^{13}C n.m.r. spectral assignments and hexad comonomer sequence determination in stereoregular ethylene–propylene copolymer

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Hexad comonomer sequences in stereoregular ethylene–propylene (E–P) copolymer were analysed on the basis of ^{13}C nuclear magnetic resonance (n.m.r.) spectra. The chemical shifts of methylene resonances, which depend on the hexad comonomer sequences, were given by the chemical shifts calculation using the gamma effect on ^{13}C n.m.r. chemical shift and the Mark's rotational isomeric state model for E–P copolymer. From comparisons between the observed and calculated chemical shifts, the hexad methylene peaks were assigned. Further, the overlap between methine and methylene peaks was discriminated by an INEPT (insensitive nuclei enhancement by polarization transfer) experiment. From these analytical results, the tetrad sequence distribution in stereoregular E–P copolymer was accurately determined. The validity of our hexad assignments was confirmed by the good correspondence between the observed tetrad sequence distribution and that predicted by the two-site statistical model for the E–P copolymerization mechanism.

INTRODUCTION

Ethylene–propylene (E–P) copolymer is an industrially important material, because some of the properties of polypropylene products, such as impact strength, flexibility and transparency, are improved by copolymerization with ethylene. Tacticity and comonomer sequence distribution are both essential factors dominating the mechanical properties of E–P copolymers. ^{13}C nuclear magnetic resonance (n.m.r.) is the most powerful method of determining these two factors. In recent years, because of the improvement in sensitivity and resolution of n.m.r. spectra, we have been able to observe tactic- and comonomer-sequence dependent hexad or heptad resonances.

Chemical shift calculations using the gamma effect on the ^{13}C n.m.r. chemical shift and the rotational isomeric state model have been applied to the assignments of the ^{13}C n.m.r. spectra of polypropylene[1-6], regioirregular polypropylene[7], and poly(1-butene)[3]. The assignments of hexad and heptad tactic resonances have been given successfully by this calculation for atactic and isotactic polypropylenes[1,2]. These calculated results indicate that the stereosequence dependent ^{13}C chemical shifts of polypropylene can be explained by the different magnitude of the gamma effect on the carbon of interest.

The effect of the different stereosequences on the chemical shifts of the methylene carbons included in the respective ethylene units of regularly alternating E–P copolymer and E–P copolymer of low ethylene content has been investigated by chemical shift calculations via the gamma effect[8,9]. Recently, Cheng[10] has explained the complex ^{13}C n.m.r. spectral features of E–P rubbers as resulting from ethylene–propylene sequence placements, inverted propylene structures, and propylene tacticity. He has analysed the large amounts of chemical shift data for E–P copolymer and related compounds, and has proposed an empirical rule for E–P copolymers, which accounts for the substituent effect as well as for configurational sequences[11].

Nowadays, methylene peaks depending on up to hexad comonomer sequences can be resolved in the spectrum of stereoregular E–P copolymer. If these peaks can be assigned, more accurate determination of the tetrad sequence distribution in E–P copolymer and detailed investigation of the E–P copolymerization mechanism will become possible. However, the assignments of the hexad comonomer sequence dependent resonances in E–P copolymer have never been proposed. The pioneering empirical rules proposed by Paul and Grant[12] and by Lindeman and Adams[13] cannot reflect the effect of comonomer sequences longer than pentads. Ray et al.[14] and Carman et al.[15] have proposed the assignments widely used for sequential analyses[10,16-18] of E–P copolymers. Paxon and Randall[16] have confirmed the method for the quantitative n.m.r. measurement of E–P copolymer with a low ethylene content. These previous studies have allowed us to determine sequence distribution in E–P copolymer only as far as triad level,

because the previous assignments[14] have ambiguities in the PPEP, EPEP, PPEE and EPEE tetrads due to contributions from sequences longer than tetrad.

In a previous paper[19], we demonstrated that the gamma effect on [13]C n.m.r. chemical shifts is sensitive to the change of comonomer sequences in the stereoregular E–P copolymer. It has been confirmed that the chemical shift calculation via the gamma effect is applicable for the prediction of the ^{13}C chemical shifts of the comonomer sequence dependent resonances. In this study, we determine the assignments of hexad methylene peaks in the [13]C n.m.r. spectrum of stereoregular E–P copolymer on the basis of this calculation method. The chemical shifts of the hexad methylene resonances in $S_{\alpha\alpha}$, $S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\gamma\gamma}$ and $S_{\gamma\delta}$ carbons (where the nomenclature proposed by Carman *et al.*[20] is used for the designation of carbon types) are calculated in two cases: Case I, the comonomer sequences of interest are isolated in the isotactic polypropylene chain; case II, the comonomer sequences of interest are isolated in the polyethylene chain. Cases I and II correspond to the sequences in stereoregular E–P copolymers of low and high ethylene contents, respectively. From comparisons between the observed and calculated chemical shifts of methylene carbons of stereoregular E–P copolymer with a low ethylene content, the assignments of hexad resonances are provided. Further, the overlap between the methine $(T_{\beta\delta})$ and methylene $(S_{\gamma\gamma})$ peaks are discriminated by the ^{1}H decoupled INEPT (insensitive nuclei enhancement by polarization transfer) spectrum[21,22]. The width of the hexad peak splitting in $S_{\gamma\gamma}$ carbon is reasonably predicted by the gamma effect calculation. From these analytical results, tetrad sequence distribution in stereoregular E–P copolymer of low ethylene content is determined by using the relationship between tetrad and triad E–P comonomer sequences. The validity of our hexad assignments of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons is confirmed by comparison of the observed tetrad sequence distribution in E–P copolymer with that predicted by the two-site statistical model for the E–P copolymerization mechanism.

EXPERIMENTAL

Material

The E–P copolymers of low ethylene content, PE-1 and PE-2, prepared with the δ-TiCl$_3$/Et$_2$AlCl catalytic system were generous gifts from Tokuyama Soda Co. Ltd. It was confirmed that head-to-head and tail-to-tail arranged propylene units are undetected by [13]C n.m.r. spectra of these samples, referring to the study of regioirregularity in the chain[7,23,24]. The ethylene contents of PE-1 and PE-2 were determined to be 0.8 and 7.0 mol % from the relative peak areas of methylene resonances.

N.m.r. measurements

[13]C n.m.r. spectra were recorded at 120°C on a JEOL GSX-270 spectrometer operated at 67.8 MHz. The sample solutions in a 10 mm o.d. glass tube were prepared in o-dichlorobenzene (90 vol %)/benzene-d$_6$ (10 vol %) to give 0.1 g (polymer) cm^{-3} (solvent). Benzene-d$_6$ provided the signal for the [2]H n.m.r. internal lock. In all measurements broadband noise decoupling was used to remove [13]C–[1]H couplings, the pulse angle was 90°, the pulse repetition time was 15 s, and 10 000 free induction

decays were stored in 32 000 data points using a spectral window of 10 000 Hz. Hexamethyldisiloxane was used as an internal reference (2.03 ppm downfield from the resonance of tetramethylsilane). [1]H decoupled INEPT[21,22] method, in which the delay time (Δ) before data acquisition is equal to $3/4J$ (where J is the [1]H–[13]C spin–spin coupling constant), was used to distinguish methylene peaks from methine or methyl peaks.

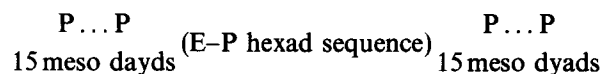### [13]C n.m.r. chemical shift calculations

[13]C n.m.r. chemical shifts of the hexad methylene resonances in stereoregular E–P copolymer were calculated using the gamma effect on the [13]C n.m.r. chemical shift and the Mark rotational isomeric state (RIS) model[25] for E–P copolymer. In the RIS model, the value of the statistical weight, η, was taken to be 1.0, and the values of four-bond pentane interferences (ω) and three bond *gauche* interactions (τ)[26] were characterized with $E_\omega = 8400$ J mol^{-1} and $E_\tau = 2000$ J mol^{-1}, respectively, Tonelli[1] proposed that the value of the gamma effects of methine carbons on methylene carbons is -3.7 ppm in a study of ^{13}C chemical shift calculations of various stereoisomers in polypropylene. In this study, the value of -3.7 ppm was assumed as the gamma effect of methyl and methylene carbons on the ^{13}C chemical shift of methylene carbons in E–P copolymer. The temperature assumed in the calculation was 120°C, corresponding to the experimental conditions.
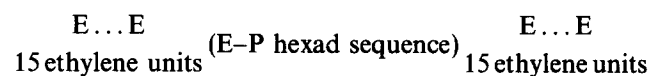
RESULTS AND DISCUSSION

Chemical shift calculations

The chemical shifts due to the gamma effects for the hexad methylene resonances were calculated using the gamma effect on the ^{13}C chemical shift and Mark's RIS model in two cases:

Case I:

$$\underset{\text{15 meso dyads}}{\text{P}\ldots\text{P}}\ \text{(E–P hexad sequence)}\ \underset{\text{15 meso dyads}}{\text{P}\ldots\text{P}}$$

Case II:

$$\underset{\text{15 ethylene units}}{\text{E}\ldots\text{E}}\ \text{(E–P hexad sequence)}\ \underset{\text{15 ethylene units}}{\text{E}\ldots\text{E}}$$

where P and E denote monomeric units of propylene and ethylene, respectively.

In Case I comonomer sequences are sandwiched between two isotactic polypropylene sequences, each of which is composed of 15 meso dyads. In Case II the comonomer sequences are between two polyethylene sequences, each composed of 15 ethylene units. These surrounding sequences simulate propylene and ethylene rich chains. Thus Cases I and II correspond to the sequences in E–P copolymers of low and high ethylene contents, respectively.

Table 1 shows the calculated chemical shifts due to the gamma effect for the hexad and pentad methylene resonances of stereoregular E–P copolymer. By using these calculated values, the chemical shift differences among the methylene carbons arising from the differences in hexad comonomer sequences are shown by stick

Table 1 Calculated ^{13}C n.m.r. chemical shifts due to the gamma effect for methylene carbons in ethylene–propylene copolymer

| Carbon type	No.	Sequence type	Chemical shift due to the gamma effect		
			Case I (ppm)	Case II (ppm)	Case I – case II (ppm)
$S_{\alpha\alpha}$	1	PPPPPP	−3.582	−3.406	−0.176
	2	PPPPPE	−3.350	−3.254	−0.096
	3	EPPPPE	−3.114	−3.100	−0.014
	4	PPPPEP	−3.544	−3.441	−0.103
	5	PPPPEE	−3.536	−3.439	−0.097
	6	EPPPEP	−3.288	−3.273	−0.015
	7	EPPPEE	−3.280	−3.271	−0.009
	8	PEPPEP	−3.406	−3.390	−0.016
	9	PEPPEE	−3.395	−3.386	−0.009
	10	EEPPEE	−3.385	−3.382	−0.003
$S_{\alpha\gamma}$	11	PPPEPP	−3.125	−3.031	−0.094
	12	PPPEPE	−3.173	−3.069	−0.104
	13	EPPEPP	−2.843	−2.843	0.0
	14	EPPEPE	−2.889	−2.881	−0.008
	15	PEPEPP	−2.805	−2.805	0.0
	16	PEPEPE	−2.850	−2.842	−0.008
	17	EEPEPP	−2.789	−2.797	0.008
	18	EEPEPE	−2.834	−2.834	0.0
$S_{\alpha\delta}$	19	PPPEEP	−3.669	−3.565	−0.104
	20	PPPEEE	−3.681	−3.576	−0.105
	21	EPPEEP	−3.384	−3.376	−0.008
	22	EPPEEE	−3.396	−3.387	−0.009
	23	PEPEEP	−3.340	−3.331	−0.009
	24	PEPEEE	−3.351	−3.342	−0.009
	25	EEPEEP	−3.323	−3.323	0.0
	26	EEPEEE	−3.335	−3.334	−0.001
$S_{\beta\beta}$	27	PPEPP	−8.944	−8.885	−0.059
	28	PPEPE	−8.793	−8.760	−0.033
	29	EPEPE	−8.644	−8.636	−0.008
$S_{\beta\delta}$	30	PPEEP	−6.013	−5.979	−0.034
	31	PPEEE	−5.941	−5.911	−0.030
	32	EPEEP	−5.858	−5.855	−0.003
	33	EPEEE	−5.792	−5.786	−0.006
$S_{\gamma\gamma}$	34	PPEEPP	−1.903	−1.918	0.015
	35	PPEEPE	−1.939	−1.950	0.011
	36	EPEEPE	−1.979	−1.981	0.002
$S_{\gamma\delta}$	37	PPEEEP	−2.410	−2.419	0.009
	38	PPEEEE	−2.422	−2.429	0.007
	39	EPEEEP	−2.448	−2.450	0.002
	40	EPEEEE	−2.459	−2.460	0.001
$S_{\delta\delta}$	41	PEEEP	−3.087	−3.076	−0.011
	42	PEEEE	−3.014	−3.007	−0.007
	43	EEEEE	−2.911	−2.938	0.027
	44	PEEEEP	−2.916	−2.918	0.002
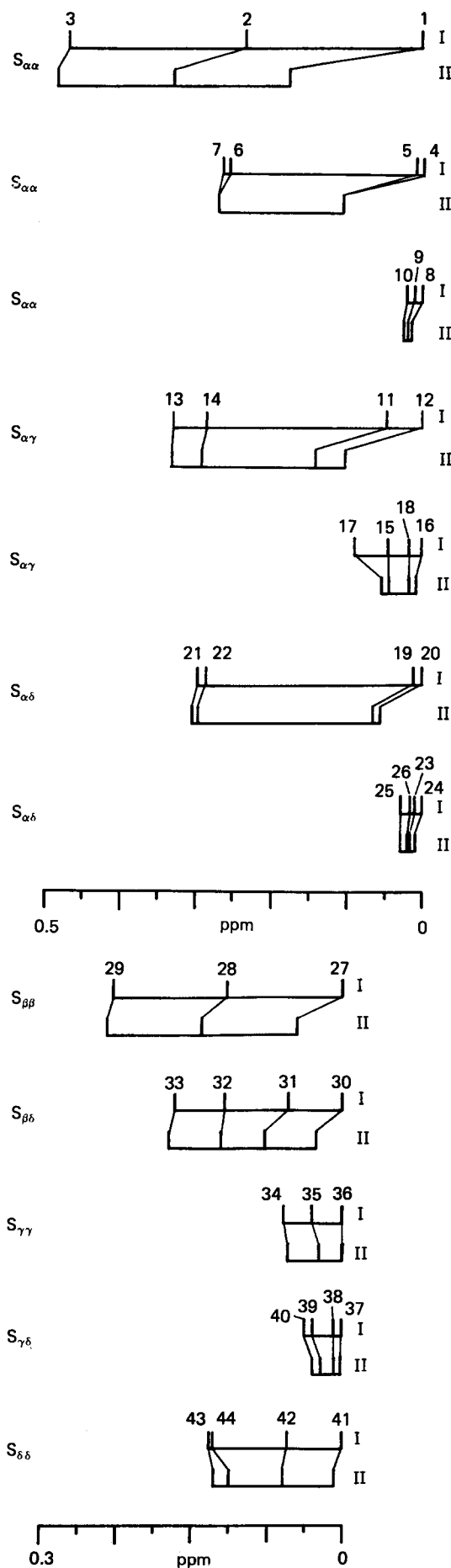
Figure 1 Comonomer sequence dependent chemical shift differences in the respective methylene carbons of ethylene–propylene copolymer. I, case I; II, case II (explained in text)

spectra in *Figure 1*. For all types of methylene carbons, the chemical shift differences among hexad and pentad sequence dependent resonances in Case I are larger than those in Case II, as shown in *Figure 1*. This suggests that the methyl groups of the propylene unit in the surrounding sequences influence the chemical shifts due to the gamma effect for the methylene carbons of interest through long-range conformational changes of the bonds in Case I, while such an influence is absent in Case II. As shown by the stick spectra of $S_{\alpha\alpha}$ carbons in *Figure 1*, the chemical shift differences among the resonances of relatively ethylene rich sequences (EPPE-centred hexads) are much smaller than those among the resonances of propylene rich sequences (PPPP- and PPPE-centred hexads) in both cases. Similar trends are found for $S_{\alpha\gamma}$

Table 2 Chemical shifts (v) of $S_{\alpha\alpha}$, $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons in ethylene–propylene copolymer and chemical shift differences (Δv_e) among these carbons calculated by the Lindeman–Adams empirical rule[13]

Carbon type	Sequence type	v (ppm)	$\Delta v_e{}^a$ (ppm)
$S_{\alpha\alpha}$	PPPP	44.36	0.0
	PPPE	44.11	−0.25
	EPPE	43.86	−0.25
$S_{\alpha\gamma}$	PPEP	37.41	0.0
	EPEP	37.16	−0.25
$S_{\alpha\delta}$	PPEE	37.16	0.0
	EPEE	36.91	−0.25

^{a} Expressed relative to the chemical shift of the peak appearing at the lowest field

carbons in the PPEP- and EPEP-centred hexads, and $S_{\alpha\delta}$ carbons in the PPEE- and EPEE-centred hexads. Further, as shown by the hexads of $S_{\alpha\alpha}$, $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons in Table 1, the differences (Case I − Case II) between the calculated chemical shifts due to the gamma effect for Cases I and II in the hexads with continuous* propylene sequences (PPPPP and PPPPE of $S_{\alpha\alpha}$, PPPEPP and PPPEPE of $S_{\alpha\gamma}$, PPPEEP and PPPEEE of $S_{\alpha\delta}$) are much larger than those in the hexads with interrupted propylene sequences (EPPPPE of $S_{\alpha\alpha}$, EPPEPP of $S_{\alpha\gamma}$, EPPEEP of $S_{\alpha\delta}$).

These results indicate that the methyl substituents in the surrounding sequences influence the chemical shifts due to the gamma effect strongly through the propylene unit, but insufficiently through the ethylene unit. Cases I and II are extremely simplified chains of copolymers of low and high ethylene contents. The chemical shifts of the ethylene rich sequences are predicted to be unchanged with an increase of the ethylene content and, thus, are applicable to the assignments of the ethylene rich sequences in E–P copolymer of low and high ethylene contents, respectively. If the surrounding sequences are composed of ethylene and propylene units, the chemical shifts of the methylene resonances of propylene rich sequences are predicted to be in the intermediate regions between these two cases.

In this study, we assigned the hexad methylene resonances in E–P copolymer (sample PE-2) with an ethylene content of 7.0 mol% using the chemical shifts calculated for Case I. The propylene rich sequences in Case II were neglected, because the fraction of propylene rich chain should be larger than that of ethylene rich chain, and the fraction of propylene rich sequences in the ethylene rich chain should be much smaller than that in the propylene rich chain.

The other effect which can cause chemical shift differences among the comonomer sequence dependent resonances is the four-bond effect. We estimated the four-bond effect by using the Lindeman–Adams empirical rule[13]. This effect should be taken into consideration for the prediction of the chemical shifts of $S_{\alpha\alpha}$ carbons in the PPPP-, PPPE-, and EPEE-centred hexads, $S_{\alpha\gamma}$ carbons in the PPEP- and EPEP-centred hexads and $S_{\alpha\delta}$ carbons in the PPEE- and EPEE-centred hexads. The chemical shift differences (Δv_c) arising from the four-bond effect are shown in Table 2.

* The term 'continuous' means that a continuous propylene sequence (PPP) appears on at least one side of the central methylene carbon of interest

Assignments of hexad resonances

Figure 2 shows the ^{13}C n.m.r. spectra of the samples PE-1 and PE-2. Using the assignments of Ray et al.[14], triad comonomer sequence distributions were determined on the basis of the method proposed by Kakugo et al.[18]. Tables 3 and 4 show the results of the area measurements and the determined triad sequence distributions. The analytical results for PE-1 indicate that all ethylene units are isolated in the polypropylene sequences, because the peaks of triad and tetrad resonances containing more than two ethylene units were undetected.

Figure 3 shows the $S_{\beta\beta}$ and $S_{\alpha\gamma}$ carbon resonance regions in the ^{13}C n.m.r. spectra of PE-1. Both carbons show the respective single-peak resonances with a sharp line shape. Referring to the observed spectrum of the model compound for the isolated ethylene unit in E–P copolymer[27] and the chemical shift calculation for the methylene carbons in the isolated ethylene unit sandwiched by polypropylene sequences[9], it is confirmed that the tacticities of the surrounding propylene sequences are isotactic and the configuration determined by the steric relationship between the methyl substituents across the isolated ethylene unit is only meso (m) in PE-1.
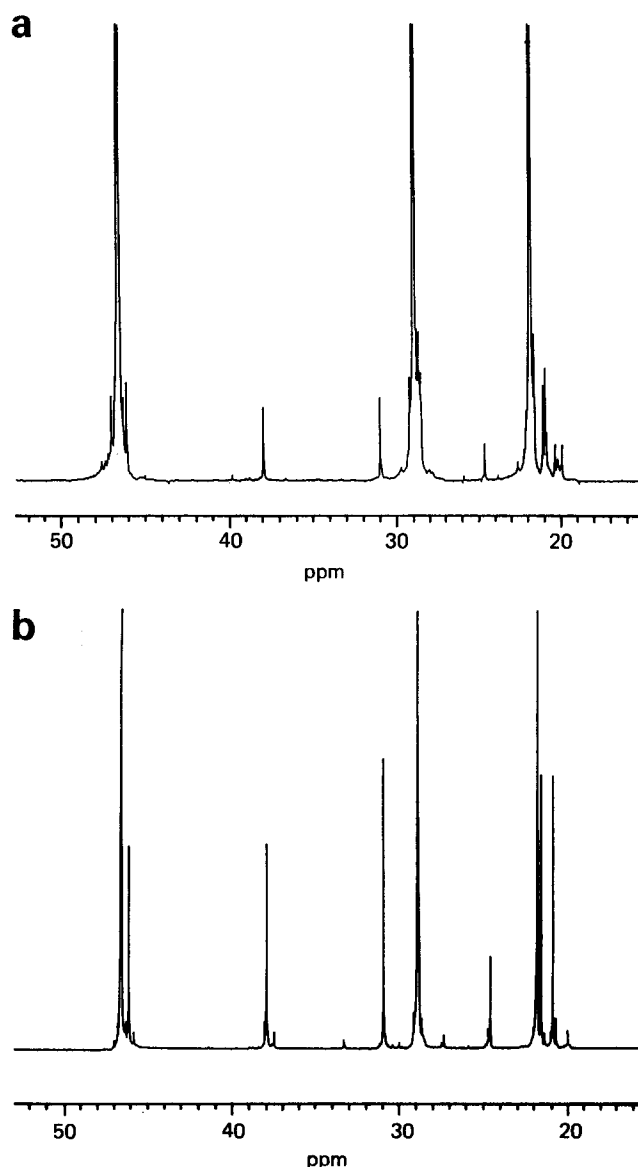

a

b

Figure 2 ^{13}C n.m.r. spectra of (a) PE-1 and (b) PE-2

Table 3 Relative peak intensities for samples PE-1 and PE-2

Carbon type	Sequence type	Area[a]	
		PE-1	PE-2
$S_{\alpha\alpha}$	PPPP	0.320	0.262
	PPPE	0.005	0.031
	EPPE	0.0	0.002
$S_{\alpha\gamma}$	PPEP + EPEP	0.005	0.039
$S_{\alpha\delta}$	PPEE + EPEE	0.0	0.004
$S_{\beta\beta}$	PEP	0.003	0.020
$S_{\beta\delta}$	PEE	0.0	0.004
$S_{\gamma\gamma}$[b]	PEEP	0.0	0.001
$S_{\gamma\delta}$	PEEE	0.0	0.001
$S_{\delta\delta}$	EEE$_n$	0.0	0.001
$T_{\beta\beta}$	PPP	0.328	0.282
$T_{\beta\delta}$	PPE	0.005	0.038
$T_{\delta\delta}$	EPE	0.0	0.002
$P_{\beta\beta}$	PPP + PPE + EPE	0.338	0.314

[a] Intensities were determined from the peak areas and are normalized to 1.00

[b] $[S_{\gamma\gamma}] = 0.5\ ([S_{\beta\delta}] - [S_{\gamma\delta}])$

Table 4 n-ad distributions for samples PE-1 and PE-2

n-ad	PE-1 obs.	PE-2		
		Obs.	Calc. (model M)	Calc. (model MM)
P	0.992	0.930	0.930	0.930
E	0.008	0.070	0.070	0.070
PP	0.984	0.868	0.868	0.868
PE	0.016	0.125	0.125	0.125
EE	0.0	0.007	0.007	0.007
PPP	0.976	0.813	0.810	0.813
PPE	0.016	0.111	0.116	0.111
EPE	0.0	0.007	0.004	0.007
PEP	0.008	0.057	0.056	0.057
PEE	0.0	0.010	0.013	0.010
EEE	0.0	0.002	0.001	0.002
SS[a]/10^{-4}			0.54	0.0

[a] Sum of the squares of the deviations between the observed and calculated triad sequence distributions

The structure of the isolated ethylene unit is as shown in Scheme 1.

polypropylene chain   ethylene   polypropylene chain
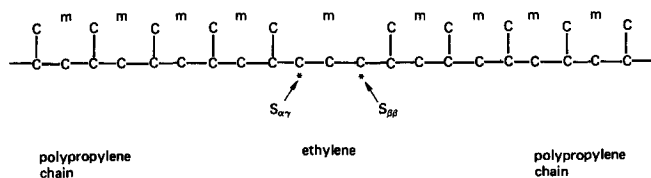
Scheme 1

As shown by the triad sequence distribution in *Table 4*, the PPP sequence is much more abundant than the other sequences in PE-2. Thus we can safely assume that in PE-2 the comonomer sequences of interest are isolated in the isotactic polypropylene sequences and that the configuration determined by the steric relationship between the methyl substituents across one and more than two ethylene units is only meso. This assumption corresponds to the calculation in Case I. So it is reasonable that the highest peak in each resonance region in the spectrum of PE-2 is attributable to the resonance of the most propylene(P)-rich sequence. The chemical shift differences predicted by the gamma effect calculation are

expressed in a unified way by referring to the peak of the central carbon in the most P-rich sequence in each resonance region. The predicted shifts are shown as stick spectra in *Figures 4–10*.

Figure 4 shows the $S_{\beta\beta}$ region of the spectrum of PE-2. The assignments of the split peaks are shown in *Table 5* and in *Figure 4*. Comparing the observed and calculated spectra shows that the observed chemical shift differences (Δv) among PEP-centred pentads correspond well with those (Δv_y) predicted by the gamma effect calculation. Further, our assignments agree with those proposed by Ray *et al.*[14]. The chemical shift calculation via the gamma effect also provides reasonable assignments for the split peaks in the $S_{\beta\delta}$ region, as shown in *Table 6* and *Figure 5*. These results assure the excellent applicability of the chemical shift calculation via the gamma-effect for the prediction of the comonomer sequence dependent chemical shifts.

Figure 6 shows the $S_{\alpha\alpha}$ region in the spectrum of PE-2 and the stick spectrum of the calculated chemical shifts of $S_{\alpha\alpha}$ carbons. *Table 7* shows the observed and calculated
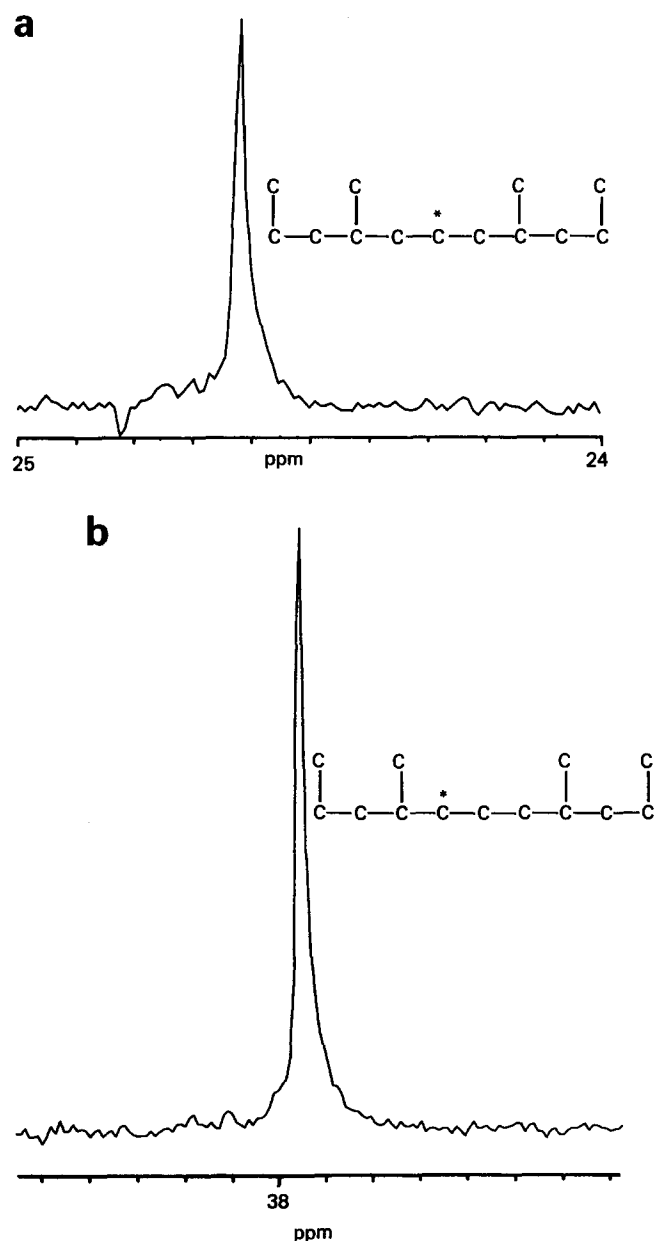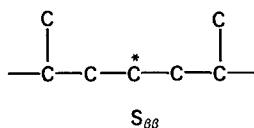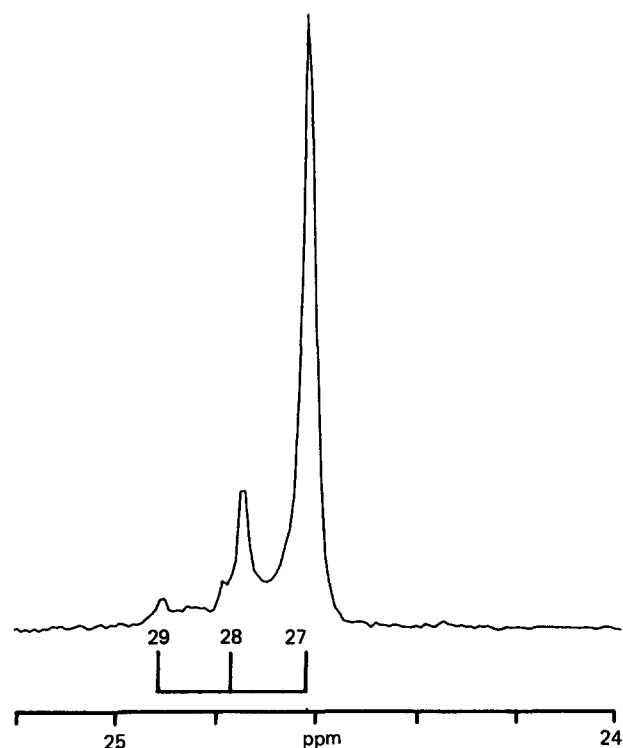
a

b

Figure 3 ^{13}C n.m.r. spectra of (a) $S_{\beta\beta}$ and (b) $S_{\alpha\gamma}$ resonance region of PE-1

Table 5 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of S$_{\beta\beta}$ carbons

```
        C              C
        |              |
   —C—C—C—C—C—
              *
           S$_{\beta\beta}$
```

No.	Sequence type	Δv$_\gamma$^{a,b} (ppm)	v (ppm)	Δv$_{obs.}$^{b} (ppm)
27	(P)PPEPP(P)	0.0	24.617	0.0
28	(P)PPEPE(P)	0.151	24.743	0.126
29	(P)EPEPE(P)	0.300	24.905	0.288

^{a} Calculated by the chemical shift calculation via the gamma effect
^{b} Chemical shift differences are expressed relative to the peak of PPEPP resonance, which is set to be 0.00 ppm
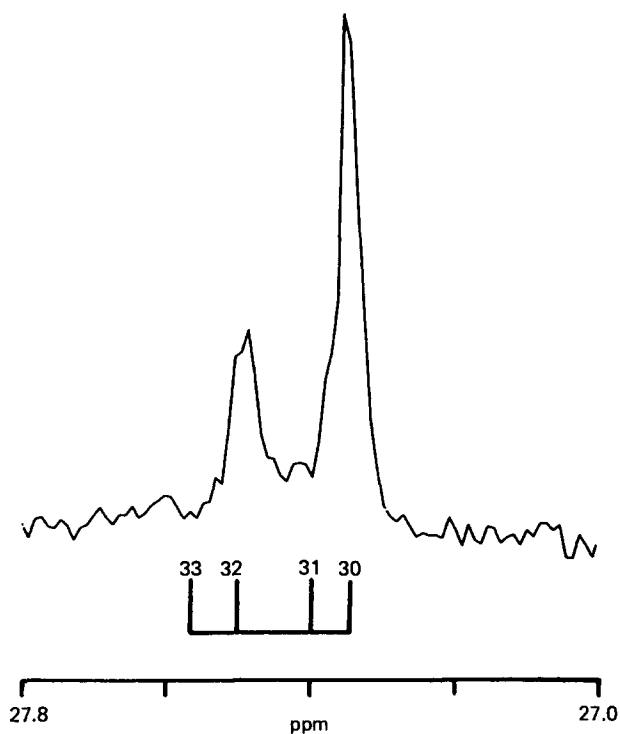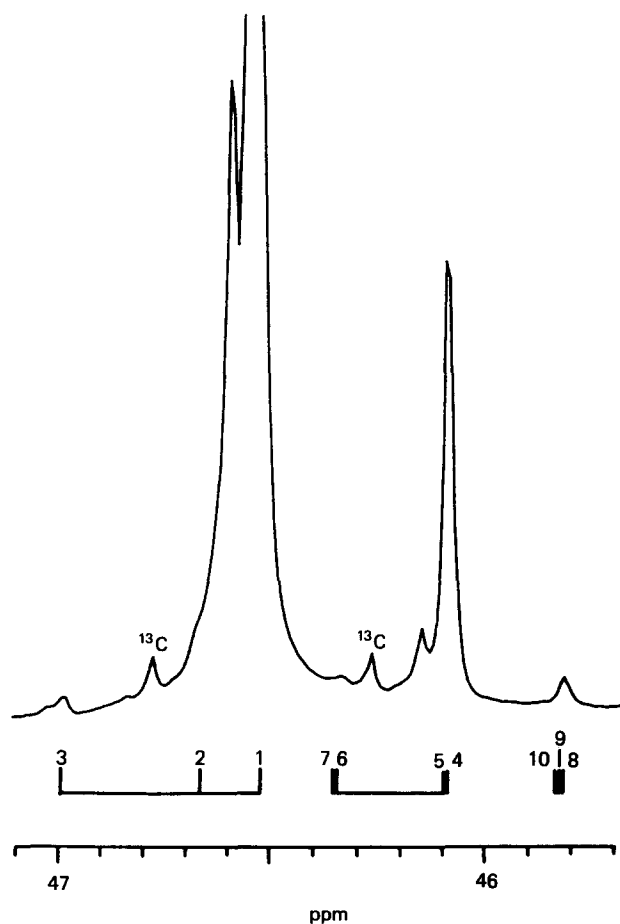

Figure 4 ^{13}C n.m.r. spectrum of the S$_{\beta\beta}$ resonance region of PE-2. The predicted chemical shifts are shown as the stick spectrum at the bottom of the figure. Peak assignments are shown in *Table 5*

Table 6 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of S$_{\beta\delta}$ carbons

```
        C                    C
        |                    |
   —C—C—C—C—C—C—C—
              *
           S$_{\beta\delta}$
```
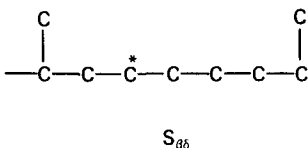
No.	Sequence type	Δv$_\gamma$^{a,b} (ppm)	v (ppm)	Δv$_{obs}$^{b} (ppm)
30	(P)PPEEP(P)	0.0	27.349	0.0
31	(P)PPEEE(P)	0.072	27.405	0.056
32	(P)EPEEP(P)	0.155	27.483	0.134
33	(P)EPEEE(P)	0.221	–	–

^{a} Calculated by the chemical shift calculation via the gamma effect
^{b} Chemical shift differences are expressed relative to the peak of PPEEP resonance, which is set to be 0.00 ppm
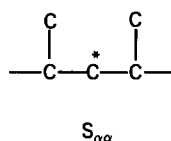

Figure 5 ^{13}C n.m.r. spectrum of the S$_{\beta\delta}$ resonance region of PE-2. The predicted chemical shifts are shown as the stick spectrum at the bottom of the figure. Peak assignments are shown in *Table 6*

Figure 6 ^{13}C n.m.r. spectrum of the S$_{\alpha\alpha}$ resonance region of PE-2. The predicted chemical shifts are shown as the stick spectrum at the bottom of the figure. The ^{13}C satellite peaks are marked as '^{13}C'. Peak assignments are shown in *Table 7*

Table 7 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of $S_{\alpha\alpha}$ carbons

$$\begin{array}{ccc} & \overset{\displaystyle C}{\underset{\displaystyle |}{}} & \overset{\displaystyle C}{\underset{\displaystyle |}{}} \\ -C & \!\!-C\!\!\underset{*}{-} & C- \end{array}$$

$S_{\alpha\alpha}$

Carbon no.	Sequence type: hexad	Δv_γ [a,b] (ppm)	v (ppm)	$\Delta v_{obs.}$ [b] (ppm)
1	PPPPPP	0.000	46.531	0.000
2	PPPPPE	0.232	46.593	0.062
3	EPPPPE	0.468	46.989	0.458
4	PPPPEP	0.000	46.093	0.000
5	PPPPEE	0.008	46.153	0.060
6	EPPPEP	0.256	46.342	0.249
7	EPPPEE	0.264	46.342	0.249
8	PEPPEP	0.000	45.821	0.000
9	EEPPEP	0.011	–	–
10	EEPPEE	0.021	–	–

[a] Calculated by the chemical shift calculation via the gamma effect
[b] Chemical shift differences are expressed relative to the peak of PPPPPP, PPPPEP and PEPPEP resonances, which are set to be 0.00 ppm
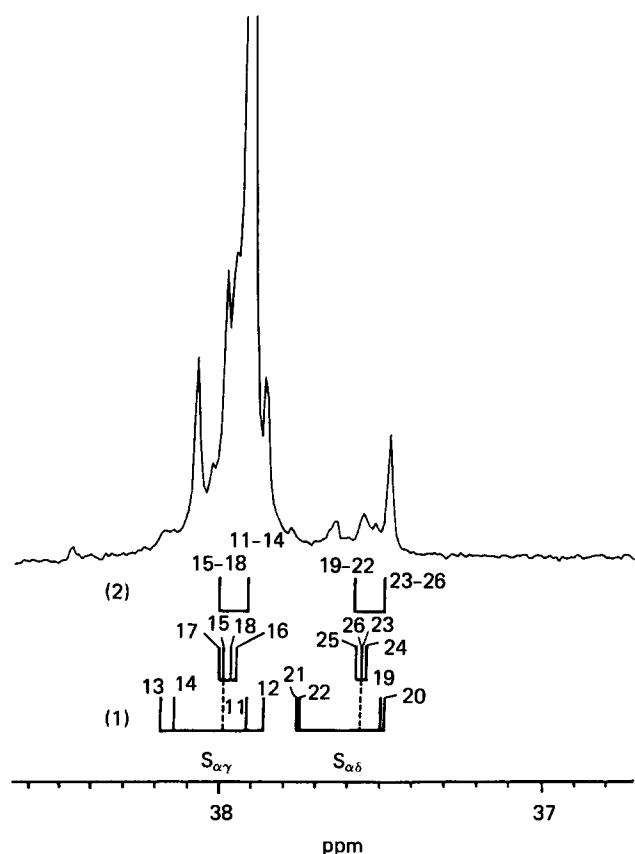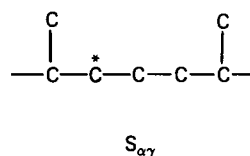

Figure 7 [13]C n.m.r. spectrum of the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ resonance regions of PE-2. The assignments by Ray et al.[14] (top) and the chemical shifts predicted by us (bottom) are shown as the stick spectra at the bottom of the figure. Assignments by Ray et al.[14]: 11–14, PPEP$_E$; 15–18, EPEP$_E$; 19–22, PPEE$_n$; 23–26, EPEE$_n$. Assignments from our study are shown in *Tables 8* and *9*

chemical shift differences and the peak assignments. The chemical shift differences among the comonomer sequence dependent hexads are predicted by contributions from the gamma effect only, because the observed peaks of PPPP, PPPE and EPPE tetrads are
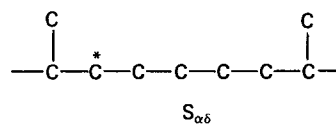
clearly separated, referring to the assignments by Ra*y et al.*[14], and the gamma effect calculation indicates that PPPP-, PPPE- and EPPE-centred hexads do not overlap with each other, as shown by the stick spectrum in *Figure 6*. Our hexad assignments of the PPPPPP, PPPPEP and PEPPEP resonances are consistent with the tetrad assignments of PPPP, PPPE and EPPE resonances proposed by Ray *et al.*[14].

Figure 7 shows the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ regions in the spectrum of PE-2. *Tables 8* and *9* show the predicted chemical shift differences (Δv_s), which are calculated from the contributions of the gamma effect (Δv_γ) and the four-bond effect (Δv_e) in Lindeman–Adams' empirical rule[13]. The chemical shifts predicted by us and those proposed by Ray *et al.*[14] are shown by the stick spectra in *Figure 7*. A number of peaks observed in these regions are unidentified from the tetrad assignments and are attributable to the hexad resonances. The chemical shifts of EPPEPP and EPPEPE hexads are predicted from our

Table 8 Observed chemical shifts (v) and the observed and the calculated chemical shift differences (Δv) of $S_{\alpha\gamma}$ carbons

$$\begin{array}{ccccc} \overset{\displaystyle C}{\underset{\displaystyle |}{}} & & & & \overset{\displaystyle C}{\underset{\displaystyle |}{}} \\ -C & \!\!-\underset{*}{C}\!\!- & C & \!\!-C\!\!- & C- \end{array}$$

$S_{\alpha\gamma}$

No.	Sequence type	Δv_e [a,b] (ppm)	Δv_γ [b,c] (ppm)	Δv_s [b,d] (ppm)	v (ppm)	Δv_{obs} [b] (ppm)
11	(P)PPPEPP(P)	0.0	0.0	0.0	37.941	0.0
12	(P)PPPEPE(P)	0.0	−0.048	−0.048	37.887	−0.054
13	(P)EPPEPP(P)	0.0	0.284	0.284	38.094	0.153
14	(P)EPPEPE(P)	0.0	0.234	0.234	38.049	0.108
15	(P)PEPEPP(P)	−0.25	0.320	0.070	38.004	0.063
16	(P)PEPEPE(P)	−0.25	0.275	0.025	37.977	0.036
17	(P)EEPEPP(P)	−0.25	0.336	0.086	38.004	0.063
18	(P)EEPEPE(P)	−0.25	0.291	0.041	37.977	0.036

[a] Calculated by the Lindeman–Adams empirical rule[13]
[b] Chemical shift differences are expressed relative to the peak of PPPEPP resonance, which is set to be 0.00 ppm
[c] Calculated by the chemical shift calculation via the gamma effect
[d] Sum of the chemical shift differences Δv_γ and Δv_e: $\Delta v_s = \Delta v_\gamma + \Delta v_e$

Table 9 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of $S_{\alpha\delta}$ carbons

$$\begin{array}{ccccccc} \overset{\displaystyle C}{\underset{\displaystyle |}{}} & & & & & & \overset{\displaystyle C}{\underset{\displaystyle |}{}} \\ -C & \!\!-\underset{*}{C}\!\!- & C & \!\!-C\!\!- & C & \!\!-C\!\!- & C- \end{array}$$

$S_{\alpha\delta}$

No.	Sequence type	Δv_e [a,b] (ppm)	Δv_γ [b,c] (ppm)	Δv_s [b,d] (ppm)	v (ppm)	Δv_{obs} [b] (ppm)
19	(P)PPPEEP(P)	0.0	0.0	0.0	37.501	0.0
20	(P)PPPEEE(P)	0.0	0.012	0.012	37.501	0.0
21	(P)EPPEEP(P)	0.0	0.285	0.285	37.672	0.171
22	(P)EPPEEE(P)	0.0	0.273	0.273	37.672	0.171
23	(P)PEPEEP(P)	−0.25	0.329	0.079	37.582	0.081
24	(P)PEPEEE(P)	−0.25	0.318	0.068	37.546	0.045
25	(P)EEPEEP(P)	−0.25	0.346	0.096	37.582	0.081
26	(P)EEPEEE(P)	−0.25	0.334	0.084	37.582	0.081

[a] Calculated by the Lindeman–Adams empirical rule[13]
[b] Chemical shifts are expressed relative to the peak of PPPEEP resonance, which is set to be 0.00 ppm
[c] Calculated by the chemical shift calculation via the gamma effect
[d] Sum of the chemical shift differences Δv_γ and Δv_e: $\Delta v_s = \Delta v_\gamma + \Delta v_e$
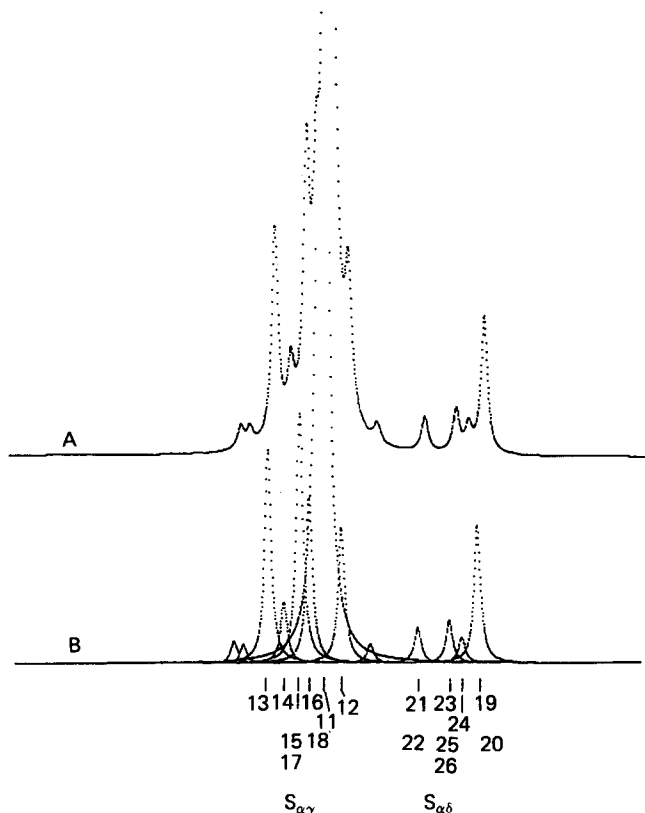
Figure 8 Curve fitting results for the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ resonances of PE-2: A, reproduced spectrum; B, results of curve resolution
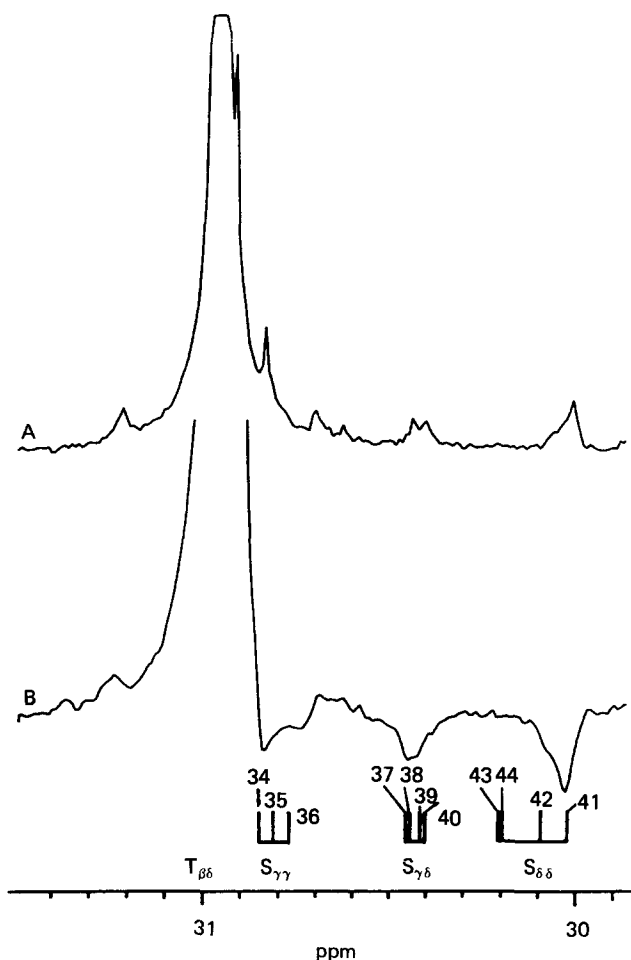

Figure 9 A, ^{13}C n.m.r. and, B, ^{1}H decoupled INEPT ($\Delta = 3/4J$) spectra of the $T_{\beta\delta}$, $S_{\gamma\gamma}$, $S_{\gamma\delta}$ and $S_{\delta\delta}$ resonance regions of PE-2. The predicted chemical shifts are shown as the stick spectra at the bottom of the figure. Peak assignments are shown in *Tables 10–12*

calculation to be in the lower field region from the EPEP-centred hexads. Thus our assignments of PPEP-centred resonances in *Table 8* differ from the previous assignments by Ray *et al.*[14]. On the basis of hexad assignments, the fractions of PPEP, EPEP, PPEE and EPEE tetrads were determined separately by the curve resolution method[28], as shown in *Figure 8*.

Figure 9 shows the $T_{\beta\delta}$, $S_{\gamma\gamma}$, $S_{\gamma\delta}$ and $S_{\delta\delta}$ resonance regions in the spectrum of PE-2. The overlap of $T_{\beta\delta}$ and $S_{\gamma\gamma}$ resonances is resolved in the ^{1}H decoupled INEPT spectrum with $\Delta = 3/4J$, as shown in *Figure 9*. *Table 10* and the stick spectra in *Figure 9* show the calculated chemical shift differences among PEEP-centred hexads. The width of the hexad peak splitting in $S_{\gamma\gamma}$ carbon is reproduced well from the calculated values. The assignments of these hexad peaks in $S_{\gamma\gamma}$ carbon are also shown in *Table 10*. The areas of $S_{\gamma\gamma}$ resonances were determined by the curve resolution method as shown in *Figure 10*. The intensities of $S_{\gamma\gamma}$ peaks should satisfy the relation[14]

$$[S_{\gamma\gamma}] = 0.5([S_{\beta\delta}] - [S_{\gamma\delta}])$$

The observed ratio of $[S_{\gamma\gamma}]$ to $0.5([S_{\beta\delta}] - [S_{\gamma\delta}])$ is approximately equal to unity (1.10), supporting the validity of our assignments of $S_{\gamma\gamma}$ peaks. *Figure 9* also shows the calculated chemical shifts of $S_{\gamma\delta}$ and $S_{\delta\delta}$ carbons as stick spectra on the basis of the chemical shift differences shown in *Tables 11* and *12*. The assignments of the split peaks in $S_{\gamma\delta}$ and $S_{\delta\delta}$ regions are summarized in *Tables 11* and *12*, respectively.

Tetrad sequence distribution

On the basis of our assignments, the tetrad sequence distribution in PE-2 is accurately determined using the curve resolution method with the aid of the relationship

$$[EEE] = [EEEE] + 0.5[PEEE]$$

where

$$[EEE] = 0.5[S_{\delta\delta}] + 0.25[S_{\gamma\delta}]$$

and

$$[PEEE] = [S_{\gamma\gamma}]$$

as shown in *Table 13*. Further, we investigated the statistical model for the ethylene–propylene copolymerization mechanism in detail on the basis of the tetrad sequence distribution. Since the ratios [EPPE]/[PEEP]

Table 10 Observed chemical shifts (ν) and the observed and calculated chemical shift differences ($\Delta\nu$) of $S_{\gamma\gamma}$ carbons

$S_{\gamma\gamma}$

No.	Sequence type	$\Delta\nu_{\gamma}^{a,b}$ (ppm)	ν (ppm)	$\Delta\nu_{obs}^{b}$ (ppm)
34	(P)PPEEPP(P)	0.0	30.844	0.0
35	(P)PPEEPE(P)	−0.036	30.790	−0.059
36	(P)EPEEPE(P)	−0.076	–	–

[a] Calculated by the chemical shift calculation via the gamma effect
[b] Chemical shift differences are expressed relative to the peak of PPEEPP resonance, which is set to be 0.00 ppm
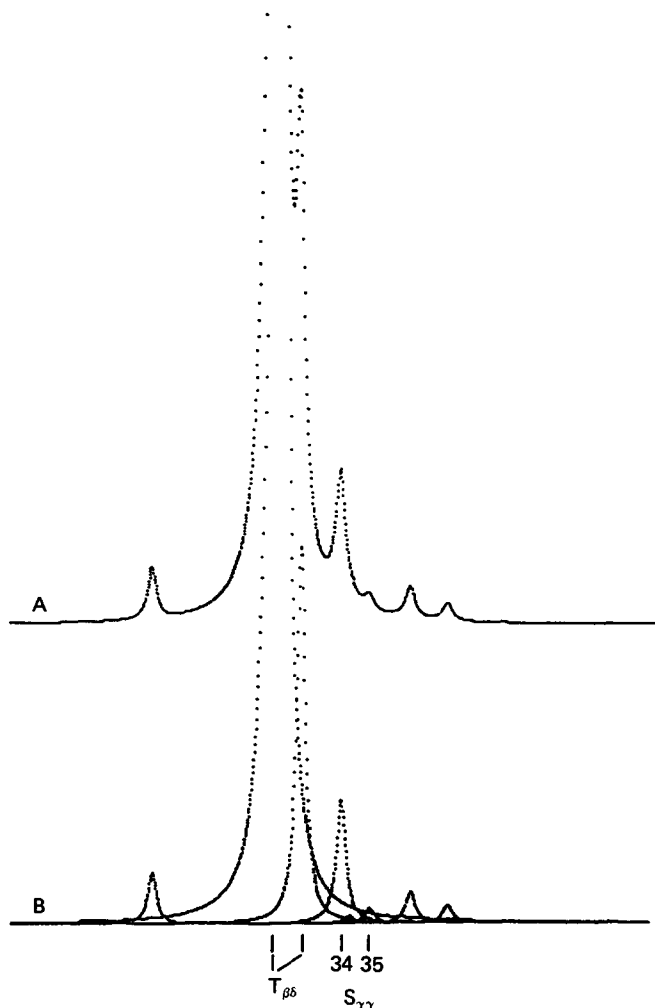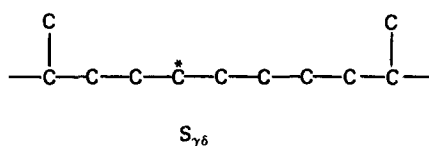
Figure 10 Curve fitting results for the $T_{\beta\delta}$ and $S_{\gamma\gamma}$ resonances: A, Reproduced spectrum; B, results of curve resolution

Table 11 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of $S_{\gamma\delta}$ carbons

$S_{\gamma\delta}$

No.	Sequence type	$\Delta v_\gamma{}^{a,b}$ (ppm)	v (ppm)	$\Delta v_{obs}{}^{b}$ (ppm)
37	(P)PPEEEP(P)	0.0	30.448	0.0
38	(P)PPEEEE(P)	−0.012	30.448	0.0
39	(P)EPEEEP(P)	−0.038	30.410	−0.038
40	(P)EPEEEE(P)	−0.049	30.410	−0.038

^{a} Calculated by the chemical shift calculation via the gamma effect
^{b} Chemical shift differences are expressed relative to the peak of PPEEEP resonance, which is set to be 0.00 ppm

and [EPEP]/[PPEE] are not equal to unity, but are 1.50 and 1.57, respectively, and the ratios [PPEE]/[EPPE] and [EPEP]/[PEEP] are 1.17 and 2.75, respectively, far from 2.0, neither one- nor multi-site Bernoullian models[29-32] can provide satisfactory fittings for the tetrad distribution. So we investigated the following two low-order Markovian models, M and MM.

Model M is an one-site model in which copolymerization proceeds under the control of first-

order Markovian statistics. The parameters of model M are P_{11} and P_{22}, which are the probabilities of ethylene and propylene adding to ethylene- and propylene-ended chains, respectively (in general, P_{mn} means the probability of an n-monomer adding to an m-monomer ended chain, where 1 and 2 represent the ethylene and propylene units, respectively). The probabilities P_{21} and P_{12} are equal to $1 - P_{22}$ and $1 - P_{11}$, respectively.

Model MM is a two-site model in which the copolymerization obeys the respective first-order Markovian statistics at two different catalytic sites. The parameters of model MM are the respective probabilities P_{11} and P_{22} at two different sites and the mole fraction (f_p) of the copolymer produced at one of the two sites.

The adequacy of model MM for describing the triad distribution in E–P copolymer has been confirmed by statistical analyses in a previous paper[33]. The optimization of the parameters of model MM was performed by the non-linear least squares routine. Model M gives an adequate fit for the triad sequence distribution (*Table 4*), but the fit for the tetrad distribution by model M produces large deviations in the calculated fractions of EPEP, PPEE, EPEE and PEEP tetrads (*Table 8*). The values of P_{22} and P_{11} for model M are 0.933 and 0.107, respectively. Model MM reproduces perfectly the dyad and triad sequence distributions and provides excellent fits to the tetrad distribution. The optimum value of f_p,

Table 12 Observed chemical shifts (v) and the observed and calculated chemical shift differences (Δv) of $S_{\delta\delta}$ carbons

$S_{\delta\delta}$
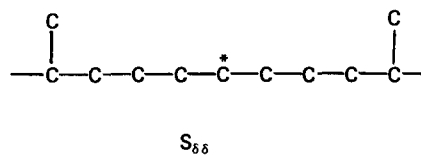
No.	Sequence type	$\Delta v_\gamma{}^{a,b}$ (ppm)	v (ppm)	$\Delta v_{obs}{}^{b}$ (ppm)
41	(P)PEEEP(P)	0.0	30.017	0.0
42	(P)PEEEE(P)	0.073	30.070	0.053
43	(P)EEEEE(P)	0.176	−	−
44	(P)PEEEEP(P)	0.171	−	−

^{a} Calculated by the chemical shift calculation via the gamma effect
^{b} Chemical shift differences are expressed relative to the peak of PEEEP resonance, which is set to be 0.00 ppm

Table 13 Tetrad distributions for samples PE-1 and PE-2

Tetrad	PE-1 obs.	PE-2		
		Obs.	Calc. (model M)	Calc. (model MM)
PPPP	0.968	0.771	0.756	0.762
PPPE	0.016	0.091	0.109	0.102
EPPE	0.000	0.006	0.004	0.005
PPEP	0.016	0.096	0.104	0.104
EPEP	0.000	0.011	0.008	0.010
PPEE	0.000	0.007	0.013	0.006
EPEE	0.000	0.003	0.001	0.003
PEEP	0.000	0.004	0.007	0.004
PEEE	0.000	0.002	0.001	0.003
EEEE	0.000	0.001	0.000	0.001
SS^a/10^{-4}		6.77		2.70

^{a} Sum of the squares of the deviations between the observed and calculated sequence distributions

Table 14 Observed and calculated fractions of hexad sequences in $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons

Carbon type	Sequence type	Obs.	Calc. (M)	Calc. (MM)
$S_{\alpha\gamma}$	PPPEPP	0.077	0.090	0.090
	PPPEPE	0.006	0.006	0.007
	EPPEPP	0.010	0.006	0.007
	EPPEPE	0.003	0.000	0.001
$S_{\alpha\gamma}$	PEPEPP + EEPEPP	0.011	0.007	0.008
	PEPEPE + EEPEPE	0.008	0.000	0.003
$S_{\alpha\delta}$	PPPEEP + PPPEEE	0.006	0.011	0.005
	EPPEEP + EPPEEE	0.002	0.001	0.001
$S_{\alpha\delta}$	PEPEEP + EEPEEP + EEPEEE	0.002	0.001	0.003
	PEPEEE	0.001	0.000	0.001

which is the mole fraction of the copolymer produced at site 1, is 0.979, and the optimum values of P_{22} and P_{11} at two different sites are as follows:

$$\text{site 1:} \quad P_{22}=0.939, \quad P_{11}=0.041$$

$$\text{site 2:} \quad P_{22}=0.418, \quad P_{11}=0.454$$

These parameters clearly indicate the two-site nature of the catalytic system, i.e. at site 1 propylene preferentially polymerizes and at site 2 ethylene and propylene copolymerize randomly. The validity of our hexad assignments is confirmed by the comparisons between the experimentally determined fractions of hexad sequences in $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ resonances and those calculated by model MM, as shown in *Table 14*. The fractions predicted by model MM correspond well to the observed fractions, except for the fractions of EPPEPE and PEPEPE + EEPEPE, while model M cannot predict the existence of EPPEPE, PEPEPE, EEPEPE and PEPEEE sequences.

CONCLUSIONS

^{13}C n.m.r. chemical shifts of hexad methylene resonances in stereoregular ethylene–propylene copolymer were calculated by using the gamma effect on ^{13}C chemical shifts and Mark's RIS model. The chemical shift due to the gamma effect is sensitive to the species of comonomer sequences because of its strong dependence on the bond conformational probability. ^{13}C chemical shifts of the hexad comonomer sequences in $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons were reasonably assigned from the predicted chemical shift differences, which are calculated from the contribution of the gamma effect and from that of the four-bond effect in Lindeman–Adam's empirical rule. Further, an INEPT experiment and the curve resolution method resolved the overlap of $T_{\beta\delta}$ and $S_{\gamma\gamma}$ resonances.

On the basis of our analytical results, the tetrad sequence distribution in E–P copolymer was determined. From the data of the sequence distribution, the E–P copolymerization mechanism was found to be reasonably described by the two-site model (model MM), in which

the respective copolymerization mechanisms at two different sites are under the control of first-order Markovian statistics. Model MM reproduced well the observed fractions of hexad sequences in $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons, supporting our assignments for the hexad methylene resonances.

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