^{13}C nuclear magnetic resonance spectral analysis of stereosequences in ethylene–propylene copolymer

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A number of split peaks dependent on both comonomer sequences and stereosequences were observed in the ^{13}C nuclear magnetic resonance (n.m.r.) spectrum of ethylene–propylene (E-P) copolymer. The ^{13}C chemical shifts of methylene carbon in stereoisomers of the respective hexad comonomer sequences were predicted by a chemical-shift calculation using the gamma effect on ^{13}C chemical shifts and Mark's rotational isomeric state model for E-P copolymer. Assignments of the split peaks that arise from different hexad stereosequences were given by comparison between the observed and calculated chemical shifts. Reference was made to the hexad assignments of comonomer-sequence-dependent peak splittings determined in our previous calculation of ^{13}C n.m.r. chemical shifts of stereoregular E-P copolymers. The tacticities were estimated for successive (not separated by ethylene units) propylene units in the hexad sequences.

(Keywords: ^{13}C nuclear magnetic resonance; chemical-shift calculation; ethylene–propylene copolymer; stereosequence-dependent hexads; comonomer-sequence-dependent hexads)

INTRODUCTION

The mechanical properties of ethylene–propylene (E-P) copolymers depend strongly on their microstructures. The E-P comonomer sequence distribution and the tacticity of the propylene units are very important factors in elucidation of the microstructure of E-P copolymer. ^{13}C n.m.r. is the most powerful method to determine these two factors. Owing to improvement in the sensitivity and the resolution of ^{13}C n.m.r. spectroscopy, a number of split peaks dependent on hexad sequence structures have been observed in the spectrum of E-P copolymer.

The ^{13}C chemical-shift assignments of stereoregular E-P copolymer proposed by Ray *et al.*[1] have been widely used for sequence analyses[2–4]. However, their assignments have ambiguities in PPEP, EPEP, PPEE and EPEE tetrads, owing to the contributions from sequences longer than tetrad. The influence of the tacticity of the propylene units on the ^{13}C chemical shifts of methylene carbons in the ethylene unit of E-P copolymers with a low ethylene content has been investigated by a chemical-shift calculation (gamma-effect method) using the gamma effect on ^{13}C chemical shifts and the rotational isomeric state (RIS) model[5]. From the ^{13}C n.m.r. spectrum of model compounds for the isolated ethylene unit in polypropylene sequences, Zambelli *et al.*[6] have indicated that this influence causes the splitting of such methylene peaks. Recently, Cheng[7] has characterized the structures of E-P rubbers on the basis of the ^{13}C n.m.r. spectra, which were complicated as a result of ethylene and propylene displacement, the presence of inverted propylene units and the tacticity of polypropylene sequences. He has proposed an empirical rule for ^{13}C chemical shifts of E-P copolymer[8], which accounts for substituent effects as well as for configurational sequences, from a statistical treatment of the large amounts of ^{13}C chemical-shift data for E-P copolymer and related compounds.

Chemical-shift calculation via the gamma effect has been applied to the prediction of the chemical shifts of pentad, hexad and heptad stereoisomers in atactic and isotactic polypropylenes[9,10]. The results confirmed that the chemical shift due to the gamma effect is very sensitive to differences in stereosequences. In our preceding paper[11], we have demonstrated that the chemical shift due to the gamma effect is sensitive not only to the tacticity of the polypropylene sequences but also to the displacement between the ethylene and propylene units. The applicability of the gamma-effect method to the prediction of chemical-shift differences dependent on the comonomer sequences has been confirmed by comparison between the observed and calculated chemical shifts of model compounds for the E-P copolymer. The ^{13}C chemical-shift assignments of the peak splittings dependent on hexad comonomer sequences in stereoregular E-P copolymer have been examined by a chemical-shift calculation via the gamma effect[12]. As for the chemical-shift, differences of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons (where the nomenclature proposed by Carman *et al.*[13] is used for the designation of carbon types) among the different hexad comonomer sequences have been reasonably predicted by contributions from the gamma effect and the four-bond effect in the Lindeman–Adams empirical rule[14].

In this study, we calculate the chemical shifts due to

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the gamma effect of methylene carbons in stereoisomers of the respective hexad comonomer sequences using the gamma-effect method. ^{13}C chemical-shift assignments of the split peaks that arise from different hexad stereosequences are given from comparisons between the observed and calculated chemical shifts, with reference to the hexad assignments[12] of comonomer-sequence-dependent peak splittings in the ^{13}C n.m.r. spectrum of stereoregular E-P copolymer. The tacticities of successive propylene units in hexad sequences are estimated on the basis of the hexad assignments of the resonance regions of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons.

EXPERIMENTAL

Material

The ethylene–propylene (E-P) copolymer of low ethylene content, sample PEW*, prepared with a δ-$TiCl_3/Et_2AlCl$ catalytic system, is a generous gift from Tokuyama Soda Co. Ltd. The other sample, PES7, is the fraction of the whole polymer (PEW) soluble in n-heptane at room temperature (23°C). It was confirmed that head-to-head and tail-to-tail arranged propylene units are not detected in ^{13}C n.m.r. spectra of these samples, referring to the study of regio-irregularity in the chain[15–17]. The ethylene contents of PEW and PES7 were determined to be 7.0 and 21.7 mol% from the relative peak areas of methylene resonances.

^{13}C 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. 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 broad-band 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).

^{13}C n.m.r. chemical-shift calculation

^{13}C n.m.r. chemical shifts of the methylene carbons in the stereoisomers of hexad ethylene–propylene comonomer sequences were calculated using the gamma effect on ^{13}C chemical shifts and Mark's[18] RIS model 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 interference ω and three-bond *gauche* interactions τ[19] were characterized with $E_\omega = 8400\ \mathrm{J\,mol^{-1}}$ and $E_\tau = 2100\ \mathrm{J\,mol^{-1}}$, respectively. Schilling *et al.*[9] proposed that the value of the gamma effects of methine carbons on methylene carbons is -3.7 ppm in their study on the chemical-shift calculation of various stereoisomers of atactic polypropylene. In this study, the value of -3.7 ppm was assumed for the gamma effect of methyl and methine carbons on the ^{13}C chemical shifts of methylene carbons. The temperature assumed in the calculation was 120°C, corresponding to the experimental conditions.

RESULTS AND DISCUSSION

In *Figure 1* are shown the ^{13}C n.m.r. spectra of PEW and PES7, respectively. In the spectrum of the whole polymer, PEW, split peaks dependent on only comonomer sequences are observed. ^{13}C chemical-shift assignments of the methylene carbons in the pentad and hexad comonomer sequences of stereoregular E-P copolymer were provided from the chemical-shift calculation via the gamma effect[12]. The observed and calculated chemical-shift differences of $S_{\beta\beta}$ and $S_{\alpha\gamma}$ carbons among methylene-centred pentad and hexad comonomer sequences are illustrated as stick spectra in *Figure 2*, on the basis of the expanded resonance regions and the calculated chemical shifts of these carbons previously reported[12] (in Figures 4 and 7 and Tables 5 and 7 in ref. 12). In this figure are also shown the chemical-shift differences of $S_{\beta\beta}$ and $S_{\alpha\gamma}$ carbons calculated by using the empirical rule proposed by Cheng[8]. As for the $S_{\beta\beta}$ carbon resonances, both calculation methods reasonably predict the chemical-shift differences. However, the empirical rule cannot predict the chemical-shift differences among EPEP-centred hexads (peaks 15–18), and those between

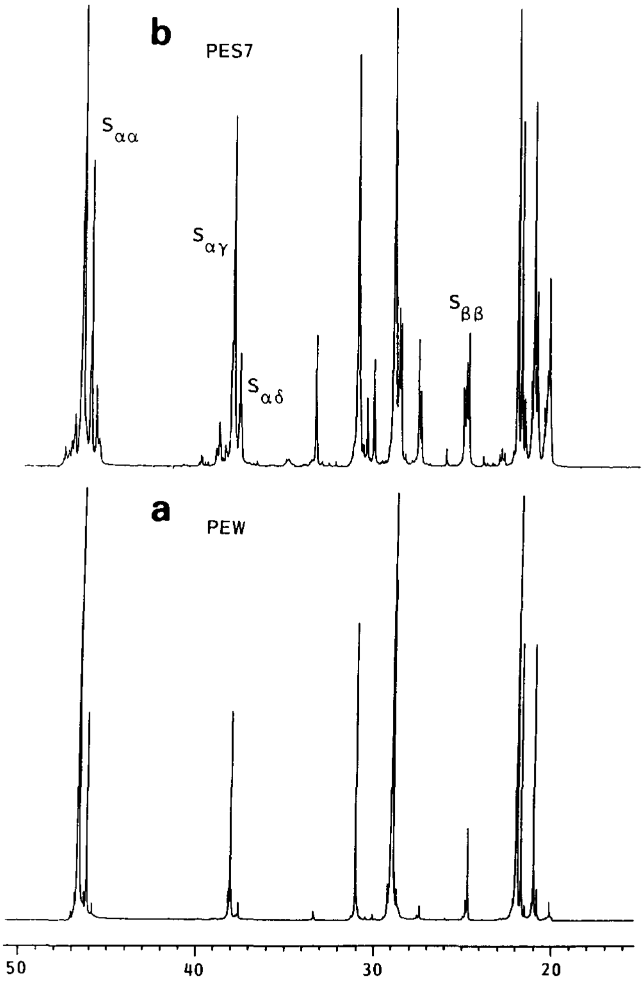

Figure 1 ^{13}C n.m.r. spectra of PEW (a) and PES7 (b)

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* Sample PEW is identical with the sample PE-2 in our preceding paper[12]

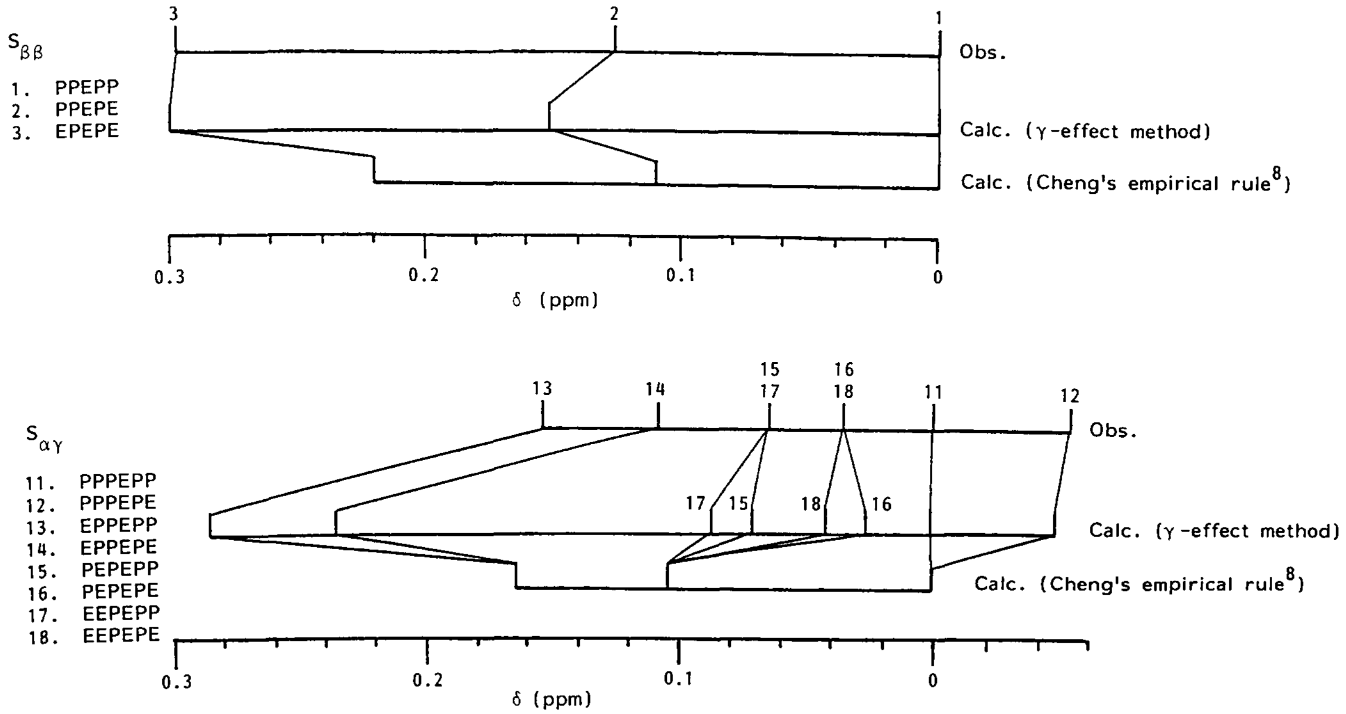

Figure 2 The observed and calculated chemical-shift differences of S$_{\beta\beta}$ and S$_{\alpha\gamma}$ carbons among methylene-centred pentad and hexad comonomer sequences

PPPEPP and PPPEPE hexads (peaks 11 and 12) and between EPPEPP and EPPEPE hexads (peaks 13 and 14) for the S$_{\alpha\gamma}$ carbon resonances. The reliability of our assignments of S$_{\alpha\gamma}$ and S$_{\alpha\delta}$ carbons has been supported by the good correspondence between the respective fractions of PE-centred hexads and those predicted by the two-site model for the E-P copolymerization mechanism[12].

As shown in *Figure 1b*, further complicated split peaks attributable to the different stereosequences are observed in the spectrum of PES7. In order to assign these complicated split peaks, the chemical shifts due to the gamma effect were calculated for the methylene carbons (S$_{\alpha\alpha}$, S$_{\alpha\gamma}$, S$_{\alpha\delta}$ and S$_{\beta\beta}$) in the stereoisomers of the respective hexad (S$_{\alpha\alpha}$, S$_{\alpha\gamma}$ and S$_{\alpha\delta}$) and pentad (S$_{\beta\beta}$) comonomer sequences. In *Figure 3* are shown the model compounds used for the calculation of the chemical shifts of hexad and pentad methylene-centred sequences of S$_{\beta\beta}$, S$_{\alpha\gamma}$ and S$_{\alpha\delta}$ carbons, respectively. Model compounds for the respective comonomer sequences are shown in *Table 1*.

Since the sample PES7 is a propylene-rich copolymer, these model compounds have isobutyl end groups as an analogue to the elucidated chain-end structures of this copolymer. The chemical shifts due to the gamma effect of the carbons marked by asterisks were calculated for all types of the stereoisomers of these model compounds. The assignments of methylene carbon (S$_{\alpha\gamma}$, S$_{\alpha\delta}$ and S$_{\beta\beta}$) resonances in the spectrum of PES7 are given from comparisons between the observed and calculated chemical shifts, referring to the assignments of comonomer-sequence-dependent peak splittings in the spectrum of PEW.

In *Figure 4* is shown the S$_{\beta\beta}$ resonance region in the spectrum of PES7. The observed and calculated chemical-shift differences are shown in *Table 2*, where the designations P^{m}P or P^{r}P and PE^{m}P or PE^{r}P mean that the configuration determined by the steric relationships between the successive propylene (P) units and those between the propylene units across the ethylene (E) unit are *meso* (m) or *racemo* (r), respectively. (In *Figure 2*, the superscript 'm' is omitted, because such configurations in the sample PEW are only *meso*[12].) In *Figure 4* are also shown the observed and calculated chemical-shift differences as stick spectra. The peaks 1, 2 and 3 that arise from the different pentad comonomer sequences, P^{m}PE^{m}P^{m}P, P^{m}PE^{m}PE and EPE^{m}PE, are observed in spectra of both PEW and PES7. Thus, the calculated chemical shifts of the methylene carbons in the stereoisomers of PPEPP, PPEPE and EPEPE pentad sequences are shown with reference to the peaks of P^{m}PE^{m}P^{m}P (1), P^{m}PE^{m}PE (2) and EPE^{m}PE (3). Broken lines on the stick spectra show the chemical shifts of pentad comonomer sequences observed in the spectrum of PEW. The calculated spectra correspond well to the peak splittings in the observed spectrum. In *Table 2* are shown the assignments of the split peaks made from comparisons between the observed and calculated chemical shifts.

Figure 5 shows the spectrum of the resonance regions of S$_{\alpha\gamma}$ and S$_{\alpha\delta}$ carbons. Referring to the spectral analysis of E-P copolymers by Cheng[7], stereosequence-dependent split peaks are observed in the region from 38.3 to 39.1 ppm. Using a similar method for the S$_{\beta\beta}$ resonance region, the calculated chemical-shift differences listed in *Table 3* are shown as stick spectra. The calculated results indicate that each peak numbered 27, 28 and 29–34 may arise from different stereoisomers of the respective hexad sequences. Thus, these peaks are composed of a number of methylene resonances that arise from different hexad comonomer sequences and stereosequences. For example, peak 34 is composed of the respective methylene resonances in P^{m}P^{r}PEPP and P^{m}P^{r}PEPE hexad sequences, where the designation P^{m}P^{r}PEPP means that the triad structure of PPP sequence is mr and other tactic structures of PEP and PP sequences are *meso* or *racemo*

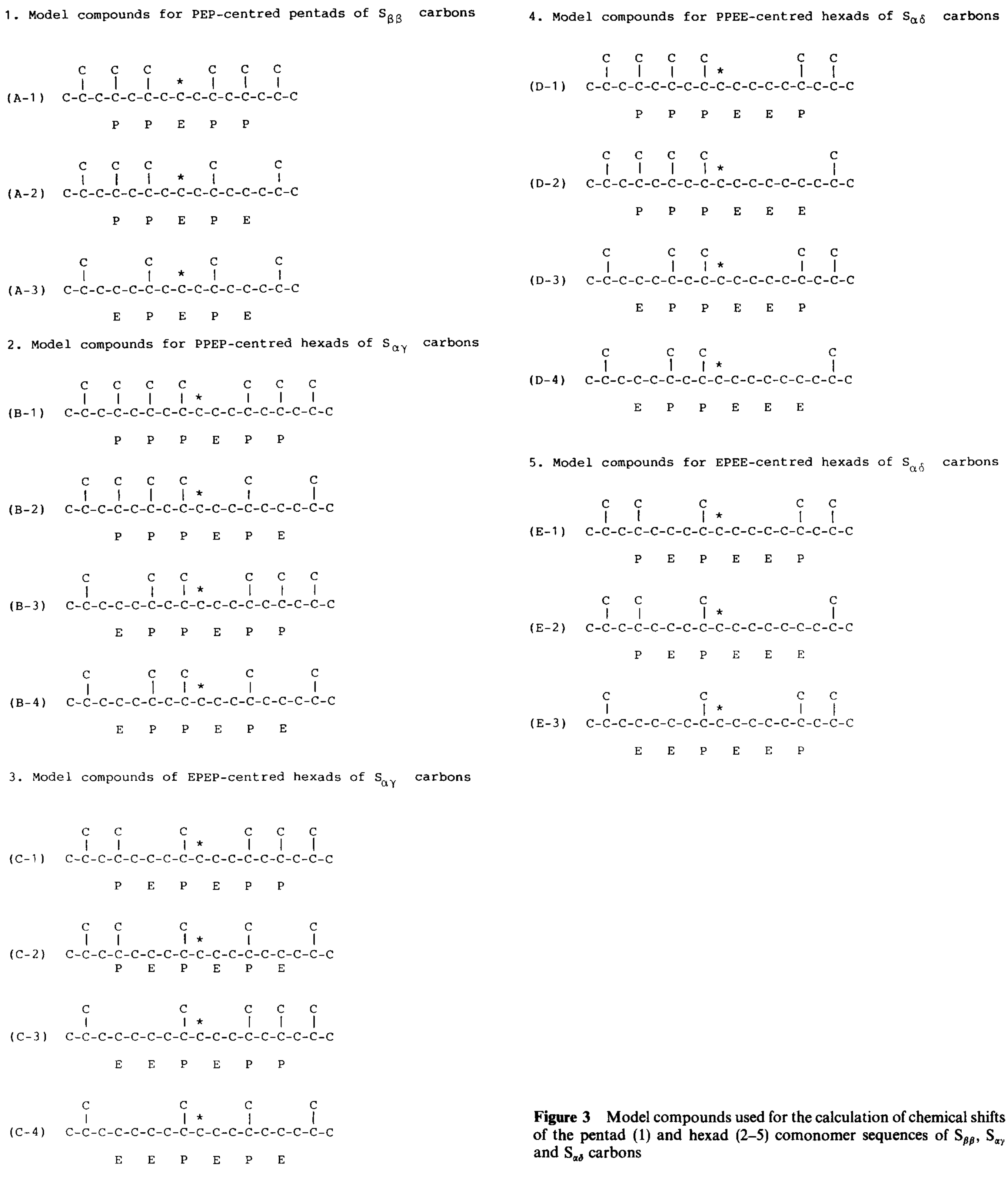

Figure 3 Model compounds used for the calculation of chemical shifts of the pentad (1) and hexad (2–5) comonomer sequences of $S_{\beta\beta}$, $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons

(namely, P^mP^rPEPP corresponds to the sum of $P^mP^rPE^mP^m$, $P^mP^rPE^rP^mP$, $P^mP^rPE^mP^rP$ and $P^mP^rPE^rP^rP$ hexads). The broader linewidths of these peaks than those of peaks 11–20 support the occurrence of overlaps of a number of resonances. The chemical-shift differences of $S_{\alpha\gamma}$ carbons in PEPEPP (*Table 3*) and other EPEP-centred hexads dependent on stereosequences are negligibly small. Similarly, the chemical-shift differences of $S_{\alpha\delta}$ carbons in EPEE-centred hexads dependent on stereosequences are also negligible. In *Tables 3* and *4* are given the resultant assignments of these split peaks in $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ regions. The peaks 27 and 29–31 are assigned to the resonances of $S_{\alpha\delta}$ carbons and the peaks 28 and 32–34 are assigned to the resonances of $S_{\alpha\gamma}$ carbons. Our assignments agree with those proposed by Cheng[7] with regard to the carbon types of the peaks 29–34. There still remains an ambiguity in the assignments of the peaks 29 and 30, because the calculated chemical shifts for the stereoisomers of P^rP^rPEEP and P^rP^rPEEE hexads and those of EP^rPEEP and EP^rPEEE hexads are very close

Table 1 Model compounds for comonomer sequences

Carbon type	Model compound	Pentad and hexad	Carbon type	Model compound	Hexad
$S_{\beta\beta}$	A-1	PPEPP	$S_{\alpha\delta}$	D-1	PPPEEP
	A-2	PPEPE		D-2	PPPEEE
	A-3	EPEPE		D-3	EPPEEP
				D-4	EPPEEE
$S_{\alpha\gamma}$	B-1	PPPEPP			
	B-2	PPPEPE	$S_{\alpha\delta}$	E-1	PEPEEP
	B-3	EPPEPP		E-2	PEPEEE
	B-4	EPPEPE		E-3	EEPEEP
				–	EEPEEE*
$S_{\alpha\gamma}$	C-1	PEPEPP			
	C-2	PEPEPE			
	C-3	EEPEPP			
	C-4	EEPEPE			

* Omitted from the calculation, because no stereoisomers are defined for a model compound of EEPEEE sequence

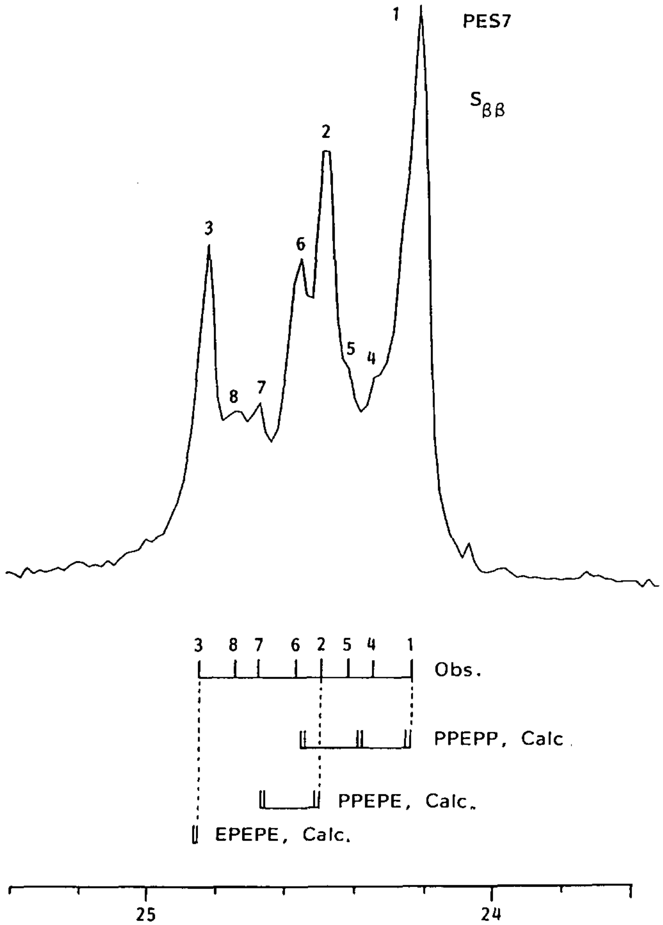

Figure 4 ^{13}C n.m.r. spectrum of the $S_{\beta\beta}$ region of PES7. The observed and calculated chemical shifts are shown as stick spectra at the bottom of this figure

to each other in the region from 38.3 to 38.5 ppm. Peak 30 was tentatively assigned to the stereoisomers of $\mathrm{EP^rPEEP}$ and $\mathrm{EP^rPEEE}$ hexads and peak 29 to the stereoisomers of $\mathrm{P^rP^rPEEP}$ and $\mathrm{P^rP^rPEEE}$ hexads because of closeness in their predicted chemical shifts. For the same reason, a similar ambiguity also remains in the assignments of peaks 32 and 33.

Table 2 Calculated and observed chemical-shift differences of $S_{\beta\beta}$ carbons among the stereosequence-dependent hexads

Pentad	Calc.[a]	Obs.[a]	Peak no.
$\mathrm{P^mPE^mP^mP}$	0	0	1
$\mathrm{P^mPE^rP^mP}$	0.003	0	1
$\mathrm{P^mPE^mP^rP}$	0.069	0.054	4
$\mathrm{P^mPE^rP^rP}$	0.076	0.090	5
$\mathrm{P^rPE^mP^rP}$	0.147	0.162	6
$\mathrm{P^rPE^rP^rP}$	0.157	0.162	6
$\mathrm{P^mPE^mPE}$	0	0	2
$\mathrm{P^mPE^rPE}$	0.008	0	2
$\mathrm{P^rPE^mPE}$	0.078	0.084	7
$\mathrm{P^rPE^rPE}$	0.082	0.120	8
$\mathrm{EPE^mPE}$	0	0	3
$\mathrm{EPE^rPE}$	0.005	0	3

[a] Expressed relative to the chemical shifts of $S^{\beta\beta}$ carbons in $\mathrm{P^mPE^mP^mP}$, $\mathrm{P^mPE^mPE}$ and $\mathrm{EPE^mPE}$ sequences, respectively, which are set to be 0 ppm

Table 3 Calculated and observed chemical-shift differences of $S_{\alpha\gamma}$ carbons among the stereosequence-dependent hexads

Hexad	Calc.[a]	Obs.[a]	Peak no.
$\mathrm{P^mP^mPE^rP^rP}$	−0.052	0	11
$\mathrm{P^mP^mPE^rP^mP}$	−0.040	0	11
$\mathrm{P^mP^mPE^mP^rP}$	−0.030	0	11
$\mathrm{P^mP^mPE^mP^mP}$	0	0	11
$\mathrm{P^rP^mPE^rP^rP}$	0.216	0.224	28
$\mathrm{P^rP^mPE^rP^mP}$	0.228	0.224	28
$\mathrm{P^rP^mPE^mP^rP}$	0.236	0.224	28
$\mathrm{P^rP^mPE^mP^mP}$	0.265	0.224	28
$\mathrm{P^rP^rPE^rP^rP}$	0.793	0.799	32
$\mathrm{P^rP^rPE^rP^mP}$	0.807	0.799	32
$\mathrm{P^rP^rPE^mP^rP}$	0.808	0.799	32
$\mathrm{P^rP^rPE^mP^mP}$	0.835	0.854	33
$\mathrm{P^mP^rPE^rP^rP}$	1.009	1.034	34
$\mathrm{P^mP^rPE^mP^rP}$	1.022	1.034	34
$\mathrm{P^mP^rPE^rP^mP}$	1.025	1.034	34
$\mathrm{P^mP^rPE^mP^mP}$	1.047	1.034	34
$\mathrm{P^mP^mPE^rPE}$	−0.027	0	12
$\mathrm{P^mP^mPE^mPE}$	0	0	12
$\mathrm{P^rP^mPE^rPE}$	0.242	0.278	28
$\mathrm{P^rP^mPE^mPE}$	0.266	0.278	28
$\mathrm{P^rP^rPE^rPE}$	0.819	0.853	32
$\mathrm{P^rP^rPE^mPE}$	0.837	0.853	32
$\mathrm{P^mP^rPE^rPE}$	1.035	1.088	34
$\mathrm{P^mP^rPE^mPE}$	1.050	1.088	34
$\mathrm{EP^mPE^mP^rP}$	−0.028	0	13
$\mathrm{EP^mPE^mP^mP}$	0	0	13
$\mathrm{EP^mPE^rP^mP}$	0.037	0.071	28
$\mathrm{EP^mPE^rP^rP}$	0.049	0.071	28
$\mathrm{EP^rPE^rP^rP}$	0.630	0.646	32
$\mathrm{EP^rPE^rP^mP}$	0.644	0.646	32
$\mathrm{EP^rPE^mP^rP}$	0.644	0.646	32
$\mathrm{EP^rPE^mP^mP}$	0.670	0.701	33
$\mathrm{EP^mPE^rPE}$	−0.025	0	14
$\mathrm{EP^mPE^mPE}$	0	0	14
$\mathrm{EP^rPE^rPE}$	0.655	0.691	32
$\mathrm{EP^rPE^mPE}$	0.673	0.691	32
$\mathrm{PE^mPE^rP^rP}$	−0.041	0	15
$\mathrm{PE^mPE^mP^rP}$	−0.026	0	15
$\mathrm{PE^mPE^rP^mP}$	−0.026	0	15
$\mathrm{PE^rPE^rP^rP}$	−0.007	0	15
$\mathrm{PE^mPE^mP^mP}$	0	0	15
$\mathrm{PE^rPE^rP^mP}$	0.007	0	15
$\mathrm{PE^rPE^mP^rP}$	0.007	0	15
$\mathrm{PE^rPE^mP^mP}$	0.033	0	15

[a] Expressed relative to the chemical shifts of $S_{\alpha\gamma}$ carbons in $\mathrm{P^mP^mPE^mP^mP}$, $\mathrm{P^mP^mPE^mPE}$, $\mathrm{EP^mPE^mP^mP}$, $\mathrm{EP^mPE^mPE}$ and $\mathrm{PE^mPE^mP^mP}$ sequences, respectively, which are set to be 0 ppm

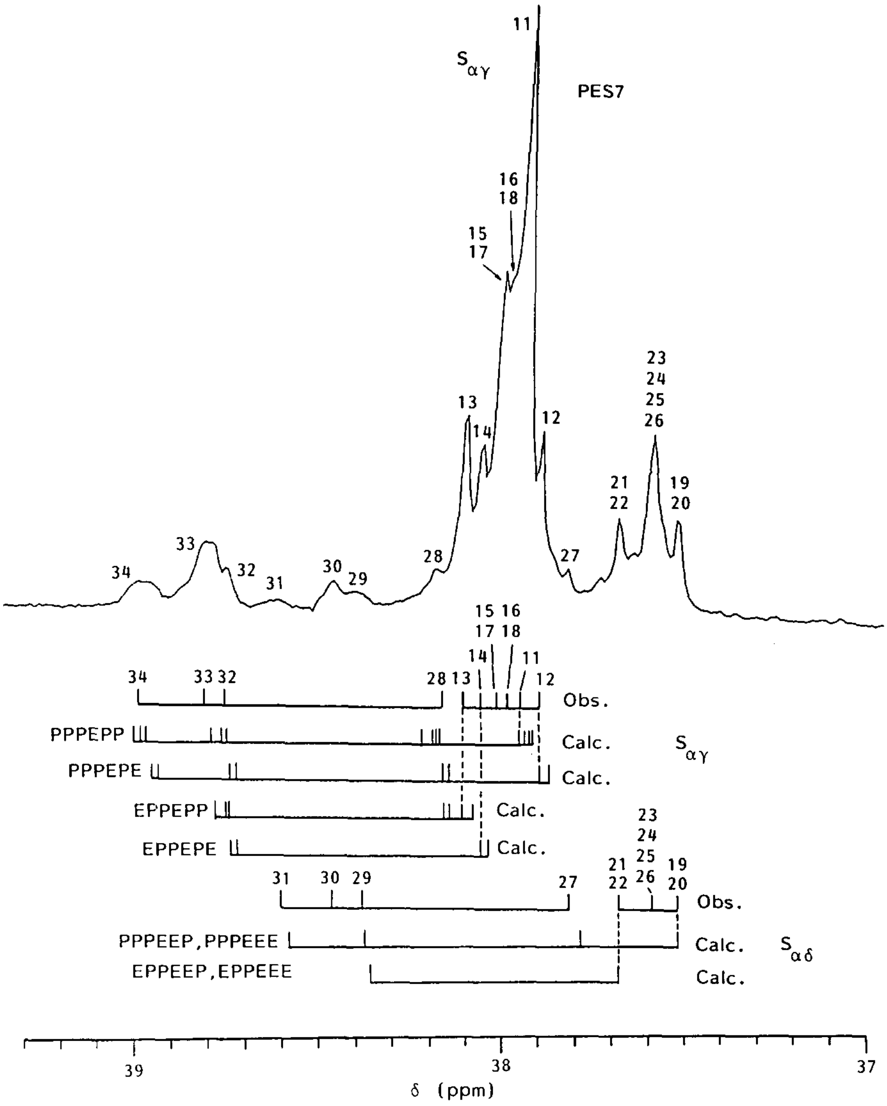

Figure 5 ^{13}C n.m.r. spectrum of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ regions of PES7. The observed and calculated chemical shifts are shown as stick spectra at the bottom of this figure

In *Figure 6* is shown the spectrum of the $S_{\alpha\alpha}$ carbon resonance region. Chemical shifts due to the gamma effect of $S_{\alpha\alpha}$ carbons in the stereoisomers of PPPPPP, PPPPPE, EPPPPE, PPPPEP, PPPPEE and PEPPEP hexads were calculated for the model compounds (not listed in *Figure 3*) corresponding to these hexad sequences. The calculated results are shown as stick spectra referring to the chemical shifts of the $S_{\alpha\alpha}$ carbons in the hexad comonomer sequences[12]. The calculated (stick) spectra indicate that the chemical-shift differences due to the hexad stereoisomers should be estimated by the contributions from the stereoisomers of not only PPPPPP hexad but also PPPPPE, EPPPPE, PPPPEP, PPPPEE and PEPPEP hexads. The only possible explanation for the broad peaks observed at 47–47.8, 46.3–46.5 and 45.6–45.7 ppm is overlapping of a number of resonances that arise from different hexad comonomer sequences and stereosequences. Therefore, it is impossible to resolve PPPP, PPPE and EPPE tetrads from the ^{13}C n.m.r. spectrum of PES7. It is remarkable that only the fraction of PP dyad is determined from the $S_{\alpha\alpha}$ resonance region.

On the basis of the hexad assignments in this study, the dyad and triad tacticities of successive (not separated by ethylene units) propylene sequences in PPEP- and PPEE-centred hexads were determined from the relative peak areas of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons, using the curve resolution method[20]. In *Table 5* are shown the values of tacticities and numbers of the peaks corresponding to the respective sequences. The fraction of tactic dyad P^mPEP is larger than that of P^mPEE. The sum of the fractions of tactic triads P^mP^mPEPP and P^mP^mPEPE is also larger than that of the fractions of P^mP^mPEEP and P^mP^mPEEE. These results indicate that the propylene tacticity in the propylene-rich sequences is more isotactic than that in the relatively ethylene-rich sequences.

CONCLUSIONS

^{13}C chemical shifts of methylene carbons in stereoisomers of the respective hexad E-P comonomer sequences were predicted by a chemical-shift calculation via the gamma effect. Referring to the assignments of the hexad comonomer-sequence-dependent peak splittings in stereoregular E-P copolymer, ^{13}C chemical-shift assignments of the split peaks dependent on hexad stereosequences were given from the observed and calculated chemical

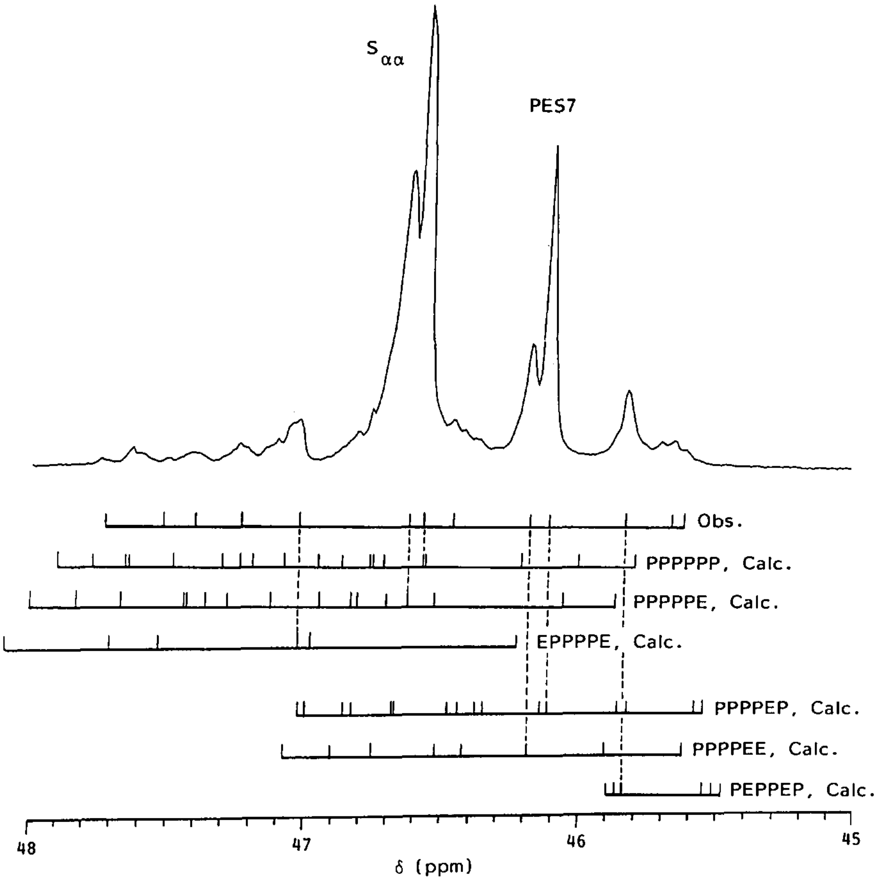

Figure 6 ^{13}C n.m.r. spectrum of the $S_{\alpha\alpha}$ carbon region of PES7. The observed and calculated chemical shifts are shown as stick spectra at the bottom of this figure

Table 4 Calculated and observed chemical-shift differences of $S_{\alpha\delta}$ carbons among the stereosequence-dependent hexads

Hexad	Calc.[a]	Obs.[a]	Peak no.
$P^{m}P^{m}PEE^{r}P$	−0.002	0	20
$P^{m}P^{m}PEE^{m}P$	0	0	20
$P^{r}P^{m}PEE^{r}P$	0.265	0.298	27
$P^{r}P^{m}PEE^{m}P$	0.267	0.298	27
$P^{r}P^{r}PEE^{r}P$	0.841	0.936	30
$P^{r}P^{r}PEE^{m}P$	0.842	0.936	30
$P^{m}P^{r}PEE^{r}P$	1.056	1.086	31
$P^{m}P^{r}PEE^{m}P$	1.057	1.086	31
$P^{m}P^{m}PEEE$	0	0	19
$P^{r}P^{m}PEEE$	0.267	0.298	27
$P^{r}P^{r}PEEE$	0.842	0.936	30
$P^{m}P^{r}PEEE$	1.057	1.086	31
$EP^{m}PEE^{r}P$	−0.002	0	21
$EP^{m}PEE^{m}P$	0	0	21
$EP^{r}PEE^{r}P$	0.675	0.710	29
$EP^{r}PEE^{m}P$	0.676	0.710	29
$EP^{m}PEEE$	0	0	22
$EP^{r}PEEE$	0.676	0.710	29
$PE^{m}PEE^{r}P$	−0.002	0	23
$PE^{m}PEE^{m}P$	0	0	23
$PE^{r}PEE^{r}P$	0.032	0	23
$PE^{r}PEE^{m}P$	0.033	0	23

[a] Expressed relative to the chemical shifts of $S_{\alpha\delta}$ carbons in $P^{m}P^{m}PEE^{m}P$, $P^{m}P^{m}PEEE$, $EP^{m}PEE^{m}P$, $EP^{m}PEEE$ and $PE^{m}PEE^{m}P$ sequences, respectively, which are set to be 0 ppm

Table 5 Dyad and triad tacticities of successive propylene units in PPEP- and PPEE-centred hexads in PES7

Peak no.	Sequence type	Fraction
	$P^{m}PEP$	0.858
	$P^{r}PEP$	0.142
	$P^{m}PEE$	0.774
	$P^{r}PEE$	0.226
11, 12	$P^{m}P^{m}PEPP$, $P^{m}P^{m}PEPE$	0.674
28	$P^{r}P^{m}PEPP$, $P^{r}P^{m}PEPE$	0.184
13, 14	$EP^{m}PEPP$, $EP^{m}PEPE$	
32, 33	$P^{r}P^{r}PEPP$, $P^{r}P^{r}PEPE$	0.115
	$EP^{r}PEPP$, $EP^{r}PEPE$	
34	$P^{m}P^{r}PEPP$, $P^{m}P^{r}PEPE$	0.027
21, 22	$EP^{m}PEEP$, $EP^{m}PEEE$	0.356
29	$EP^{r}PEEP$, $EP^{r}PEEE$	0.067
19, 20	$P^{m}P^{m}PEEP$, $P^{m}P^{m}PEEE$	0.356
27	$P^{r}P^{m}PEEP$, $P^{r}P^{m}PEEE$	0.063
31	$P^{m}P^{r}PEEP$, $P^{m}P^{r}PEEE$	0.054
30	$P^{r}P^{r}PEEP$, $P^{r}P^{r}PEEE$	0.105

shifts. The overlaps of a number of resonances that arise from different hexad comonomer sequences and stereosequences result in broad methylene peaks when the stereosequence of successive propylene units is rather irregular. The dyad and triad tacticities of successive propylene units in E-P copolymer were estimated on the basis of the hexad assignments of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbons for the first time. It was found that the tacticity of successive propylene units in PPEP sequences is more isotactic than that in PPEE sequences. Therefore, the ^{13}C chemical-shift assignments presented in this paper are useful to elucidate the influence of coexistent ethylene monomer on the steric control in propylene polymerization.

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