Microstructure in polypropylenes prepared with $TiCl_4/MgCl_2$–Et_3Al and $Ti(OBu)Cl_3/MgCl_2$–Et_3Al catalytic systems

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Microstructures were studied for polypropylenes prepared with $TiCl_4/MgCl_2$–Et_3Al and $Ti(OBu)Cl_3/MgCl_2$–Et_3Al catalytic systems. Pentad tacticities, chain-end structures, and regioirregularity in these polypropylenes were determined from ^{13}C n.m.r., ^1H n.m.r., and INEPT (insensitive nuclei enhancement by polarization transfer) spectra. The propylene polymerization mechanism was statistically analysed on the basis of the two-site model from the pentad tacticities. It was confirmed that these polypropylenes are composed of the isotactic and atactic polymers produced at the IPP and APP catalytic sites, which produce the isotactic and atactic polymers, respectively. The optimum values of the two-site model parameters elucidated that the displacement of Cl ligand around the titanium by OBu reduces the strength of the steric control at the IPP site. The detected chain-end structures verified that the chain transfer of propagation species to the propylene monomer terminates the propagation reaction and regenerates initiation species. The two-site model analysis for the tactic structures at the chain-end indicated that the steric controls of the initiation reactions at both sites are as strong as those of propagation reactions. Further, it was found that these polypropylenes contain head-to-head and tail-to-tail structures whose contents (monomer unit per chain) are 10^{-3} order.

(Keywords: polypropylene; Ziegler–Natta catalyst; ^{13}C n.m.r.; ^1H n.m.r.; tacticity; chain-end structure; polymerization mechanism; propylene polymerization)

INTRODUCTION

Since the discovery of Ziegler–Natta catalysts, a number of workers have investigated a large number of different combinations of metal alkyls and transition metal salts to make catalytic systems which are active for polymerization of ethylene, propylene and higher olefins, and copolymerization of these monomers. In recent years, supported catalysts have been used for the industrial scale process of ethylene[1–6] and propylene polymerization[7–9], because these catalysts were shown to be highly efficient.

^{13}C n.m.r. is the most powerful method to determine the microstructures in polypropylene. Tactic and chain-end structures, and the regioirregularity in polypropylenes have been investigated in detail from the high resolution ^{13}C n.m.r. spectra. ^{13}C n.m.r. assignments of methyl carbons in pentad and heptad stereoisomers have been confirmed by the chemical shift calculation using the gamma-effect on ^{13}C n.m.r. chemical shift and rotational isomeric state model[10,11]. A mechanism of stereospecific polymerization has been statistically analysed from the values of tacticities in polypropylenes prepared with various Ziegler–Natta catalytic systems[10–16]. The two-site model[13,14], in which at one site propylene polymerization proceeds according to the asymmetric Bernoullian statistics (selection between dextro and levo[17]) and at the other site to symmetric Bernoullian statistics (selection between meso and racemo), has been found to be adequate for the description of the propylene polymerization mechanism[11,15,16].

Analyses of chain-end structures in polypropylene have thrown light on the study of the mechanisms of the initiation and termination reactions. Zambelli *et al.*[18–21] elucidated the mechanism of the initiation and termination reactions of propylene polymerization with various types of Ziegler–Natta catalytic systems from the ^{13}C n.m.r. spectra of ^{13}C enriched polypropylenes and selectively ^{13}C enriched end groups of polypropylenes. In an earlier paper[22], we determined the chain-end structures in polypropylene prepared with δ-$TiCl_3/Et_2AlCl$ catalytic system in the presence of hydrogen. Triad and tetrad tacticities at the chain-end have been evaluated from the quantitative analyses of the split peaks arising from the different tactic structures at the chain-end[22]. These results have provided useful information on steric controls of the initiation reaction.

Regioirregularity in polypropylene chains has been studied from the ^{13}C n.m.r. spectra[23–25]. Asakura *et al.*[25] calculated the ^{13}C chemical shifts due to the gamma-effect of carbons in regioirregular polypropylene by taking into account the effect of tacticity on chemical shifts. Their calculated shifts are in good agreement with the observed

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ones, and with the calculated ones[23] based on the empirical rule.

The analysis of microstructures in polypropylene prepared with supported catalysts is of great interest, because microstructures in polypropylenes reflect the kinetic schemes and steric control of the propylene polymerization as mentioned above. In this study, the microstructures in polypropylenes prepared with supported catalytic systems, $TiCl_4/MgCl_2$–Et_3Al and $Ti(OBu)Cl_3/MgCl_2$–Et_3Al, in the absence of hydrogen are studied by ^{13}C and ^1H n.m.r. spectroscopy, and the polymerization mechanism is statistically analysed on the basis of the two-site model from the pentad tacticities. The chain-end structures are also determined by ^{13}C and ^1H n.m.r. spectra. Proton decoupled INEPT (insensitive nuclei enhanced by polarization transfer)[26,27] spectra obtained with the delay times (Δ) of $3/4J$ and $2/4J$ prior to the data acquisition are used for the spectral assignments of carbons situated at the chain-end and at the inverted propylene units. The initiation and termination reactions of propylene polymerization are elucidated from the chain-end structures.

EXPERIMENTAL

Polypropylenes

Polypropylenes A and B were prepared with $TiCl_4/MgCl_4$–Et_3Al and $Ti(OBu)Cl_3/MgCl_2$–Et_3Al catalytic systems, respectively. Polymerization was performed at 40°C for 2 h under atmospheric pressure (pressure of propylene = 660 T). n-Heptane was used as the polymerization medium. Samples AS6 and BS6 are fractions of A and B soluble in boiling hexane, respectively. Weight fractions of AS6 and BS6 to the whole polymers A and B are 0.53 and 0.63, respectively. The weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights of polypropylenes were determined by g.p.c.. A molecular weight calibration curve for polypropylene was obtained on the basis of the universal calibration[28,29] curve for polystyrene determined from seven standard polystyrenes of molecular weights from 950 to 6 750 000. In *Table 1* are shown the molecular weights of these samples. The values of molecular weights for AS6 and BS6 have ambiguity due to the poor reliability of the calibration curve in the range of molecular weight less than 1000 (the lowest molecular weight of standard polystyrenes is 950), because AS6 and BS6 have considerable amounts of low molecular weight components less than 1000. AS6 and BS6 were used for the analysis of chain-end structures.

N.m.r. measurement

^{13}C and ^1H n.m.r. spectra were recorded at 120°C on a Jeol GSX-270 FT spectrometer operated at 67.8 and 270.1 MHz, respectively. The sample solutions in 10 mm o.d. glass tube were prepared in *o*-dichlorobenzene (90 vol%)/benzene-d_6 (10 vol%) to give 0.15 g (polymer) cm^{-3} (solvent). Benzene-d_6 was used for the ^2H n.m.r. internal lock.

In ^{13}C n.m.r. measurements, broad band noise decoupling was used to remove ^{13}C–^1H couplings. The pulse angle was 90°, and 8000 free induction decays were stored in 64K data points using a spectral window of 12 000 Hz. For the quantitative measurement, the pulse repetition time was set to be 25 s, which is more than five times the spin-lattice relaxation times of the most mobile methyl carbons at the chain-end (4.0–4.8 s (ref. 30)).

The ^1H decoupled INEPT method[26,27], in which the delay times (Δ) prior to data acquisition are $3/4J$ and $2/4J$ (where J is a ^1H–^{13}C spin–spin coupling constant), was used to discriminate methylene peaks from methine peaks and the selective observation of methine peaks, respectively.

In ^1H n.m.r. measurement, the pulse angle was 90°, and 500 free induction decays were stored in 32K data points using a spectral window of 10 000 Hz.

In all measurements hexamethyldisiloxane was used as an internal reference (2.03 (^{13}C) and 0.07 (^1H) ppm downfield from the resonances of tetramethylsilane).

Table 1 Molecular weights of polypropylene samples

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
A	190 000	14 000	13.6
AS6	ca. 50 000	ca. 8 000	ca. 6.3
B	140 000	14 000	10.0
BS6	ca. 50 000	ca. 8 000	ca. 6.3

RESULTS AND DISCUSSION

Tactic structures

In *Figures 1a* and *b* are shown the methyl resonance regions of ^{13}C n.m.r. spectra of samples A and B, and AS6 and BS6, respectively. The ^{13}C n.m.r. chemical shift assignments of methyl pentad peaks proposed by Zambelli *et al.*[31], which have been confirmed from the chemical shift calculation via the gamma effect[10,11] are also shown in *Figure 1b*. Pentad tacticities were accurately determined from the relative peak areas using curve resolution method[12] as listed in *Table 2*. From these data propylene polymerization mechanism was analysed on the basis of the two-site model[11,13–16]. The parameters of this model and their meanings are as follows:

α, the probability of selecting a d(dextro)-unit at a d-preferring site in the asymmetric Bernoullian model site;

σ, the probability of selecting a meso dyad configuration in the symmetric Bernoullian model site;

ω, the weight fraction of the polymer produced at the asymmetric Bernoullian model site.

The optimum values of model parameters were determined by the nonlinear least squares method. The results are shown in *Table 3*. Pentad stereosequence distributions in samples A, B, AS6, and BS6 predicted by the two-site model are in good agreement with those determined experimentally within standard deviations of less than 5.0×10^{-3}, indicating the suitability of the two-site model for the mechanism of propylene polymerization. Optimum values of these parameters indicate that the isotactic polymer is predominantly produced at the asymmetric model site (IPP-site) and the atactic polymer at the symmetric model site (APP-site). This conclusion is in agreement with our previous study[11,14–16].

As shown in *Figure 1a* (Sample A (top), Sample B (bottom)) and *Table 2*, fractions of mmmr, mmrr, and mrrm in B are larger than those in A. This result is

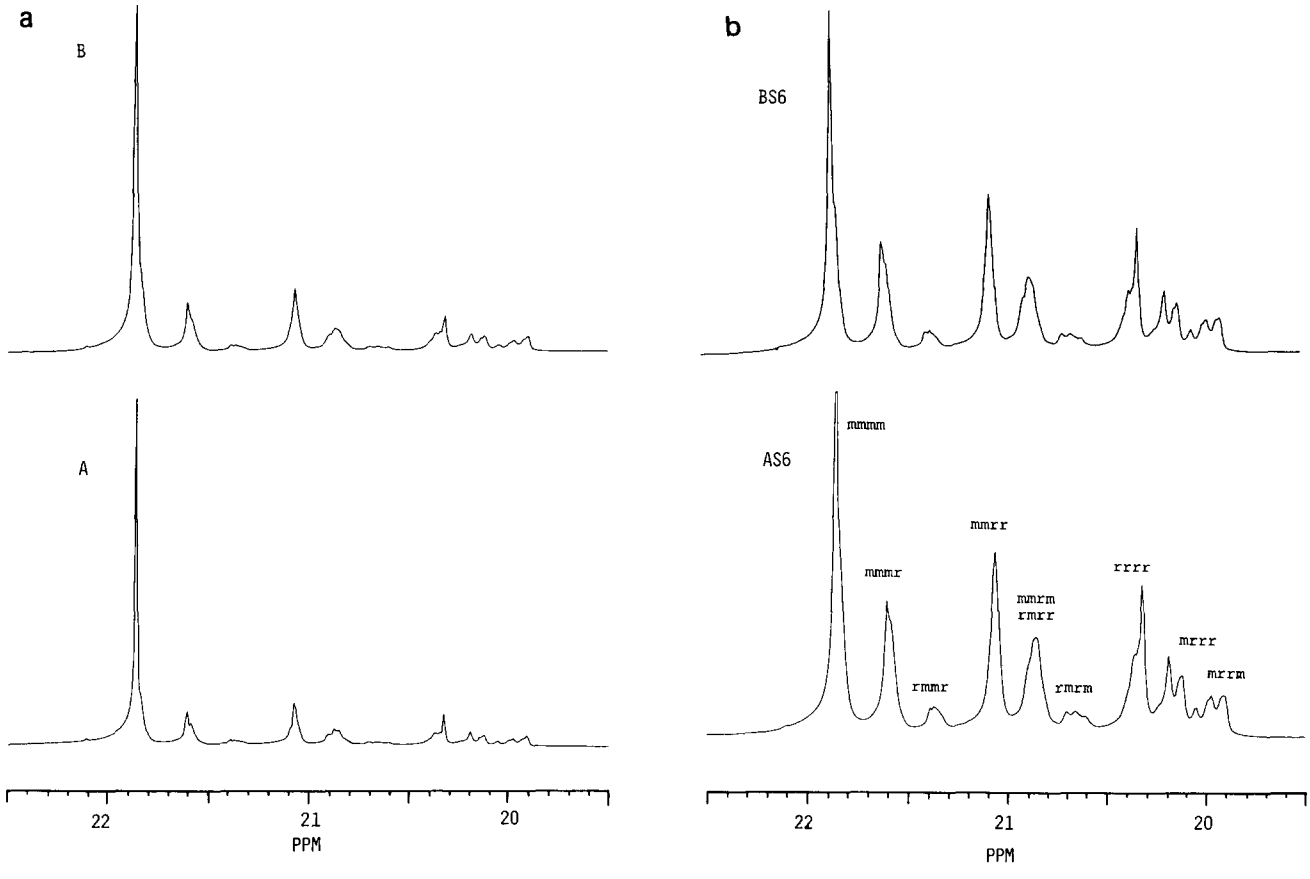


Figure 1 Methyl resonance regions in ^{13}C n.m.r. spectra of (a) polypropylenes A and B and (b) AS6 and BS6

Table 2 Pentad tacticities of polypropylenes

Sample	A		B		AS6		BS6	
pentad	observed	calculated[a]	observed	calculated[a]	observed	calculated[a]	observed	calculated[a]
mmmm	0.646	0.647	0.605	0.607	0.265	0.264	0.294	0.297
mmmr	0.052	0.053	0.075	0.075	0.111	0.114	0.111	0.111
rmmr	0.014	0.010	0.013	0.010	0.030	0.026	0.027	0.022
mmrr	0.061	0.064	0.082	0.085	0.141	0.131	0.123	0.126
mmrm + rmrr	0.059	0.059	0.060	0.057	0.130	0.134	0.119	0.121
rmrm	0.020	0.020	0.020	0.021	0.048	0.052	0.050	0.044
mrrm	0.037	0.032	0.045	0.042	0.070	0.066	0.060	0.064
mrrr	0.048	0.050	0.043	0.047	0.092	0.099	0.092	0.093
rrrr	0.063	0.065	0.057	0.056	0.113	0.114	0.124	0.122
SD[b]/10^{-3}		2.73		2.54		4.99		3.40

[a] Based on the two-site model. Parameters for the calculation are listed in *Table 3*
[b] Standard deviations between the observed and calculated fractions of pentad stereoisomers

Table 3 The optimum values of the parameters for the two-site model

Sample	ω	α	σ
A	0.770	0.966	0.273
B	0.797	0.947	0.281
AS6	0.640	0.836	0.270
BS6	0.660	0.851	0.243

reasonably described by using optimum values of model parameters as follows.

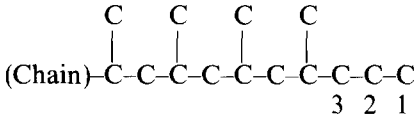
The mmmr, mmrr, and mrrm sequences are isolated rr defects in the isotactic polypropylene chains and the peak assigned to mmmr pentad arises mainly from mmmmrr heptad[11]. The optimum value (0.966) of α for sample A (prepared with $TiCl_4/MgCl_2$ catalyst) is larger than that (0.947) for sample B (prepared with $Ti(OBu)Cl_3/MgCl_2$ catalyst), although the difference is small. This elucidates that the displacement of Cl ligand around the titanium by OBu reduces the strength of the steric control at the IPP site.

As shown in *Figure 1b* and *Table 2*, the pentad tacticities of boiling hexane soluble fractions AS6 and BS6 are close to each other. The values of parameter α for AS6 and BS6 are different from those of whole polymers, A and B (*Table 3*), while the values of σ are almost constant among these polymers. This indicates

that, besides molecular weight fractionation, the tacticity fractionation (separation of polypropylene into fractions of different tacticities) occurs for the isotactic polymer produced at the asymmetric site in the boiling hexane extraction, and that the molecular weight fractionation mainly occurs for the atactic polymer produced at the symmetric site[32].

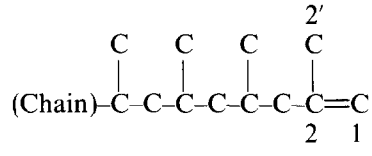
Chain-end structures

Referring to our previous study on chain-end structures[22], peaks of methyl carbon 1 and methylene carbon 3 in chain-end structure I can be found in the spectra of AS6, as shown in *Figures 2* and *3* (^{13}C n.m.r. spectra of BS6 and AS6 are practically identical over the whole resonance regions).

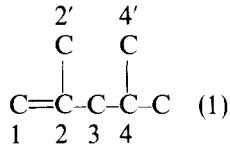


Structure I

In *Figures 4* and *5* are shown ^{13}C resonance regions of AS6 from 22 to 24 and from 110.5 to 112.5 ppm, respectively. The intensity of the peak observed at 22.56 ppm is nearly equal to that of the peak of carbon 1 in structure I. The INEPT spectrum in *Figure 5*, obtained with the delay time of $3/4J$ ($J = 160$ Hz) indicates that the peak at 111.60 ppm is a methylene carbon resonance. This suggests the existence of structure II, referring to the ^{13}C n.m.r. chemical shift assignments[33] of 2,4-dimethyl-1-pentene (1).



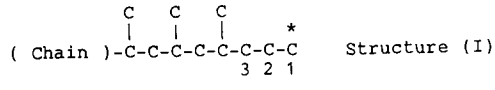
Structure II



(1)

^{13}C chemical shift assignments of 2,4-dimethyl-1-pentene (1)

Carbon No.	Chemical shift/ppm
1	111.60
2	144.34
2'	22.56



Structure (I)

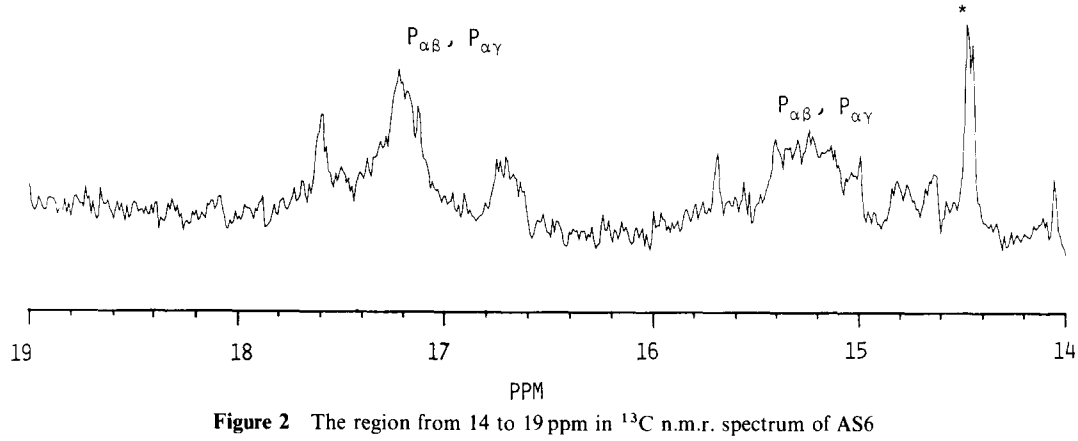
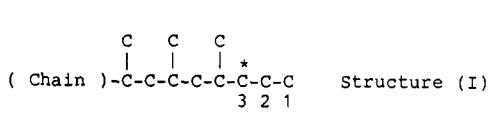
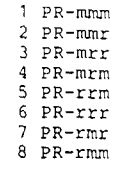


Figure 2 The region from 14 to 19 ppm in ^{13}C n.m.r. spectrum of AS6



Structure (I)



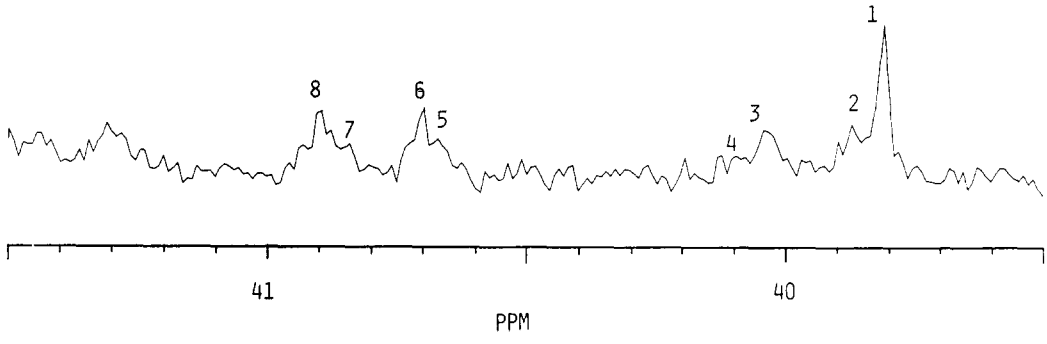


Figure 3 ^{13}C n.m.r. spectrum of methylene carbon 3 in chain-end structure (I) of AS6

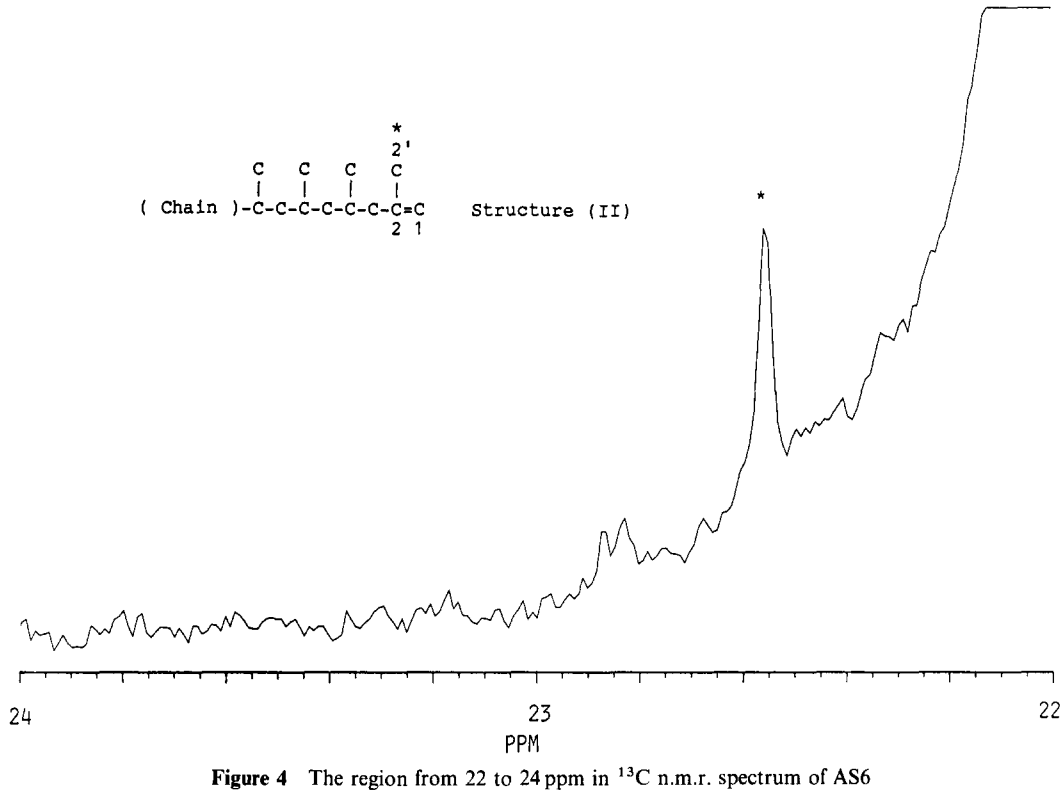


Figure 4 The region from 22 to 24 ppm in ^{13}C n.m.r. spectrum of AS6

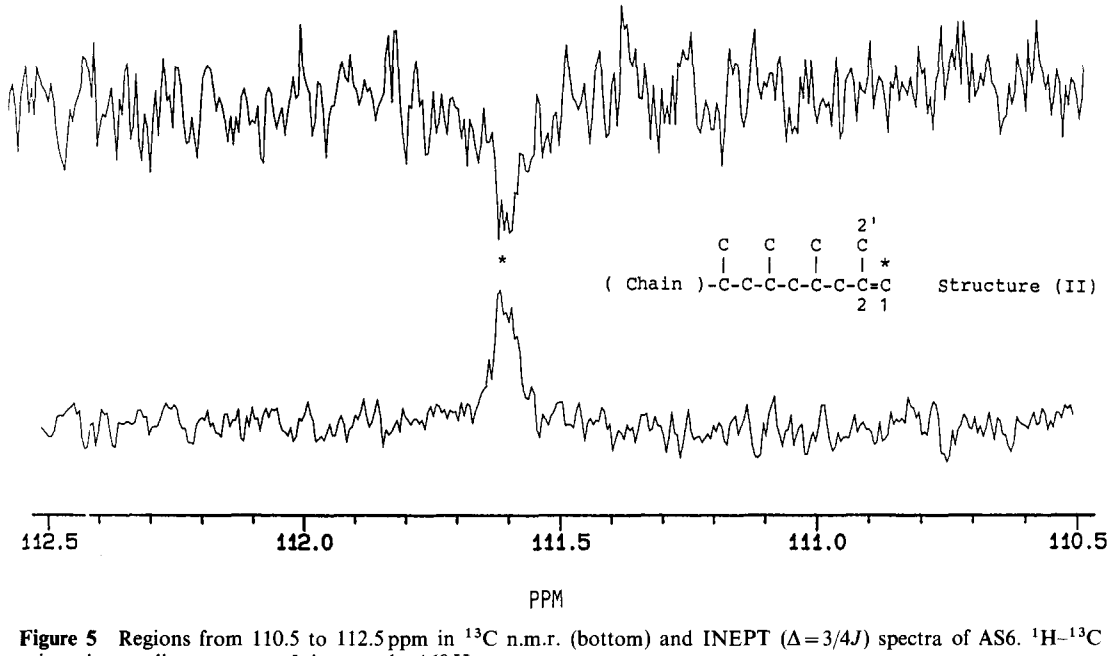


Figure 5 Regions from 110.5 to 112.5 ppm in ^{13}C n.m.r. (bottom) and INEPT ($\Delta = 3/4J$) spectra of AS6. ^{1}H–^{13}C spin–spin coupling constant, J, is set to be 160 Hz

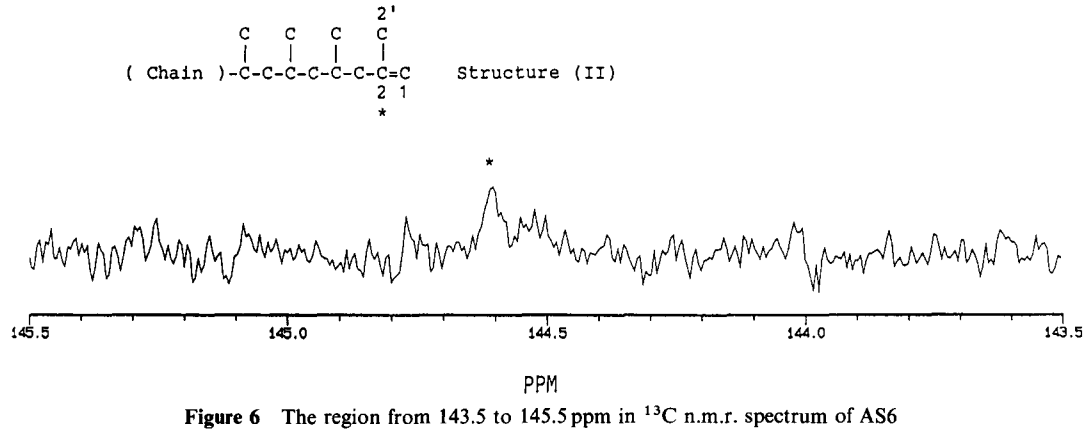


Figure 6 The region from 143.5 to 145.5 ppm in ^{13}C n.m.r. spectrum of AS6

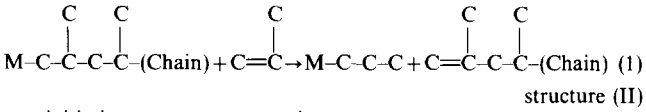
In *Figure 6*, a small peak observed at 144.6 ppm is assigned to carbon 2 in structure (II). The reason for the small intensity of this peak is attributable to the long spin–lattice relaxation time and the ineffective NOE of carbon 2, because this carbon being at the chain-end may be highly mobile, and further it has no directly attached protons.

In *Figure 7* is shown the ^{1}H n.m.r. spectrum of sample AS6. Two peaks observed at 4.67 and 4.73 ppm are assigned to the protons attached to methylene carbon 1 in structure II, referring to the ^{1}H n.m.r. spectrum of 2,4-dimethyl-1-pentene[34].

Schemes for the formation of chain-end structures

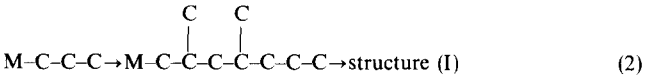
Under the polymerization conditions employed in this study, the termination and initiation reactions are expected to occur through the chain transfer reaction of the propagating species to the propylene monomer. In the case of the primary insertion of propylene, chain-end structures I and II are formed as follows.

termination



structure (II) (1)

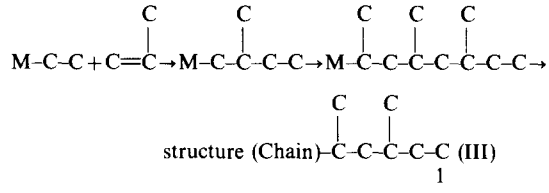
initiation propagation



M = Transition metal (titanium) (2)

According to the well known schemes for the initiation reaction[35], the initiating species produced at the initial stage of the polymerization should be M–Et (where ethyl(Et) group is derived from Et_3Al). The primary insertion to this species should produce chain-end structure (III) as follows.

primary insertion propagation



structure (Chain)–C–C–C–C (III)
1

However, the peak of carbon 1 in structure III was not detected at about 11 ppm (ref. 22) in the spectrum of AS6. Thus, the relative content of this structure may be too small to be detected in the spectrum of the AS6 owing to the higher molecular weight ($\bar{M}_n = 8000$) of boiling hexane soluble fraction (AS6), compared with that ($\bar{M}_n = 1000$) of boiling heptane soluble fraction of polypropylene prepared with δ-$TiCl_3/Et_2AlCl$ catalytic system[22]. The number average molecular weight estimated from the relative areas of peaks of methyl carbon 1 in chain-end structure I and of inner-chain methyl carbon is 9300. Since the peak area of methyl carbon 1 in structure I is nearly equal to that of methyl carbon 2′ in structure II, the value of M_n is reliable, indicating that most parts of polymer chains are formed by the chain transfer reaction.

Tacticity at the region of chain-end structure I is determined from the relative areas of split peaks of carbon 3, on the basis of the chain-end tetrad assignments[22] shown in *Figure 3*. The notations, PR–mmm (1), PR–mmr (2), ..., and PR–rrr (8) denote a n-propyl group at the chain-end followed by dyad configurations of meso, meso, and meso(1), meso, meso and racemo(2), ..., and racemo, racemo, and racemo(8) in the order from the chain-end. In *Table 4* are shown the assignments of split peaks arising from PR–tetrad sequences. The triad

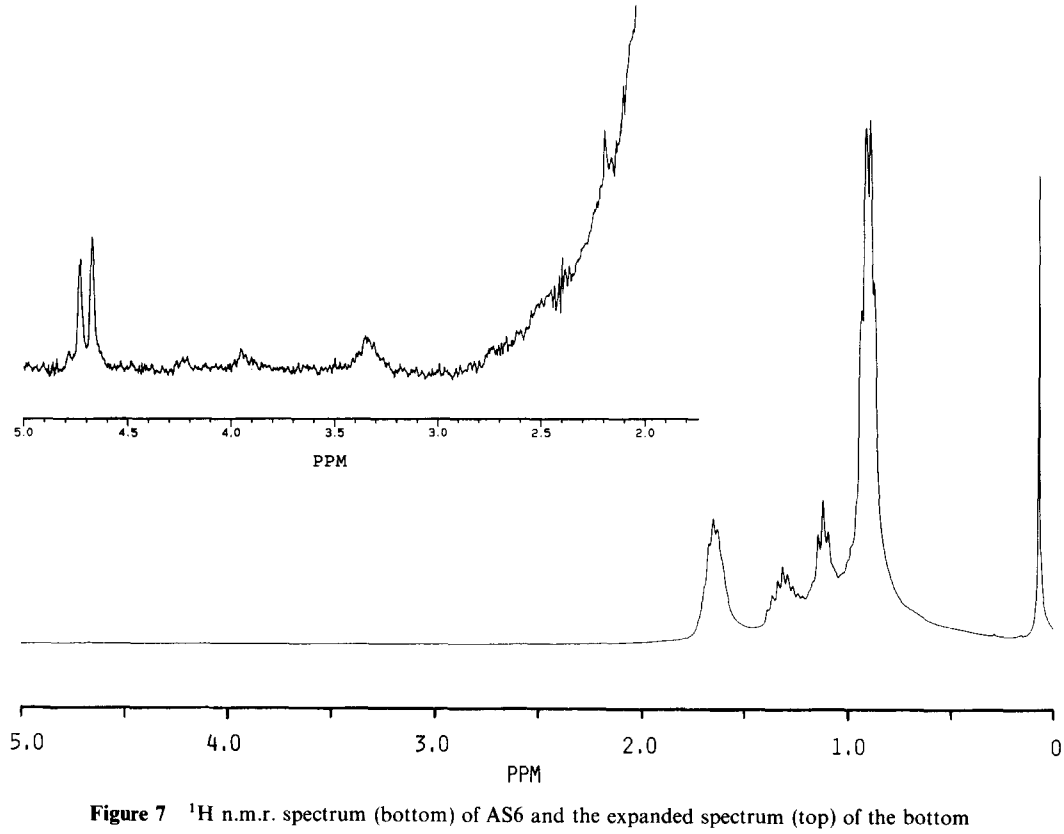
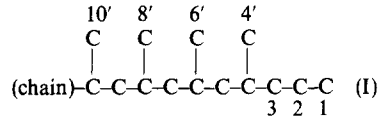


Figure 7 ^{1}H n.m.r. spectrum (bottom) of AS6 and the expanded spectrum (top) of the bottom

tacticity of chain-end structure I is similar to that of inner-chain as shown in *Table 5*. Further, fractions of PR–triads were well reproduced by the calculation using parameters of the two-site model. Optimum values of model parameters, ω, α, and σ are 0.750, 0.785, and 0.289, respectively. These values are similar to those determined by the triad fractions of the inner chain. Thus, the steric controls of the initiation reactions at both sites are as strong as those of the propagation reactions, as confirmed for the polypropylene prepared with δ-$TiCl_3/Et_2AlCl$ catalytic system[22].

Table 4 Chain-end tetrad assignments and individual fractions of split peaks of carbon 3 in structure (I) for AS6 (PR-tetrad is defined by the steric relationships among methyl carbons 4′, 6′, 8′ and 10′)



Chemical shift	Assignment PR–tetrad
39.81	PR–mmm
39.87	PR–mmr
40.04	PR–mrr
40.08	PR–mrm
40.68	PR–rrm
40.70	PR–rrr
40.84	PR–rmr
40.90	PR–rmm

Regioirregularity

In *Figure 8* are shown the resonance regions from 31.0 to 39.0 ppm in ^{13}C n.m.r. and INEPT ($\Delta = 2/4J$, $3/4J$) spectra of AS6. From the INEPT ($3/4J$) spectrum obtained with $\Delta = 3/4J$, it is found that peaks h, i, and j

Table 5 The fractions of chain-end PR–triads and inner-chain triads for AS6

PR–triad	fraction observed	fraction calculated[a]	inner-chain triad	fraction observed
PR–mm	0.389	0.389	mm	0.406
PR–mr	0.164	0.178	mr	0.319
PR–rm	0.193	0.178		
PR–rr	0.254	0.254	rr	0.275

[a] Based on the two site model: $\omega = 0.750$, $\alpha = 0.785$, $\sigma = 0.289$

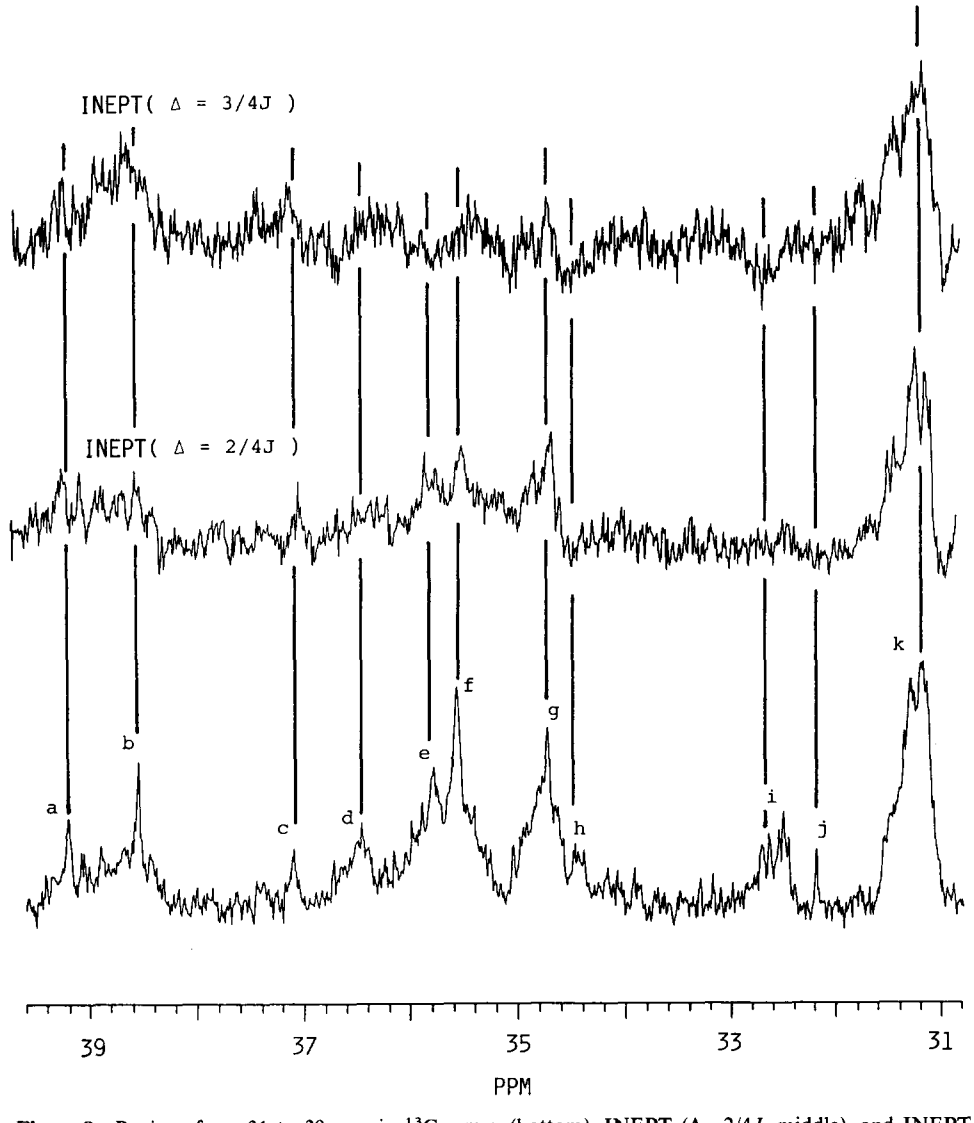
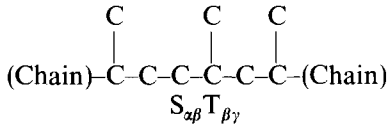


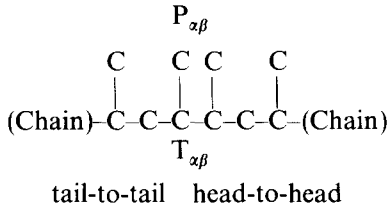
Figure 8 Regions from 31 to 39 ppm in ^{13}C n.m.r. (bottom), INEPT ($\Delta = 2/4J$, middle), and INEPT ($\Delta = 3/4J$, top) spectra of AS6. ^1H–^{13}C spin–spin coupling constant, J, is set to be 125 Hz

are methylene resonances and peak c is a methine resonance. INEPT spectrum obtained with $\Delta = 2/4J$, where only methine peaks are observed, indicates that peaks a, b, e, f, g and k are composed of methine resonances. Line shapes of peaks a, b, e, f, g, and k in the ^{13}C normal spectrum are different from those in the INEPT spectrum ($\Delta = 2/4J$). In the INEPT spectrum ($\Delta = 3/4J$), peaks a, b, e, f, and g are not observed clearly and the profile of the peak k is different from that in the ^{13}C n.m.r. and INEPT ($\Delta = 2/4J$) spectra. These results suggest that overlaps of methylene and methine resonances occur in this spectral region. According to previous assignments[24,25], peaks h, i and j are assigned to $S_{\gamma\alpha\beta\gamma}$, and $S_{\beta\alpha\beta\gamma}$ or $S_{\beta\alpha\beta\delta}$ carbons, respectively, and peaks a, b, e, f, g and k arise from resonances of $T_{\alpha\gamma}$ (peaks a and b), $T_{\alpha\beta}$ (peaks e, f, and g), and $T_{\beta\gamma}$ (peak k) carbons. The methine peak c has never been identified. Overlapping of methylene and methine resonances is supported by broad chemical shift bands of $S_{\alpha\beta}$ and $T_{\alpha\beta}$ carbons calculated via the gamma effect method[25]. In *Figure 2* are shown peaks of $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ carbons. Thus, present polypropylenes contain the following head-to-head and tail-to-tail arranged propylene units.

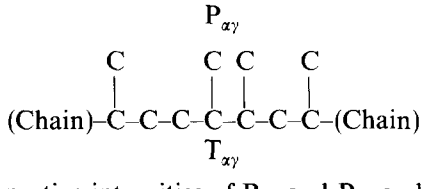
tail-to-tail



head-to-head



tail-to-tail head-to-head



The respective intensities of $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ carbon peaks are nearly equal to that of carbon 1 in the structure I. Therefore, the contents of head-to-head and tail-to-tail arranged units per chain are 10^{-3} order.

CONCLUSIONS

Microstructures in polypropylenes (A, B) prepared with $TiCl_4/MgCl_2$–Et_3Al and $Ti(OBu)Cl_3/MgCl_2$–Et_3Al catalytic systems were determined by ^{13}C and ^1H n.m.r. spectroscopy. Pentad tacticities of these samples were reasonably reproduced by the two-site model for the stereospecific polymerization. The optimum values of the model parameters elucidated that the displacement of Cl ligand around the titanium by OBu reduces the strength of the steric control at the IPP site. The chain-end structures were investigated by ^1H and ^{13}C n.m.r. spectra of boiling hexane soluble fractions (AS6 and BS6) of whole polymers. (^{13}C n.m.r. spectra of AS6 and BS6 are practically identical over the whole resonance regions.) The detected structures verified that the chain transfer of propagating species to the propylene monomer terminates the propagation reaction and regenerates initiating species. The two-site model analysis for the tactic structures at the chain end indicated that the steric controls of the initiation reactions at both sites are as strong as those of the propagation reactions. Further, it was found that these polypropylenes contain the regioirregularity such as head-to-head and tail-to-tail structures whose contents per chain are 10^{-3} order.

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