Short chain branching in high density polyethylene: ^{13}C n.m.r. study

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The character and amount of branching has been determined by ^{13}C. n.m.r. spectroscopy, in a series of samples of high density polyethylene (HDPE) and in some ethylene copolymers of high density. HDPE samples prepared by different methods were studied and only methyl branches were found; however, the number of branches differs considerably in various polymers. The quantitative determination of the branches is in good agreement with the results of infra-red spectroscopy. The relation between the type of branches and the crystallinity of polyethylene is discussed.

INTRODUCTION

Many physical properties of solid polyethylene (PE) are largely dependent on the type and amount of short chain branching[1]. The branching of low density PE (LDPE) has been studied by various methods (infra-red spectroscopy, γ radiolysis and pyrolysis gas chromatography) which indicate the presence of ethyl and butyl branches, with a predominance of the former[1–4] (see also refs cited in ref 4). Utilizing recent progress in ^{13}C n.m.r. spectroscopy, Dorman *et al.*[5] and, independently, Randall[6] were the first to show that both type and quantity of branches in LDPE can be determined by ^{13}C n.m.r. Subsequently, ^{13}C n.m.r. was applied to the quantitative characterization of short chain branching in LDPE in a number of papers[7–11]. In most of these it was shown that n-butyl branches predominate in LDPE[5–10]; smaller amounts of ethyl, n-amyl and longer branches were also found. However, in a recent paper Axelson *et al.*[12] have called attention to the fact that in the cited papers (refs 5–11), conditions for the correct quantitative determination of branches of various types have not always been met. If these conditions are respected, then ^{13}C n.m.r. spectroscopy, as a direct and unequivocal method, appears to be the most reliable way of determining branching in PE.

Branching of high density PE (HDPE) has so far been studied by infra-red (i.r.) spectroscopy[1] and by pyrolysis gas chromatography[2–4]. Only ethyl branches were detected in HDPE by Willbourn[1], whereas the presence of butyl[2] and longer[3] branches has been described in refs 2 and 3. A predominance of methyl branches was detected in the single sample studied by Ahlstrom *et al.*[4]. Branching of HDPE has not been studied by ^{13}C n.m.r. so far, probably because of experimental difficulties due to the very low concentration of branches in HDPE; the number of branches is lower by an order of magnitude[13] than in LDPE, LDPE containing 10–35 branches per 1000 C atoms of the main chain[5–11,13]. The quantitative characterization of branching in HDPE by means of ^{13}C n.m.r. spectroscopy is the subject of this paper.

EXPERIMENTAL

Polymers

All the studied polymers were commercial samples provided by Union Carbide (K–PE/B–2, K–PE/P, PE 1–3), Höchst (K–PE/B–1) and Mitsui Petrochemical (PE–4). The samples PE 1–4 were homopolymers. The nearly linear polymers K–PE/B–1, K–PE/B–2 and K–PE/P have been described as ethylene–butene (K–PE/B–1, K–PE/B–2) and ethylene–propylene (K–PE/P) copolymers by the producer. However, the chemical structure of these copolymers has not been clearly specified, probably on commercial grounds. The characteristics of the polymers are summarized in *Table 1*. The number-average molecular weights, $\bar{M}_n$, were determined by gel permeation chromatography (g.p.c.).

Samples and measuring conditions

Solutions of the studied polymers containing 20% (w/v) of polymer in 1,2,4-trichlorobenzene were prepared directly in the n.m.r. cells. Hexamethyl disiloxane (HMDS) was used as internal standard (2.0 ppm from TMS). The solutions were homogenized by mixing in sealed cells for several days at 110°C.

Table 1 Characterization of polymers

Sample	Trade Name	Production technology type[a]	Melt index[a]	Density[a] (g/cm^3)	$\bar{M}_n$[b]
K–PE/B–1	Hostalen GF 7740	Blowing	0.4	0.943	32000
K–PE/B–2	DMDS 3190	Extrusion	0.1	0.954	14000
K–PE/P	DMDJ 7904	Injection	4.0	0.953	12000
PE–1	DMDJ 3472	Extrusion	0.2	0.959	22000
PE–2	DMDJ 5140	Blowing	0.7	0.959	23000
PE–3	DMDJ 7006	Injection	6.2	0.960	13000
PE–4	Hizex 2200 J	Injection	4.3	0.968	16000

[a] Characterized by manufacturer; [b] relative error ± 10%

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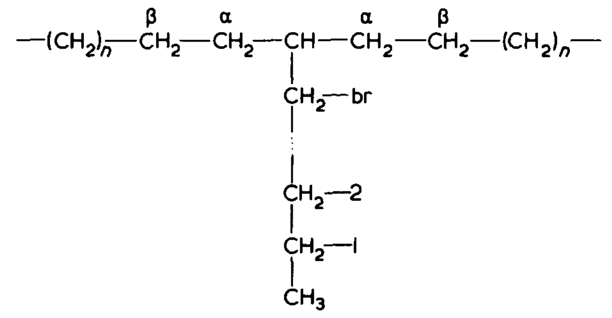
^{13}C n.m.r. spectra were measured using a Jeol FX-60 spectrometer operating at 15 MHz and 103°C with external lock. The protons were decoupled from the carbon nuclei using a random noise decoupling field. The spectral width was 4 kHz, with 8K data points. The pulse width was 13 μsec (a 60° pulse) with pulse interval 4.8 sec and 15 000–18 000 scans. The integrated line intensities were determined by the FX-60 computer. A comparison of the integrated intensities differing by 3–4 orders of magnitude was made possible by the use of the 'FX-60 System Program (8K) FAFT01/02-760415'. I.r. spectra were recorded using a Zeiss UR-10 spectrometer.

Quantitative analysis of branching by ^{13}C n.m.r.

In the quantitative analysis of ^{13}C n.m.r. spectra two factors characteristic of the measured substance have to be taken into account: (1) the nuclear Overhauser enhancement (*NOE*); (2) the spin–lattice relaxation time, T_1. Both these factors can differ for different carbon atoms. Axelson *et al.*[12] have verified that the theoretical maximum *NOE* value (*NOE* = 3) is reached for all carbons in branched LDPE, so that no problems for quantitative analysis arise from this effect. For T_1 values, the situation is more complicated. According to the study of branched PE and model ethylene copolymers by Axelson *et al.*[12], T_1 values of various carbons differ considerably. In the main chain the longest T_1 is exhibited by the $(CH_2)_n$ type carbons (see formula):



The T_1 values of CH_2 carbons in the branch depend on their distance from the branch point; only the T_1 values of CH_2–br carbons are shorter than those of $(CH_2)_n$ carbons. The T_1 values of methyl carbons are very long, evidently due to internal rotation of methyl groups. According to Axelson *et al.*[12] T_1 = 1.6–2.0 sec (at 118°C) for the $(CH_2)_n$ carbons; in HDPE, Inoue *et al.*[14] found for the same carbons T_1 = 1.35 sec (at 100°C). Since the T_1 values are temperature dependent, with an activation energy of ΔE = 10.1 kJ/mol[14], for our measuring temperature (103°C) the T_1 value of $(CH_2)_n$ carbons is expected to be 1.4–1.7 sec based on data of Axelson *et al.* in good agreement with the value T_1 = 1.4 sec based on the data of Inoue *et al.*

For correct measurement of the integrated intensity of a ^{13}C n.m.r. band, the pulse interval τ must be sufficiently long for establishment of equilibrium magnetization. This time depends on the pulse angle θ. For $\theta = 90°$, the pulse interval is subject to the condition $\tau \geq (3\text{–}4) \times T_1$[12,15]. For 60° pulses it can be shown that for 'true equilibrium spectra' the condition $\tau = (2.3\text{–}3.3) \times T_1$ is sufficient. With respect to the above cited T_1 values of $(CH_2)_n$ carbons at 103°C, the parameters used in our measurements ($\theta = 60°$ and τ = 4.8 sec) were chosen so as to be suitable for correct quantitative analysis of the content of branches based only on main chain carbons [$(CH_2)_n$, αCH_2, βCH_2, CH].

RESULTS AND DISCUSSION

The spectra of the copolymers K–PE/P and K–PE/B–1 are shown in *Figure 1*. The appearance of the spectrum of K–PE/B–2 is similar to that of K–PE/B–1. It has already been shown by Randall[6] that copolymers of ethylene with a small amount of higher mono-olefin component can serve as suitable model systems in ^{13}C n.m.r. studies of PE branching. Comparison of chemical shifts of bands of K–PE/P with the values given in refs 5 and 6 leads to the assignment shown in *Figure 1a*, indicating the presence only of methyl branches. Bands in spectra of K–PE/B–1 and 2 have been assigned in a similar manner, documenting the presence of ethyl branches in these copolymers. The band of CH_3 carbons of ethyl branches expected to appear at 11.2 ppm[5,6] is not evident in the spectra of K–PE/B copolymers. This is probably due to the long relaxation time of these carbons (T_1 ~ 5 sec[12]) for which the applied pulse interval is not of sufficient length. The nature of the band at 32.1 ppm (*Figure 1b*) will be discussed later. The results cited confirm the chemical structure of K–PE/P as an ethylene–propylene copolymer with only methyl branches, and of K–PE/B–1,2 as ethylene–butene copolymers with only ethyl branches present.

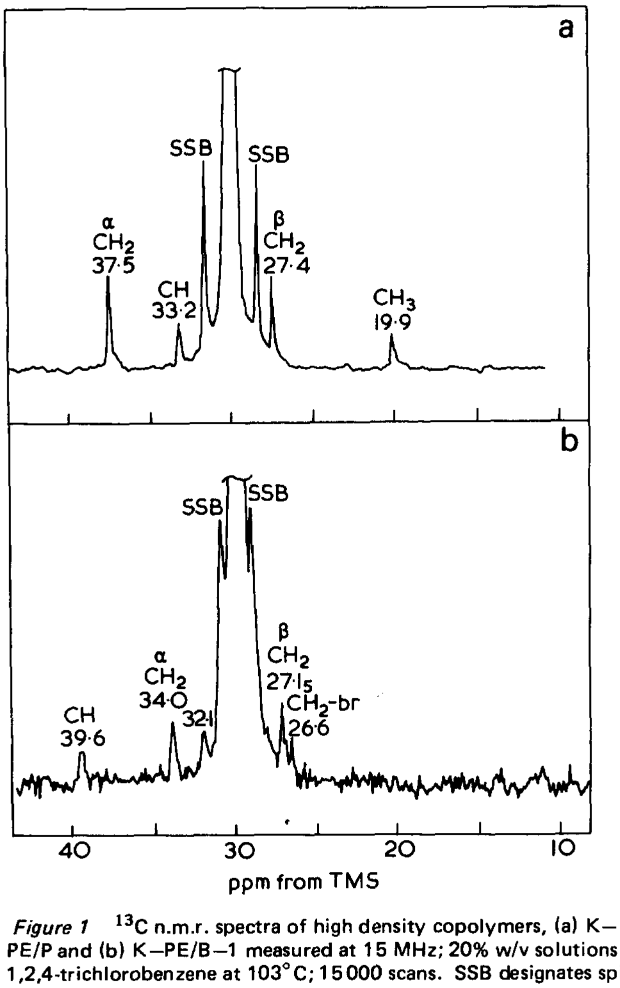


Figure 1 ^{13}C n.m.r. spectra of high density copolymers, (a) K–PE/P and (b) K–PE/B–1 measured at 15 MHz; 20% w/v solutions in 1,2,4-trichlorobenzene at 103°C; 15 000 scans. SSB designates spinning side bands to the principal methylene resonance

The spectra of the homopolymers PE–2 and PE–3 are shown in *Figure 2*. The spectra of PE–1 are similar to PE–3, those of PE–4 are similar to PE–2. In addition to the very strong band of $(CH_2)_n$ carbons at ~30 ppm, these spectra exhibit a number of lines which are assigned to carbons in the vicinity of methyl branches (αCH_2, 37.5 ppm; CH, 33.2 ppm; βCH_2, 27.4 ppm) and to carbons of methyl branches (19.9 ppm), based on a comparison with *Figure 1a* and with the data of refs 5 and 6. In samples PE–2 and PE–4 the band of CH_3 carbons is almost lost in noise. Besides the bands corresponding to methyl branches, further bands may be observed at 32.1 ppm (see also *Figure 1b*) and at 22.9 ppm (weak, only in PE–1 and PE–3). The chemical shifts of these bands correspond to CH_2–2 and CH_2–1 carbons, respectively, in long branches[6,7]. Since in the measured spectra, bands of αCH_2 carbons (34.5 ppm) and of CH carbons (38.2 ppm) of long branches[6,7] have not been observed, it may be assumed that the observed bands correspond to the nearest neighbour carbons (CH_2–1, CH_2–2) of chain end methyl groups. Carbons removed further from the chain end (CH_2–3, CH_2–4) contribute to the strong band of $(CH_2)_n$ carbons at ~30 ppm. The band of chain-end methyl groups (expected to lie at 14 ppm) is scarcely visible (*Figure 2*), probably due to a long T_1, (similarly in the ethyl branches of the copolymers K–PE/B). The relaxation time, T_1, of the carbon next to the chain-end methyl group is still so long that the condition $\tau = (2.3–3.3) \times T_1$ is not fulfilled, resulting in low intensity of the corresponding band at 22.9 ppm.

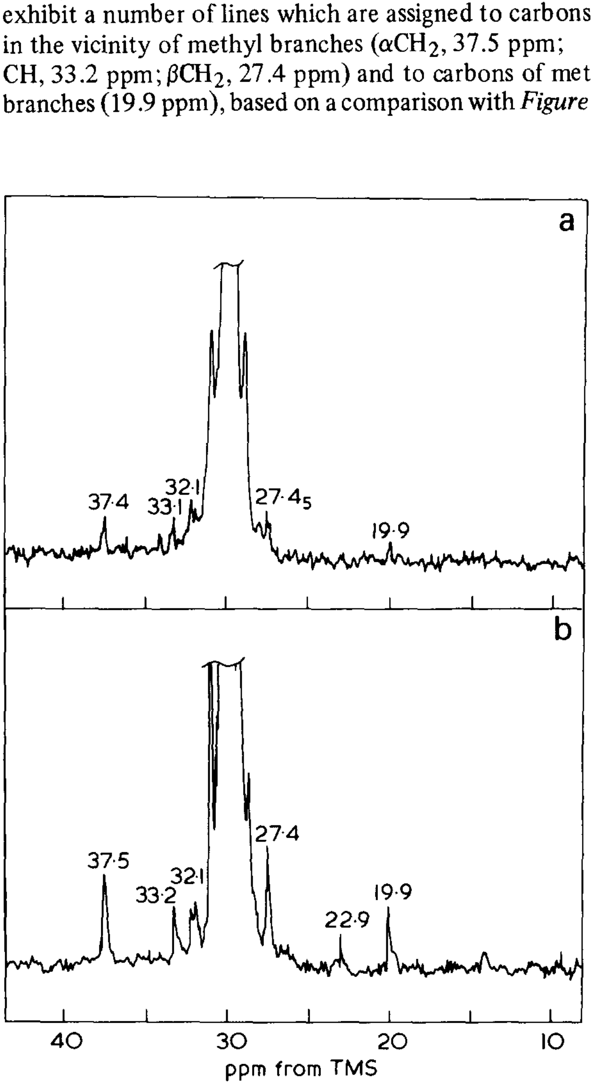


Figure 2 ^{13}C n.m.r. spectra of high density homopolymers (a) PE–2 and (b) PE–3 measured at 15 MHz; 20% w/v solutions in 1,2,4-trichlorobenzene at 103°C; 15 000 scans

The assignment of the bands at 22.9 and 32.1 ppm to the two nearest neighbours of chain-end methyl groups is confirmed by the results of the analysis of i.r. spectra, according to which all the studied polymers (with the exception of K–PE/B–2) practically do not contain unsaturated groups (vinyl, vinylidene, *trans* in chain vinylene). In the copolymer K–PE/B–2, 0.8 vinyl $=CH_2$ groups per 1000 C atoms were found. This value is in good agreement with $\bar{M}_n$ (*Table 1*), assuming that in this copolymer one end of the polymer chain is terminated by a vinyl group and the other by a methyl group. In all other polymers analysis of i.r. spectra confirms the assumption that the chains are terminated only by methyl groups. From the ratio of the integrated intensities of the band of CH_2–2 carbons of chain end-groups (at 32.1 ppm) and the sum of integrated intensities of the bands of all carbons of the main chain [including the strong band of the $(CH_2)_n$ carbons and its spinning side bands] the number of chain-end methyl groups per 1000 C was determined; this number is given in *Table 2* where it is compared with the value obtained from $\bar{M}_n$. Values are seen to agree reasonably well, with the exception of K–PE/B–1.

In all samples the number of branches was determined from the comparison of integrated intensities of bands of

Table 2 Character and number of branches in studied samples of high density polyethylene and ethylene copolymers

			Branching			
	Chain end-groups		I. r. data		^{13}C n.m.r. data	
Sample	Number of chain end CH_3/1000 C from $\bar{M}_n$	Number of chain end CH_3/1000 C from ^{13}C n.m.r.	Total number of CH_3/1000 C (including chain end CH_3)	Number of CH_3/1000 C corrected for chain end CH_3 [a]	Type of branches	Number of branches/ 1000 C
K–PE/B–1	0.9	2.0	3.2	2.8[b] 2.3[c]	Ethyl	2.5
K–PE/B–2	1.0	–[d]	2.5	2.0[b]	Ethyl	1.9
K–PE/P	2.3	–[d]	8.0	7.0[b]	Methyl	7.4
PE–1	1.2_5	1.0	1.9	1.3[b] 1.4[c]	Methyl	1.6
PE–2	1.2	0.9	2.5	2.0[b] 2.1[c]	Methyl	0.7_5
PE–3	2.1_5	3.2	5.1	4.1[b] 3.7[c]	Methyl	2.6
PE–4	1.7_5	2.1	1.4	0.6[b] 0.5[c]	Methyl	0.4

[a] See text; [b] corrected using values from $\bar{M}_n$; [c] corrected using values from ^{13}C n.m.r.; [d] undetermined

αCH_2, βCH_2 or CH carbons with the sum of integrated intensities of all main chain carbons (i.e. including the strong band at ~30 ppm and its spinning side bands). As two αCH_2 and two βCH_2 carbons correspond to each branch, the following values should be comparable: one half of the integrated intensity of the αCH_2 band, one half of the integrated intensity of the βCH_2 band and the whole integrated intensity of the CH band. These three values have been averaged and the relative deviation from the mean did not exceed ± 20%. The results are given in the last column of *Table 2*. It is interesting to compare these data with the results of i.r. spectroscopy. The number of total CH_3 groups per 1000 C atoms was obtained[16] by the classical method of measurement of the intensity of the CH_3 bending band at 1378 cm^{-1} (*Table 2*). This value includes both the chain end and the branch methyl groups. In determining the methyl groups in branches, we have to correct for chain end methyl groups. As the absorbances of both CH_3 types differ, the number of chain end methyls has to be multiplied[17] by 0.45; the values characterizing branching, obtained by the procedure described, using the number of chain-end methyls from $\bar{M}_n$ and also from ^{13}C n.m.r. are given in the fourth column of *Table 2*. It is seen that the number of branches determined in this way is in good agreement with the values obtained directly from ^{13}C n.m.r. spectra. An exception is sample PE–2 in which the difference between the results of the two methods exceeds the probable error in the ^{13}C n.m.r. spectra.

Analysis of ^{13}C n.m.r. spectra of HDPE homopolymers prepared by various methods (*Table 1*) clearly indicates that all studied samples PE 1–4 contain practically only methyl branches. No other type of branching was observed in these samples. This is in agreement with the results of Ahlstrom *et al.*[4] reached by 'pyrolysis gas chromatography' of one sample of HDPE. The number of branches differs in various HDPE samples (*Table 2*).

Finally, using the results obtained, some comments can be made on the relation between the type of branching and the crystallinity of PE. Although the crystallinity values of PE determined by various methods sometimes differ to a considerable extent[18,19], there exists a direct correlation between density and crystallinity of PE: higher density corresponds to higher crystallinity and *vice versa*[18,19]. The finding that the samples of HDPE studied contain only methyl branches and no ethyl and butyl branches (which were found in LDPE[1–11]) is in agreement with the results of a recent publication by Cutler *et al.*[11] who have come to the conclusion that ethyl and butyl branches cannot be included in crystalline domains of PE. Comparison of the data in *Tables 1* and *2* reveals that in the homopolymers PE 1–4 the values of density (and therefore also of crystallinity) do not correlate with the number of branches determined from ^{13}C n.m.r. (or i.r.) spectra. The densities of the samples PE 1–3 are practically equal even though the number of branches in these samples differs considerably. This indicates that the short methyl branches can be included in crystalline domains of PE. A similar conclusion has been reached by McRae and Maddams based on the analysis of i.r. spectra of ethylene–propylene copolymers[20].

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