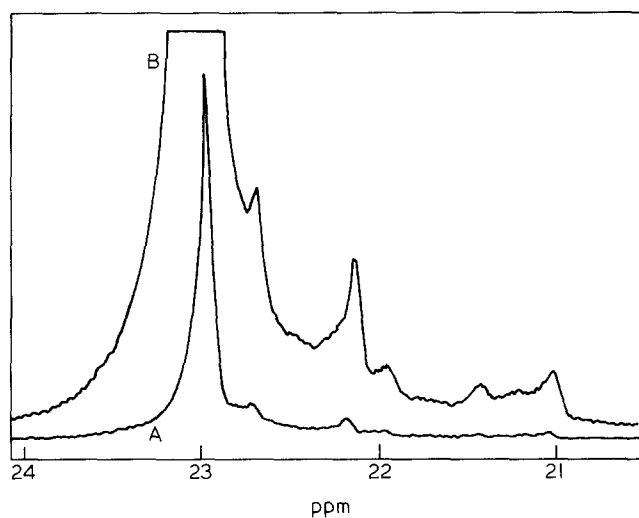


Figure 2 (a) Proton-decoupled ^{13}C n.m.r. spectrum (at 125.6 MHz) of the methyl carbon region in the (boiling-heptane) insoluble fraction (I7) of polypropylene. The spectrum is the result of 16000 accumulations. The other conditions are the same shown in the caption of Figure 1. (b) Expanded spectrum of (a). The triad and pentad assignments are shown in Figure 1

taken to be 67.4 p.p.m. downfield from the resonance of Me_4Si . The configurational triad assignments are the same as those made previously^{2,3}, which are unequivocal. The pentad assignments shown in Figures 1 and 2 are based on those proposed by Zambelli *et al.*⁹, which were theoretically supported by Tonelli^{4b,10}. The triad and pentad sequences are described in terms of combinations of m and r (meso(isotactic) and racemic(syndiotactic)diad). The values of tacticity were estimated based on the relative peak areas, which were determined using a curve resolving method^{4a,11}. As can be seen in the Figures, some pentad resonances split

further, probably due to heptad configurations^{4b}. For these resonances, the pentad intensities were estimated as the sum of relative intensities of corresponding split peaks. Some parameters for a statistical model were determined by an iterative calculation on a HITAC M-280 computer at the Information Processing Center, Tokyo Institute of Technology.

RESULTS AND DISCUSSION

The experimentally determined triad and pentad tacticity values of both polymers are shown in Table 1. The insoluble (in boiling heptane) fraction I7 is highly isotactic while the soluble fraction S7 is rather atactic. It is well known that at least two types of configurationally different polymers were therefore formed in the polymerization with the modified Ziegler-Natta catalyst. The applicability of several statistical models for the stereospecific polymerization was tested using the above tacticity values. The known statistical models can be classified into two types, a chain-end growing dependent model, in which the configuration of the monomer joining at the growing chain-end is controlled by the growing chain-end unit or units. The other model is the catalyst-dependent model.

The simplest model of the first type is the symmetric one-parameter model (Bernoullian model)¹², where the addition of the monomer to the growing chain-end is assumed to be influenced only by the end-unit of the growing chain. It is well-known that the stereochemistry in free radical polymerizations of many vinyl monomers follows this simple model^{4a}. This model was, however, found to be inappropriate for both samples, since the values of triad tacticity of both polymers do not satisfy the following relation¹³,

$$\frac{4[\text{mm}][\text{rr}]}{[\text{mrr}]^2} = 1 \quad (1)$$

i.e. the values found for the soluble and insoluble fractions, S7 and I7, were 8.82 and 29.8, respectively (Table 2).

Two more models of the chain-end control type are the first- and second-order Markovian models¹⁴, in which the steric configuration of the 'adding' monomer is influenced by the stereochemistry of the growing chain-end, which may be m or r, and mm, mr or rr, for the first- and second-order Markovian models, respectively. If the stereochemistry of the propagation reaction is controlled by first-order Markovian statistics, the following relations must hold between the values of tetrad tacticity^{15,16},

$$\frac{4[\text{mrr}][\text{rmm}]}{[\text{mrr}]^2} = 1 \quad (2)$$

$$\frac{4[\text{mrr}][\text{rrr}]}{[\text{mrr}]^2} = 1 \quad (3)$$

The tetrad tacticity appearing in these relations can be calculated from the related pentad tacticity. Similar relations between the values of pentad tacticity must

Table 1 Triad and pentad tacticities of (boiling-heptane) soluble and insoluble fractions of polypropylene prepared with a $TiCl_4/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$ system

Sample		Triad tacticity		
		[mm]	[mr]	[rr]
Heptane-soluble (S7)	Found ^a	0.51 ₆	0.23 ₉	0.24 ₄
	Calcd. ^b	0.516	0.239	0.244
Heptane-insoluble (I7)	Found ^a	0.89 ₉	0.06 ₅	0.03 ₅
	Calcd. ^b	0.902	0.064	0.035

Sample		Pentad tacticity								
		[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mrmr]	[rmrm]	[rrrr]	[mrrr]	[rmrr]
Heptane-soluble (S7)	Found ^a	0.39 ₃	0.09 ₃	0.03 ₀	0.12 ₈	0.07 ₄	0.03 ₇	0.12 ₇	0.06 ₄	0.05 ₃
	Calcd. ^b	0.400	0.101	0.016	0.114	0.094	0.032	0.112	0.076	0.055
Heptane-insoluble (I7)	Found ^a	0.82 ₇	0.06 ₀	0.01 ₂	0.04 ₄	0.01 ₃	0.00 ₈	0.01 ₁	0.00 ₉	0.01 ₅
	Calcd. ^b	0.846	0.055	0.001	0.055	0.006	0.003	0.003	0.004	0.027

^a Observed by 125.6 MHz ¹³C n.m.r. spectroscopy

^b Calculated based on the two-sites model with the values of parameters shown in Table 5

Table 2 Test for the conformity to the Bernoullian and Markovian models

Sample	Bernoullian	1-st Markovian		2-nd Markovian	
	$\frac{4 [mm] [rr]}{[mr]^2}$	$\frac{[mmr]^2}{[mmm]} + \frac{[mrr]^2}{[rrr]}$	$4 \frac{[mrmr]}{[mmmr]^2}$	$\frac{\{[mmrm] + [rmrr]\}^2}{4 [mmrr] [rmrm]}$	$4 \frac{[mrrr] [rrrr]}{[mrrr]^2}$
Heptane-soluble (S7)	8.82	0.79	5.45	0.29	6.57
Heptane-insoluble (I7)	29.8	1.83	11.03	0.12	8.15

hold if the reaction is controlled by second-order Markovian statistics as follows¹⁶:

$$\frac{4[mmmm][rmmr]}{[mmmr]^2} = 1 \quad (4)$$

$$\frac{[mmrm][rmrr]}{[mmrr][rmrm]} = 1 \quad (5)$$

$$\frac{4[mrmr][rrrr]}{[mrrr]^2} = 1 \quad (6)$$

Practically the pentad peaks of (mrmr) and (rmrr) could not be observed separately; relations (2) and (3) must be combined and modified as follows,

$$\frac{\left\{ \frac{[mmr]^2}{[mmm]} + \frac{[mrr]^2}{[rrr]} \right\}}{4\{[rmr] + [mrm]\}} = 1 \quad (7)$$

For the same reason, the relation (5) is modified as follows,

$$\frac{\{[mmrm] + [rmrr]\}^2}{4[mmrr][rmrm]} \geq 1 \quad (8)$$

with the aid of inequality,

$$\frac{2[rr]}{[mr]} = 1 \quad (10)$$

$$\frac{\{[mmrm] + [rmrr]\}^2}{4[mmrr][rmrm]} \geq \frac{[mmrm][rmrr]}{[mmrr][rmrm]} \equiv 1 \quad (9)$$

By examining the conformity of the observed values of tacticity to these relations, we can judge the applicability of Markovian statistics. The results are summarized in Table 2, which clearly indicates the inadequacy of the first- and second-Markovian models, as well as the Bernoullian model, for both polymers. Both polypropylenes should be controlled by more complex configurational statistics than the simple chain-end growing dependent model.

The applicability of the model of the second type (the catalyst-control model) was, therefore, tested. A well-known model of this type is the enantiomorphic-sites model based on the assumed presence of equal numbers of d- and l-preferring catalyst sites¹⁷. In the simplest case, that is, the one parameter (probability) model, the configuration of the growing end unit and all preceding units is assumed to have negligible influence on the configuration of monomer addition; the latter being determined by the innate preference exhibited by the catalyst site. According to this model, the following relations must hold between the triad tacticities^{17,18}.

Table 3 Test for the conformity to the one-parameter enantiomorphic-site model

Sample	$2 \frac{[rr]}{[mr]}$	$1 - \frac{4}{[mr] + 2[rr]} + \frac{1}{[rr]}$
Heptane-soluble (S7)	2.04	-0.40
Heptane-insoluble (I7)	1.07	-0.06

Table 4 Triad and pentad proportions for the two-sites model *a, b*

Triad	Weight fraction	
	ω	$1 - \omega$
[mm]	$1 - 3\beta$	σ^2
[mr]	2β	$2\sigma(1-\sigma)$
[rr]	β	$(1-\sigma)^2$
Pentad		
[mmmm]	$1 - 5\beta + 5\beta^2$	σ^4
[mmmr]	$2\beta - 6\beta^2$	$2\sigma^3(1-\sigma)$
[rmmr]	β^2	$\sigma^2(1-\sigma)^2$
[mmrr]	$2\beta - 6\beta^2$	$2\sigma^2(1-\sigma)^2$
[mrrm]	$2\beta^2$	$2\sigma^3(1-\sigma)$
[rmrr]	$2\beta^2$	$2\sigma(1-\sigma)^3$
[rmmr]	$2\beta^2$	$2\sigma^2(1-\sigma)^2$
[rrrr]	β^2	$(1-\sigma)^4$
[mrrr]	$2\beta^2$	$2\sigma(1-\sigma)^3$
[mrrm]	$\beta - 3\beta^2$	$\sigma^2(1-\sigma)^2$

^a $\beta = \alpha(1-\alpha)$

^b $\alpha, \sigma,$ and ω are the probability to select a d-unit at a d-preferring site in the enantiomorphic site, the probability to select a meso-diad configuration in the Bernoullian site, and the weight fraction of the polymer produced according to the enantiomorphic-site model in the unfractionated polymer

$$1 - \frac{4}{[mr] + 2[rr]} + \frac{1}{[rr]} = 1 \quad (11)$$

The calculated values are shown in Table 3. The results indicate the non-conformity of the catalyst-control model with the observed triad tacticity of both polymers, while the values of $2[rr]/[mr]$ for the insoluble fraction I7 are accidentally close to unity. After all (as discussed the above) all well-known models, which assume the presence of only a single catalytic centre at the growing chain-end, are inappropriate to the description of the stereospecific polymerization of propylene with the modified Ziegler-Natta catalyst. This means that the application of the single active-centre model is inadequate. The original unfractionated polypropylene (prepared with a Ziegler-Natta type catalyst) split into at least two fractions (with different tacticities by solvent fractionation). We should therefore examine a possible two catalytic sites model¹⁹. In this model at one site the stereospecific propagation proceeds in obedience to the Bernoullian statistics and at the other it proceeds under the control of enantiomorphic model. The resulting polymer should be a mixture of polymers with different configurations or a polymer with stereoblocks of different configurations. This model is a kind of 'stereoblend' model, which has been primarily introduced to describe the stereospecific

polymerization mechanism of methylmethacrylate with 9-fluorenyllithium^{16,20}. The applicability of the model of this type has been already recognized in the analyses of the stereochemical configuration of polypropylenes^{6,21}. The combination of the one-parameter Bernoullian and the one-parameter enantiomorphic models corresponds to an empirical trend that the atactic polymers are generally generated obeying the Bernoullian statistics; while the higher isotactic chains are controlled by the catalysts²². According to the two-sites model, the triad and pentad tacticities can be described with three parameters (shown in Table 4). Here, α is the probability to select a d-unit at a d-preferring site in the enantiomorphic site, σ is the probability to select a meso-diad configuration in the Bernoullian site, and ω is the weight fraction of the polymer produced according to the enantiomorphic-site model in the unfractionated original polypropylene. For convenience the term $\alpha(1-\alpha)$ is replaced by β .

The values of three parameters, which satisfactorily reproduced the triad tacticity, were determined by an iterative fitting calculation. The best values of parameters for both polymers are shown in Table 5, and the calculated values of the triad and pentad tacticity by using these parameters are shown in Table 1. For both samples, the calculated values of pentad tacticity are reasonably consistent with the observed ones, indicating the applicability of the two-sites model. The best values of α and σ for the soluble fraction S7 are in good agreement with those found for the soluble fractions in boiling hydrocarbons of polypropylenes prepared by various Ziegler-Natta type catalysts⁶.

If the polymerization of propylene with a catalyst system $TiCl_4/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$ proceeds according to the two-sites model, the tacticity values of the resulting polymers S7 and I7 must be described by the same parameters α and σ , differing only the weight fraction ω . As can be seen in Table 5, the results are somewhat far from this expectation, although the inconsistency is not so large. It is possible to point out two sources of this discrepancy.

The first is ignorance of the dynamic equilibrium of the growing chain-end between the two possible sites. Such an equilibrium has been introduced into the mechanism of stereospecific polymerization to explain the stereoblock structures which occasionally result from homogeneous anionic polymerizations²³.

The second is the insufficiency of the number of assumed sites. The presence of more than two sites is, indeed, suggested from the fact that polypropylene prepared with a Ziegler-Natta type catalyst could be fractionated into several fractions having different tacticities, e.g. boiling-heptane soluble- and insoluble-fractions, boiling-hexane soluble- and insoluble-

Table 5 The 'best-fit' values of three parameters $\omega, \alpha,$ and σ for the two-sites model

Sample	ω	α	σ
Heptane-soluble (S7)	0.70	0.89	0.23
Heptane-insoluble (I7)	0.99	0.97	0.29

Table 6 Number averaged sequence length of meso diad of the polymers generated at the enantiomorphic site ($\langle m \rangle_{n,\alpha}$) and at the Bernoullian site ($\langle m \rangle_{n,\sigma}$)

Sample	$\langle m \rangle_{n,\alpha}$	$\langle m \rangle_{n,\sigma}$
Heptane-soluble (S7)	8.5	1.3
Heptane-insoluble (I7)	31.3	1.4

fractions, etc.^{1,5} It is well-known that the difference in the tacticity of the fractionated polypropylene is dependent on the solvent used for the fractionation. The introduction of the dynamic equilibrium between the two-sites or the multi-sites (more than two) or the combination of these simultaneously, makes the model very complex to analyse. The two-sites model presented here is the simplest multi-sites model. It must be emphasized that the values of pentad tacticity of both (boiling-heptane) soluble and insoluble fractions are well described by this simple model.

According to the Bernoullian and the enantiomorphic models, the number averaged sequence length of meso diad, $\langle m \rangle_n$, is expressed by

$$\langle m \rangle_{n,\sigma} = \frac{1}{1-\sigma} \quad (12)$$

$$\langle m \rangle_{n,\alpha} = \frac{1-2\alpha(1-\alpha)}{\alpha(1-\alpha)} \quad (13)$$

respectively²⁴. The $\langle m \rangle_n$ values, calculated using the parameters σ and α listed in Table 5, are shown in Table 6. It is clear that the values of $\langle m \rangle_{n,\alpha}$ is larger than that of $\langle m \rangle_{n,\sigma}$. This result suggests that the longer isotactic-sequence is mainly generated on an enantiomorphic site of the catalyst.

It is concluded that the mechanism of the stereo-specific polymerization of propylene catalysed by a modified Ziegler-Natta catalyst system, $\text{TiCl}_4/\text{MgCl}_2/\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5/\text{Al}(\text{C}_2\text{H}_5)_3$ is well

described by the two-sites model, but not by the one-site Bernoullian, Markovian, or enantiomorphic models.

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