Carbon-13 nuclear magnetic resonance study of ethylene–1-octene and ethylene–4-methyl-1-pentene copolymers

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Detailed assignments of ^{13}C n.m.r. signals of ethylene–1-octene and ethylene–4-methyl-1-pentene copolymers, members of the linear low-density polyethylene (LLDPE) family, are presented. The equations relating signal intensities to the monomer sequences are given. Using these equations, the characterization of these copolymers by the triad monomer sequences is possible. From the analysis by the triad sequence, it is suggested that these 1-olefins have a tendency to be present isolated in the copolymer chain.

Keywords Characterization; ethylene–1-olefin copolymer; monomer sequence; structure; nuclear magnetic resonance; linear low-density polyethylene

INTRODUCTION

Recently, linear low-density polyethylenes (LLDPE) have attracted public attention as novel type polyethylenes. These are copolymers of ethylene and 1-olefin, of which ethylene–1-butene copolymer is the leading one. However, the ethylene copolymers with 4-methyl-1-pentene (EMP) and 1-octene (EO) are considered to have better mechanical properties than the ethylene–1-butene copolymers.

In the field of ^{13}C n.m.r. on copolymers, ethylene–1-olefin copolymers have been studied in relation to the analysis of the various kinds of branching structures that exist in the low-density polyethylenes. Therefore, many works on ^{13}C n.m.r. of these copolymers have been reported up to now. Ray *et al.*[1] and Hsieh *et al.*[2] recently described the detailed assignments of the ^{13}C n.m.r. signals of ethylene–1-butene copolymers. Randall[3] reported on the ^{13}C n.m.r. spectra of the ethylene copolymers with various 1-olefins (propylene to 1-octene). Cavagna[4] discussed an EO of low 1-octene content by high-resolution ^{13}C n.m.r. spectrometry. However, their interpretations for EOs have been limited to part of the isolated 1-octene unit because these EO copolymers are considered only as a reference for the analysis of hexyl branching in low-density polyethylenes. As for EMP, no reports have been published.

We have studied the ^{13}C n.m.r. spectra of several EOs and EMPs with various contents of comonomers. The assignments of ^{13}C n.m.r. signals of these copolymers were carried out by considering the relative intensity of the signals and also the chemical shifts of the model polymers as well as the empirical method by Lindeman and Adams[5]. It is the purpose of this study to present the detailed ^{13}C n.m.r. chemical shift assignments for these copolymers and a method for characterizing them in terms of the triad sequence distributions and the respective comonomer concentrations.

EXPERIMENTAL

Measurements

The proton-decoupled ^{13}C n.m.r. spectra were recorded on a JEOL FX200 n.m.r. spectrometer at 50.10 MHz. The instrumental conditions were as follows: pulse width, 8 μs (45°); pulse repetition, 10 s; spectral width, 8000 Hz; number of data points per spectrum, 16 000; and double-precision arithmetic. Sample measurements were made at 130°C.

Polymer solutions for the ^{13}C n.m.r. measurements were prepared in *o*-dichlorobenzene/deuterobenzene-d_6, with tetramethylsilane (TMS) and octamethylcyclotetrasiloxane (OMCTS) as internal reference and intervention standard, respectively. Sample concentration was ~45% w/v. The number of scans performed for each spectrum was 1000–14 000. The intensities of the signals of ^{13}C n.m.r. spectra were determined by the weights of signal portions cut out from xerox$^{(R)}$ copies. Determination of the proportion of small to large signals was carried out through the mediation of the signal of OMCTS added in the proper quantity as an intervention standard.

The pulse repetition time (10 s) adopted here is considered to be sufficient because the T_1's, except for several carbon atoms (mainly CH_3 carbons), were found to be less than 2 s in both ethylene copolymers from ^{13}C n.m.r. spin–lattice relaxation measurements according to the inversion recovery method. Therefore, the signals of methylene and methine carbons $\leqslant 2$ s in T_1 were used to satisfy the quantitative requirement (pulse repetition time $\geqslant 5T_1$).

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Materials

Ethylene–1-octene copolymers (EO). EO copolymers differing in 1-octene content were obtained by two methods. One was the polymerization method: the EO copolymer containing 11.1 mol% octene (EO(2)) was prepared at 70°C for 1 h by bulk copolymerization of ethylene and 1-octene, using the catalyst system of supported titanium ($TiCl_4$)–$AlEt_3$. The other was the solvent extraction method using a Soxhlet extractor: an EO copolymer containing 2.2 mol% octene, prepared by the polymerization method mentioned above, was extracted successively by solvents in the order ethyl acetate, ethyl ether, hexane, cyclohexane and heptane. The copolymers containing 11.9 mol% (EO(3)) and 6.6 mol% 1-octene (EO(1)) were obtained as ethyl ether and hexane extracts, respectively.

Ethylene–4-methyl-1-pentene copolymers (EMP). Three EMP copolymers containing 11.8 (EMP(3)), 19.4 (EMP(2)) and 2.0 mol% 4-methyl-1-pentene (EMP(1)) were obtained as the ethyl acetate, ethyl ether and heptane extracts, respectively, from a commercial product of EMP, ULTZEX 3010F$^{(R)}$ (Mitsui Petrochem. Co.), by the same extraction method as described above.

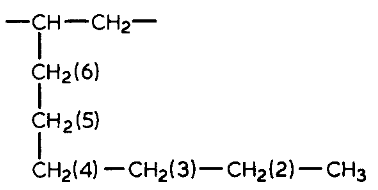
Poly(1-octene) (PO). The PO was obtained by the same polymerization method used for the preparation of EO, mentioned above.

Poly(4-methyl-1-pentene) (PMP). A commercial product, TPX-RT-18 (Imperial Chem. Ind. Co.), was used.

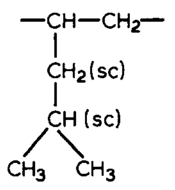
NOMENCLATURE

We have used the nomenclature suggested by Carman and Wilkes[6] for ethylene–propylene copolymers. Methylene carbons in the polymer main chain are designated by two Greek letters showing their position relative to the nearest branch carbon (i.e. methine carbon) on both sides. The symbol δ was used to indicate methylene carbons which were four or more removed from the nearest methine carbon. Methine carbons in the main chain and the side chain are designated by the symbols CH and CH(sc), respectively.

The designation of the branch carbons is as follows:

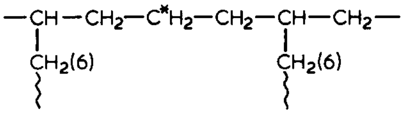


1–octene unit (O)



4-methyl-1-pentene unit (P)

The monomer units of ethylene, octene and 4-methyl-1-pentene are denoted by the symbols E, O and P, respectively. An asterisk on an E (E*) is used to indicate an ethylene unit that contains the carbon atom indicated by the rule mentioned above. This designation is also applied to the cases of O and P. For example, $\beta\beta$-OE*O designates the carbon with an asterisk in the following structure:



$$\begin{array}{c}-\underset{\underset{\wr}{CH_2(6)}}{CH}-CH_2-C^{*}H_2-CH_2-\underset{\underset{\wr}{CH_2(6)}}{CH}-CH_2-\end{array}$$

RESULTS AND DISCUSSION

EO copolymers

Table 1 shows the possible sequences for ethylene–octene copolymers and the chemical shifts corresponding to these sequences. The calculated chemical shifts for these sequences and the observed chemical shifts for PO are also listed in this Table. The assignments of signals were carried out on the basis of the chemical shifts calculated by the empirical method of Lindeman and Adams[5] and the comparisons of signal intensities as a function of monomer composition. Furthermore, the assignments of the spectra for ethylene–butene copolymers by Ray *et al.*[1] were found to be helpful in this case because the spectra for ethylene copolymers examined in this study resemble fairly closely those of ethylene–butene copolymers.

Figure 1 shows the ^{13}C n.m.r. spectra of two kinds of ethylene–octene copolymers differing in octene content. The spectrum for the low octene content (*Figure 1a*), which is practically the same as that reported by Cavagna, shows the signals arising from the sequence EOE alone. (Cavagna reported only the assignments of signals related to the sequence EOE.) Therefore, the signals in spectrum (b), except for those concerning the sequence EOE, are due to sequences such as OOO, OEO, OOE and the like. As shown in *Table 1*, a PO gives unequivocal assignments for the $\alpha\alpha$–CH_2–OOOO, CH–OOO, CH_3–OOO and the branch CH_2–OOO. The signals at 26.91, 33.86, 35.65 and 41.47 ppm in the spectrum for the high octene content (*Figure 1b*) increased by adding a small amount of PO to this sample, and then these signals are assigned to the corresponding carbons in the sequences of OOO and OOOO as listed in *Table 1*. On the basis of these assignments, the signal at 27.07 ppm in spectrum (b) is considered to be $CH_2(5)$ in the sequence OOE, because this signal lies midway between 26.91 ppm ($CH_2(5)$ in OOO) and 27.22 ppm ($CH_2(5)$ in EOE). The same assignment procedure is applied to the signal of the $\alpha\alpha$ carbon in the sequence OOOE (40.96 ppm), judging from its relationship to the sequences EOOE (40.28 ppm) and OOOO (41.47 ppm). The order of these chemical shift values is the same as that predicted by the empirical method of Lindeman and Adams.

The interpretation for the signals at 34.95, 35.07 and 35.50 ppm in spectrum (b) is quite difficult since the resolution in this region is not so high as for the case of ethylene–butene copolymers. However, the assignments of these signals are possible when one takes into consideration the comparisons of signal intensities and the similarity to the signal patterns of ethylene–butene copolymers. *Figure 2* shows the expansions of this region and the 24–28 ppm region of the spectrum in *Figure 1b*. *Table 2* shows the relative observed signal intensities for the related resonances, $\alpha\gamma$, $\beta\beta$, $\alpha\delta$, $CH_2(6)$ and CH, in the case of the CH–OOE signal intensity being unity. The $\alpha\delta$-OOE and $CH_2(6)$–OOE may not be resolved and therefore the single signal containing these two resonances must be twice as intense as the signal of CH–OOE at 35.96 ppm. From this point of view, the signal at 35.07 ppm is regarded as the $CH_2(6)$–OOE and $\alpha\delta$–OOEE. The $\beta\beta$–OEO signal at 24.60 ppm has a shoulder on the high-field side that is considered to be a symptom of the splitting by the tetrad sequences. The $\alpha\gamma$-EOEO signal at 34.95 ppm is clearly not twice as intense as the $\beta\beta$ signal at 24.60 ppm. This anomaly can be explained by the presence of an $\alpha\gamma$ carbon in the sequence

Table 1 Chemical shifts of ethylene–1-octene copolymers and reference polymer

Line no.	Type	Sequence	Chemical shifts[a] Calc.	EO (1), 6.6 mol%	EO (2), 11.1 mol%	Cavagna[4]	PO
1	CH_3	EO*E	13.86	13.99	13.99	14.19	
		OO*E	13.86				
		OO*O	13.86				14.01
2	CH_2 (2)	EO*E	22.65	22.85	22.83	22.90	
		OO*E	22.65				
		OO*O	22.65				22.90
3	$\beta\beta$	OE*O	25.08	24.62	24.60		
4	CH_2 (5)	OO*O	27.52		26.91		27.03
5	CH_2 (5)	OO*E	27.52		27.07		
6	CH_2 (5)	EO*E	27.52	27.26	27.22	27.24	
7	$\beta\delta$	OE*E	27.52	27.30	27.28	27.27	
8	$\delta\delta$	(EE*E)	29.96	29.97	29.95		
	CH_2 (4)	EO*E	29.96				
	CH_2 (4)	OO*E	29.96				
	CH_2 (4)	OO*O	29.96				30.28
9	$\gamma\delta$	OE*EE	30.21	30.47	30.46	30.44	
10	$\gamma\gamma$	OE*EO	30.46	30.94	30.98		
11	CH_2 (3)	EO*E	32.40	32.19	32.17	32.21	
	CH_2 (3)	OO*E	32.40				
	CH_2 (3)	OO*O	32.40				32.28
12	CH	OO*O	32.91		33.86		33.67
13	$\alpha\delta$	EO*EE	34.47	34.60	34.56	34.55	
	CH_2 (6)	EO*E	34.47				
14	$\alpha\gamma$	EO*EO	34.72	34.99	34.95		
15	$\alpha\delta$	OO*EE	34.72	35.09	35.07		
	CH_2 (6)	OO*E	34.72				
16	$\alpha\gamma$	OO*EO	34.97		35.50		
17	CH_2 (6)	OO*O	34.97		35.65		35.79
18	CH	OO*E	34.98	35.98	35.96		
19	CH	EO*E	37.05	38.24	38.22	38.15	
20	$\alpha\alpha$	EO*OE	38.98	40.28	40.28		
21	$\alpha\alpha$	OO*OE	39.23		40.96		
22	$\alpha\alpha$	OO*OO	39.48		41.47		41.43

[a] ppm relative to TMS

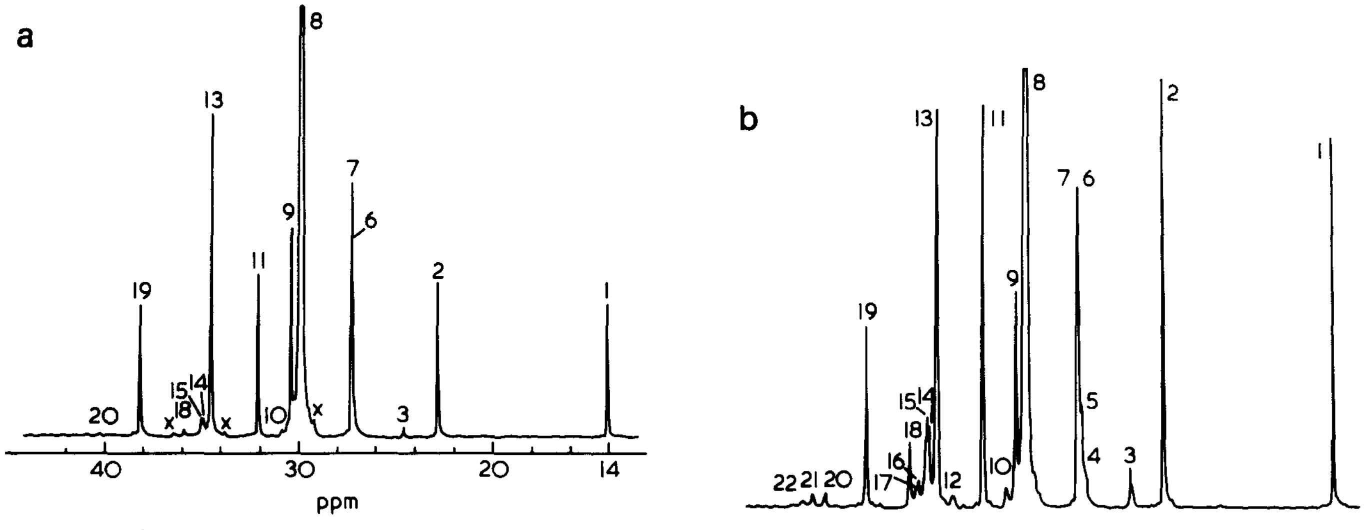


Figure 1 ^{13}C n.m.r. spectra of ethylene–1-octene copolymers: (a) EO(1), 6.6 mol% 1-octene; (b) EO(2), 11.1 mol% 1-octene. Crosses (x) denote signals due to the terminal carbons in a saturated end group of the main chain

Table 2 Intensities[a] of the various signals of the sequences OOE and OEO

CH–OO*E (*a*)	$\alpha\delta$–OO*EE and CH_2 (6)–OO*E (*b*)	$\beta\beta$–OE*O (*c*)	$\alpha\gamma$–EO*EO (*d*)	$\alpha\gamma$–OO*EO (*e*)	*b*/*a*	(*d* + *e*)/*c*
1.0	1.93	0.82	1.15	0.44	1.93	1.94

[a] Intensity of CH–OO*E is taken as unity

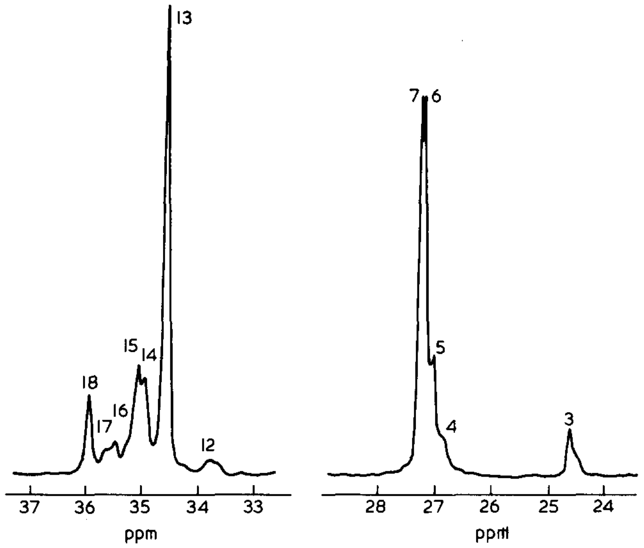


Figure 2 Expansion of the 24–28 ppm and 33–37 ppm regions of the spectrum shown in *Figure 1b*

OOEO, giving a signal at 35.50 ppm. The sum of both intensities of signals assigned to $\alpha\gamma$ carbons is about twice the intensity of the $\beta\beta$ signal at 24.60 ppm.

For the purpose of extracting the triad information from collective assignments, it is necessary to obtain the equation relating each signal intensity to the number of corresponding monomer sequences. According to the assignment for each signal established here, the signal intensities given by I_n (where the subscript denotes the number of the signal shown in *Figures 1* and *2*) are defined as follows in terms of the number of sequences of E and O units with reference to the method adopted by Randall[7]. For example, S_{EOE} indicates the number of EOE triad sequences. The number of like sequences per polymer chain is designated by $S_{\mathrm{EO...OE}}$ and $S_{\mathrm{OE...EO}}$ for the sequences EO ... OE and OE ... EO, respectively. In the following equations, $S_{\mathrm{EO...OE}}$ and $S_{\mathrm{OE...EO}}$ are described as the general terms, $S_{\mathrm{EO(O)_aOE}}$ and $S_{\mathrm{OE(E)_bEO}}$, respectively, and k denotes the n.m.r. proportionality constant.

$$I_1 = kS_{\mathrm{EOE}} + k\sum_{a=0}^{a=n}(a+2)S_{\mathrm{EO(O)_aOE}} \tag{1}$$

$$I_2 = kS_{\mathrm{EOE}} + k\sum_{a=0}^{a=n}(a+2)S_{\mathrm{EO(O)_aOE}} \tag{2}$$

$$I_3 = kS_{\mathrm{OEO}} \tag{3}$$

$$I_{4-7} = kS_{\mathrm{EOE}} + k\sum_{a=0}^{a=n}(a+4)S_{\mathrm{EO(O)_aOE}} + 2kS_{\mathrm{EEOEE}} + kS_{\mathrm{EEOEO}} \tag{4}$$

$$I_8 = k\sum_{b=0}^{b=n}(2b-1)S_{\mathrm{OE(E)_bEO}} + k\sum_{a=0}^{a=n}(a+2)S_{\mathrm{EO(O)_aOE}} + kS_{\mathrm{EOE}} \tag{5}$$

$$I_9 = 2k\sum_{b=0}^{b=n}S_{\mathrm{OE(E)_bEO}} \tag{6}$$

$$I_{10} = kS_{\mathrm{OEEO}} \tag{7}$$

$$I_{11} = kS_{\mathrm{EOE}} + k\sum_{a=0}^{a=n}(a+2)S_{\mathrm{EO(O)_aOE}} \tag{8}$$

$$I_{12} = k\sum_{a=0}^{a=n}aS_{\mathrm{EO(O)_aOE}} \tag{9}$$

$$I_{13} = kS_{\mathrm{EOE}} + 2kS_{\mathrm{EEOEE}} \tag{10}$$

$$I_{14-15} = 2kS_{\mathrm{EOEOE}} + 4k\sum_{a=0}^{a=n}S_{\mathrm{EO(O)_aOE}} + kS_{\mathrm{OOEOE}} \tag{11}$$

$$I_{16-17} = kS_{\mathrm{OOEOE}} + 2kS_{\mathrm{OOEOO}} + k\sum_{a=0}^{a=n}aS_{\mathrm{EO(O)_aOE}} \tag{12}$$

$$I_{18} = 2k\sum_{a=0}^{a=n}S_{\mathrm{EO(O)_aOE}} \tag{13}$$

$$I_{19} = kS_{\mathrm{EOE}} \tag{14}$$

$$I_{20} = kS_{\mathrm{EOOE}} \tag{15}$$

$$I_{21} = 2k\sum_{a=1}^{a=n}S_{\mathrm{EO(O)_aOE}} \tag{16}$$

$$I_{22} = k\sum_{a=1}^{a=n}(a-1)S_{\mathrm{EO(O)_aOE}}. \tag{17}$$

Each triad must be defined by the sequences of E and O units detected, and related to the appropriate signal intensities. These relations are derived from the equations described above:

$$S_{\mathrm{OOO}} = \sum_{a=0}^{a=n}aS_{\mathrm{EO(O)_aOE}} = I_{12}/k \tag{18}$$

$$S_{\mathrm{EOO}} + S_{\mathrm{OOE}} = 2\sum_{a=0}^{a=n}S_{\mathrm{EO(O)_aOE}} = I_{18}/k \tag{19}$$

$$S_{\mathrm{OEO}} = I_3/k \tag{20}$$

$$S_{\mathrm{EOE}} = I_{19}/k \tag{21}$$

$$S_{\mathrm{OEE}} + S_{\mathrm{EEO}} = 2\sum_{b=0}^{b=n}S_{\mathrm{OE(E)_bEO}} = 2\sum_{b=0}^{b=n}S_{\mathrm{OE(E)_bEO}} + 2S_{\mathrm{OEEO}} = I_9/k + 2I_{10}/k \tag{22}$$

$$S_{\mathrm{EEE}} = \sum_{b=1}^{b=n}bS_{\mathrm{OE(E)_bEO}} = I_8/2k + I_9/4k - I_2/2k. \tag{23}$$

In this case, k can be eliminated by converting S_{EEE}, $S_{\mathrm{EEO}} + S_{\mathrm{OEE}}$, etc., to the corresponding triad 'mole fractions'. The octene content is calculated from the ratio of the sum of the octene-centred triads to that of all triads, that is:

$$\text{1-octene (mol \%) content} = \frac{100 \times (S_{\mathrm{OOO}} + S_{\mathrm{OOE}} + S_{\mathrm{EOO}} + S_{\mathrm{EOE}})}{S_{\mathrm{OOO}} + S_{\mathrm{OOE}} + S_{\mathrm{EOO}} + S_{\mathrm{EOE}} + S_{\mathrm{EEE}} + S_{\mathrm{EEO}} + S_{\mathrm{OEE}} + S_{\mathrm{OEO}}} = \frac{100 \times (I_{12} + I_{18} + I_{19})}{I_{12} + I_{18} + I_{19} + (1/2)I_8 + (5/4)I_9 + 2I_{10} + I_3 - (1/2)I_2}. \tag{24}$$

EMP copolymers

For the signal assignments of EMP copolymers, the EO spectra shown before are very instructive because of the similarity to these spectra. The possible sequences for EMP copolymers and the chemical shifts corresponding to these sequences are listed in *Table 3* in the same form as described for EO copolymers. However, the correspondence between the observed chemical shift and the calculated one was not particularly good even if any

Table 3 Chemical shifts of ethylene–4-methyl-1-pentene copolymers and reference polymer

			Chemical shifts[a]				
Line no.	Type	Sequence	Calc.	EMP (1), 2.0 mol%	EMP (2), 19.4 mol%	EMP (3)[b], 11.8 mol%	PMP
1	CH_3	EP*E	22.62	23.26	23.29	23.27	
2	CH_3	PP*E	22.62		23.51	23.51	
	CH_3	PP*P	22.62				23.57
3	$\beta\beta$	PE*P	25.08	24.27	24.29	24.29	
4	CH(sc)	PP*P	25.92			26.10	25.92
		PP*E	25.92		26.12		
		EP*E	25.92	26.06			
5	$\beta\delta$	PPE*E	27.52		27.01	26.95	
6	$\beta\delta$	EPE*E	27.52	27.15	27.22	27.17	
7	$\delta\delta$	(EE*E)	29.96	29.97	30.05	29.99	
8	$\gamma\delta$	PE*EE	30.21	30.49	30.55	30.49	
9	$\gamma\gamma$	PE*EP	30.46		31.04	30.98	
10	CH	PP*E	32.91		33.90	33.86	31.45[c]
11	$\alpha\delta$	EP*EE	34.72	34.91	34.99	34.93	
12	$\alpha\delta$	PP*EE	34.97		35.48	35.42	
	$\alpha\gamma$	EP*EP	34.97	35.38			
13	$\alpha\gamma$	PP*EP	35.22		35.93	35.86	
14	CH	EP*E	34.98	36.06	36.14	36.08	
15	$\alpha\alpha$	EP*PE	39.48		41.41	41.39	
16	$\alpha\alpha$	PP*PE	39.73			42.29	
17	$\alpha\alpha$	PP*PP	39.98			42.83	42.62
18	CH_2 (sc)	EP*E	43.86	44.86	44.89	44.89	
19	CH_2 (sc)	PP*E	44.11		45.48	45.46	
20	CH_2 (sc)	PP*P	44.36			46.06	46.14

[a] ppm relative to TMS
[b] This sample is a mixture of various comonomer content copolymers
[c] CH–PP*P

empirical calculation methods were applied. In this case, some characteristic parts of the spectra of EMP copolymers that are different from those of EO copolymers will be selected and discussed.

Figure 3 shows the spectra of three kinds of EMP copolymers differing in 4-methyl-1-pentene content. The signals associated with the sequence EPE are assigned without difficulty from the lowest comonomer level spectrum (*Figure 3a*). The signal at 23.51 ppm (signal no. 2 in *Figure 3b*), which is lower than the CH_3–EPE signal (23.29 ppm), is assigned to CH_3–EPP because the CH_3–PPP signal (23.57 ppm) arising from PMP exists at the lowest field among these three CH_3 carbons. The chemical shifts of the CH_3 carbons are arranged in the order CH_3–EPE, CH_3–EPP and CH_3–PPP from high field to low field, which is the reverse of the case for ethylene–butene copolymers[1,2].

The CH(sc) carbon signals, which are not in the ethylene copolymers containing linear 1-olefin as comonomer, appear at 26.06–26.12 ppm but do not show the splitting due to the monomer sequences, although the CH carbon signals of three P-centred triads do show considerably different chemical shifts.

The $\alpha\delta$-EPEE and $\alpha\gamma$-EPEP carbons are not resolved from each other although the corresponding carbons in EO copolymer show separate chemical shifts. However, the $\alpha\gamma$-PPEP carbon shows a different chemical shift from the $\alpha\gamma$-EPEP carbon, and is located at 35.93 ppm in a region that also contains a signal due to CH–EPE.

Each $\alpha\alpha$-PP-centred tetrad carbon at 44.89–46.06 ppm shows a different chemical shift although each line width is broad. This broadening is assumed to arise from the effect of possible tacticity.

The signal intensity and triad relations are defined in the same manner as in the case of EO copolymer described before. These are as follows:

$$I_1 = 2kS_{\mathrm{EPE}} \tag{25}$$

$$I_2 = 4k\sum_{a=0}^{a=n} S_{\mathrm{EP(P)}_a\mathrm{PE}} + 2k\sum_{a=0}^{a=n} aS_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{26}$$

$$I_3 = kS_{\mathrm{PEP}} \tag{27}$$

$$I_4 = kS_{\mathrm{EPE}} + k\sum_{a=0}^{a=n} (a+2)S_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{28}$$

$$I_{5-6} = 2kS_{\mathrm{EEPEE}} + 2k\sum_{a=0}^{a=n} S_{\mathrm{EP(P)}_a\mathrm{PE}} + kS_{\mathrm{EEPEP}} \tag{29}$$

$$I_7 = k\sum_{b=1}^{b=n} (2b-1)S_{\mathrm{PE(E)}_b\mathrm{EP}} \tag{30}$$

$$I_8 = 2k\sum_{b=1}^{b=n} S_{\mathrm{PE(E)}_b\mathrm{EP}} \tag{31}$$

$$I_9 = kS_{\mathrm{PEEP}} \tag{32}$$

$$I_{10} = 2k\sum_{a=0}^{a=n} S_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{33}$$

$$I_{11} = 2kS_{\mathrm{EEPEE}} \tag{34}$$

$$I_{12} = 2kS_{\mathrm{EPEPE}} + 2k\sum_{a=0}^{a=n} S_{\mathrm{EP(P)}_a\mathrm{PE}} + kS_{\mathrm{PPEPE}} \tag{35}$$

$$I_{13-14} = kS_{\mathrm{EPE}} + kS_{\mathrm{PPEPE}} + 2kS_{\mathrm{PPEPP}} \tag{36}$$

$$I_{15} = kS_{\mathrm{EPPE}} \tag{37}$$

$$I_{16} = 2k\sum_{a=1}^{a=n} S_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{38}$$

$$I_{17} = k\sum_{a=1}^{a=n} (a-1)S_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{39}$$

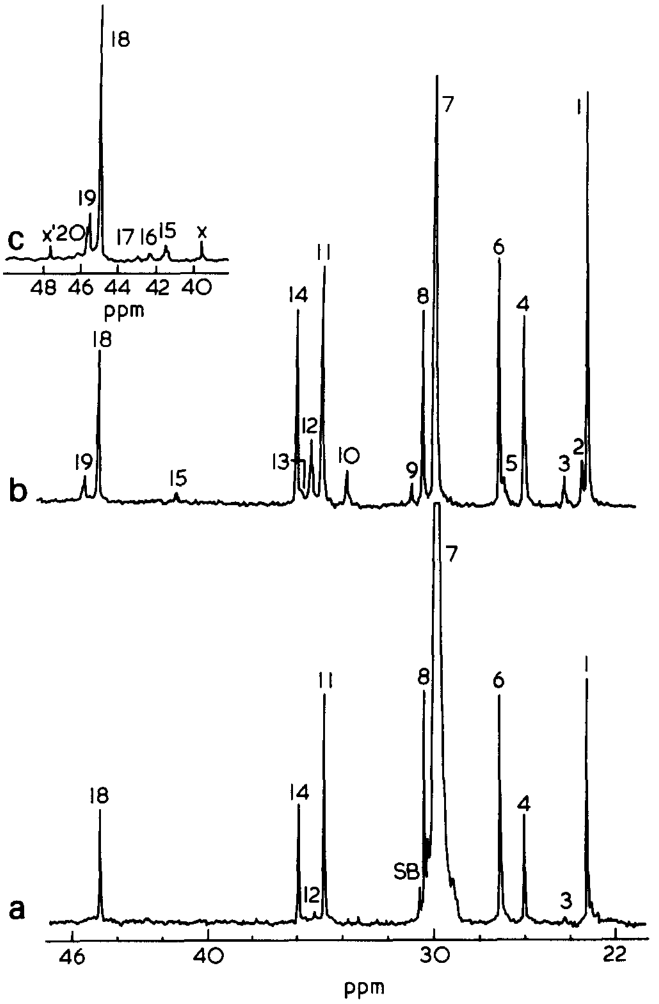


Figure 3 ^{13}C n.m.r. spectra of ethylene–4-methyl-1-pentene copolymers: (a) EMP(1), 2.0 mol% 4-methyl-1-pentene; (b) EMP(2), 19.4 mol% 4-methyl-1-pentene; (c) a part of EMP(3), 11.8 mol% 4-methyl-1-pentene spectrum. Crosses (x and x') denote signals due to the terminal carbons in a saturated end group of the main chain. SB denotes a spinning sideband signal

$$I_{18}=kS_{\mathrm{EPE}} \tag{40}$$

$$I_{19}=2k\sum_{a=0}^{a=n}S_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{41}$$

$$I_{20}=k\sum_{a=0}^{a=n}aS_{\mathrm{EP(P)}_a\mathrm{PE}} \tag{42}$$

$$S_{\mathrm{PPP}}=\sum_{a=1}^{a=n}aS_{\mathrm{EP(P)}_a\mathrm{PE}}=(I_4-I_{18}-I_{19})/k \tag{43}$$

$$S_{\mathrm{EPP}}+S_{\mathrm{PPE}}=2\sum_{a=0}^{a=n}S_{\mathrm{EP(P)}_a\mathrm{PE}}=I_{19}/k \tag{44}$$

$$S_{\mathrm{PEP}}=I_3/k \tag{45}$$

$$S_{\mathrm{EPE}}=I_{18}/k \tag{46}$$

$$S_{\mathrm{EEP}}+S_{\mathrm{PEE}}=2\sum_{b=0}^{b=n}S_{\mathrm{PE(E)}_b\mathrm{EP}}=2\sum_{b=1}^{b=n}S_{\mathrm{PE(E)}_b\mathrm{EP}}+2S_{\mathrm{PEEP}}$$

$$=(I_8+I_9)/k \tag{47}$$

$$S_{\mathrm{EEE}}=\sum_{b=1}^{b=n}bS_{\mathrm{PE(E)}_b\mathrm{EP}}=I_7/2k+I_8/4k \tag{48}$$

4-methyl-1-pentene content (mol %)

$$=\frac{(S_{\mathrm{PPP}}+S_{\mathrm{EPP}}+S_{\mathrm{PPE}}+S_{\mathrm{EPE}})\times 100}{S_{\mathrm{PPP}}+S_{\mathrm{EPP}}+S_{\mathrm{PPE}}+S_{\mathrm{EPE}}+S_{\mathrm{EEE}}+S_{\mathrm{EEP}}+S_{\mathrm{PEE}}+S_{\mathrm{PEP}}}$$

$$=\frac{I_4\times 100}{I_4+I_3+2I_9+(5/4)I_8+(1/2)I_7}. \tag{49}$$

Monomer triad distributions

The monomer triad distributions of EO and EMP copolymers can be calculated using equations (18)–(23) and (43)–(48), respectively. The observed values for EO(3) and EMP(2) samples are listed in *Table 4* and also the calculated values on the basis of Bernoullian statistics are included. For both copolymers, the observed values of S_{ECE} are larger than the calculated ones, and the values of $(S_{\mathrm{CCE}}+S_{\mathrm{ECC}})/S_{\mathrm{CEC}}$ are less than 2.0, the theoretical value in Bernoullian behaviour. This trend is found in the case of ethylene–butene copolymers shown by Hsieh *et al.*[2] These results may be attributed to the fact that these 1-olefins have a tendency to be present isolated in the copolymer chain.

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Table 4 Results of monomer triad distributions of EO and EMP copolymers

	Sample EO (3)		Sample EMP (2)	
	Observed	Calculated[a]	Observed	Calculated[a]
Mole fractions[b]	From areas by weight	$P_O = 0.119$	From areas by weight	$P_P = 0.194$
S_{CCC}	0	0.002	0.004	0.007
$S_{\mathrm{CCE}}+S_{\mathrm{ECC}}$	0.016	0.025	0.040	0.061
S_{CEC}	0.017	0.013	0.038	0.030
S_{ECE}	0.104	0.092	0.149	0.126
$S_{\mathrm{EEC}}+S_{\mathrm{CEE}}$	0.183	0.185	0.250	0.252
S_{EEE}	0.680	0.684	0.519	0.523

[a] Bernoullian result
[b] The subscript C denotes the corresponding comonomer