Analysis of ^{13}C *FT*n.m.r. spectra of low-density polyethylene by the simplex method

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High-field ^{13}C n.m.r. spectroscopy has been used on low-density polyethylene (LDPE) to determine the nature and concentration of branches. A simplex method has been used to deconvolute the spectra and determine the relative concentrations of each branch type present. Spectra have been measured on the molten polymer at 140°C and studies made to determine spin-relaxation times to confirm that this is a viable method of measuring the spectra.

(Keywords: high-field *FT*n.m.r.; linear low-density polyethylene; branches; spin-lattice relaxation time)

INTRODUCTION

The optimum degree of crystallinity that develops in linear low-density polyethylene[1] depends on the number and distribution of branches within the molecules, and is independent of the nature of the branch longer than C_2. An estimate of chain branching and some measure of the branch distribution along the chain is vital to an understanding of material properties.

Estimates have been made by a variety of techniques such as ^{13}C n.m.r. spectroscopy, infra-red spectroscopy and g.p.c. on samples etched with fuming nitric acid. I.r. spectroscopy can only measure short-chain branching (methyl and ethyl) by a method that requires prior calibration of the instrument[2]. G.p.c. is only able to give a figure relating to the amount of extra hydrodynamic volume due to all chain branches without distinguishing between the various types of chain branching[3]. ^{13}C *FT*n.m.r. alone enables the chain-branching type and concentration to be measured, but is limited to separate determinations of branches shorter than six carbon atoms.

Here we present our findings on evaluating branch concentration for linear low-density polyethylene and low-density polyethylene (LDPE) on bulk material above 140°C, and the subsequent analysis of the spectra using the simplex method of Danzig[4]. Solution ^{13}C *FT*n.m.r. spectra and i.r. spectra were also measured for comparison.

EXPERIMENTAL

^{13}C *FT*n.m.r. spectra were measured on a Brüker Spectrometer WH400, 100.6 MHz, for the ^{13}C nuclei, at the University of Warwick. Polymer samples were prepared by extruding molten polymer at 160°C through a circular die of 4 mm diameter to produce a specimen that closely fitted the n.m.r. sample tube, while being careful to exclude air-bubble inhomogeneities in the samples. Spectroscopic conditions included a pulse angle of 55°, pulse width of 10 μs and a time interval of 10 s on at least 80 scans (usually over 400 scans) to achieve a good signal to noise ratio. Machine drift was sufficiently low to do without an internal locking agent, such as deuterated toluene. White noise decoupling at the proton resonance frequency leads to energy transfer among the ^1H and ^{13}C nuclear spin levels causing Nuclear Overhauser Enhancement (NOE). Axelson *et al.*[5] have verified that the theoretical maximum NOE factor is reached for all carbons in branched LDPE so that no problems for quantitative analysis of the spectra arise from this effect. Temperature effects were measured in the range 80°C–140°C, to determine the optimum temperature for the measurements.

Fast inversion-recovery Fourier transform (f.i.r.*FT*) experiments[6] were made with a 180°–τ–90° pulse sequence to determine spin-lattice relaxation times (T_1) for the various carbon atoms. Time intervals (τ) from 0.1 to 15 s were chosen and used to determine T_1 from a three-parameter fit to equation (1).

$$s(\tau) = A + B\exp(-\tau/T_1) \qquad (1)$$

where $s(\tau)$ is the signal height, A and B machine parameters, and T_1 the spin-lattice relaxation time. Spectra with long τ-values, of the order of 10 s, gave noticeable peak-broadening due to machine drift on samples containing no locking agent and were, therefore, excluded from calculations. T_1 comparisons were made on spectra from solutions of trichlorobenzene (40% w/v) at 118°C and 67.905 MHz.[5]

PE samples were measured on a Perkin–Elmer 580B computer-interfaced i.r. spectrophotometer that had been calibrated with polystyrene. PE was moulded into approximately 3 mm thick specimens. Details of PE characteristics are given in *Table 1*.

SIMPLEX METHOD OF SPECTRAL ANALYSIS

This is a linear-programming technique[4] that iteratively solves a set of linear equations (equation (2)) in a finite

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Table 1 Polyethylene characteristics

Manufacturer	Grade number	Index number	Density (g/cm^3)	Melt index (dg/min)
Dupont Chemicals	11B	S1	0.922	0.70
	8105	S2	0.921	2.35
	8107	S3	0.921	4.24
	8109	S4	0.923	8.71
	2309	S5	0.929	10.40
	15A	S6	0.939	0.74
	2906M6	S7	0.939	0.74
Dow	2045	D1	0.920	1.15
	2035	D2	0.919	4.11
BP Chemicals	PN220	BX1	0.918	0.07
	DFDG4262	BX2	0.922	0.84
	N81382	BX3	0.921	4.31
	DFDG0159	BX4	0.928	1.91
	LL101AA	L1		
	LL102AA	L2		
	LL103AA	L3		

Table 2 Simplex table

	Integral of absorption band (ppm from TMS)
$X4 + X5 + X6$	$\leqslant 37.9 \pm 0.5$
$2X4 + 3X5 + 3X6$	$\leqslant 34.4 \pm 0.2$
$2X2 + X4$	$\leqslant 34.0 \pm 0.2$
$X5$	$\leqslant 32.6 \pm 0.3$
$X6$	$\leqslant 32.0 \pm 0.3$
$3X2 + 2X4 + 3X5 + 3X6$	$\leqslant 27.2 \pm 0.5$

Branch contributions: X2, ethyl branch; X4, n-butyl branch; X5, n-amyl branch; X6, n-hexyl and longer branches

number of steps if a solution exists, or otherwise indicates an unbounded solution.

$$\sum_{i=0}^{n} k_i x_i \leqslant a_i \qquad (2)$$

The method maximizes an equation of the type

$$\sum_{i=0}^{n} x_i = m \qquad (3)$$

by introducing slack and surplus variables into equation (2), and solves for optimum values.

Linear equations can be written for each n.m.r. absorption band in terms of contributions from each chain branch by using the assignments made by Randall *et al.*[7]. These are used to construct a simplex table of matrix elements X2, X4, X5 and X6 for the relative concentrations of ethyl, n-butyl, n-amyl and n-hexyl and longer branches (see *Table 2*). Slack and surplus variables were introduced as corrections for machine noise.

In analysing the spectra, all carbon-atom signals were used except those with the largest spin-lattice relaxation times, e.g. terminal methyls, which would not have fully relaxed in the pulse interval used. Results are reported as number of branches per 1000 main-chain carbon atoms.

RESULTS AND DISCUSSION

Typical high-field ^{13}C n.m.r. spectra for the three grades of LDPE are shown in *Figure 1*. The integrated intensities of a range of PEs when analysed by a matrix-inversion procedure for a series of linear equations gave negative values for certain branch concentrations. This was considered unacceptable and the simplex procedure adopted instead. The simplex analysis of the spectra obtained from a wide range of PEs are listed in *Tables 5* and *6* (both solution and molten PE). Two LLDPEs containing ethyl and hexyl branches were studied, as well as high-pressure polymerized material, LDPE, which clearly contained ethyl, n-butyl, n-amyl and n-hexyl and longer chain branches. The three grades are clearly distinguishable in *Figure 1*.

Temperature has a marked effect on the quality of spectra as summarized in *Figure 2*, and the integral values in *Table 3*. Peak broadening and the presence of shoulders occur when the polymer is partially melted, and the full intensities of the absorption bands are not realized until melting is complete; about 135°C, as found by differential scanning calorimetry (d.s.c.). This presumably arises because of line broadening, ^{13}C–^{1}H dipolar interactions and ^{13}C chemical-shift anisotropy below the melt. A temperature of 140°C was used in all quantitative analysis of the spectra.

Fast inversion-recovery experiments were made to determine the optimum pulse interval for measurements at 140°C (see *Figure 3*). The intensity of the signals were measured at various pulse intervals, τ, and analysed according to equation (1). In this way, spin-lattice relaxation times (T_1) for the various carbon atoms around the branch were measured in the melt and compared with those done in solution[5]. Carbon atoms at the branch were

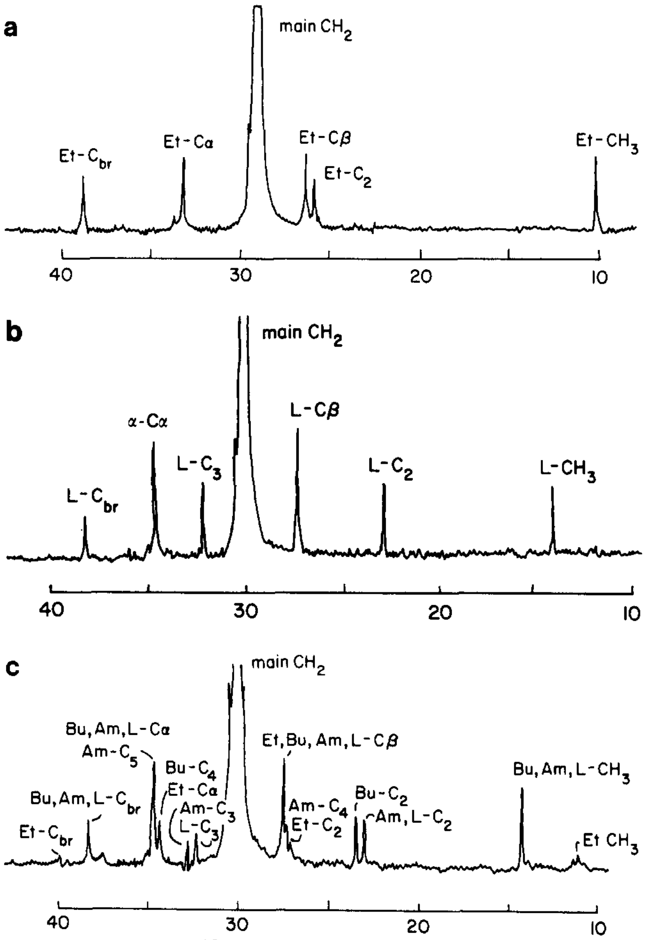


Figure 1 High-field ^{13}C n.m.r. spectra of LDPE: (a) ethyl-branched copolymer, L3; (b) hexyl-branched copolymer, D2; (c) LDPE, BX2

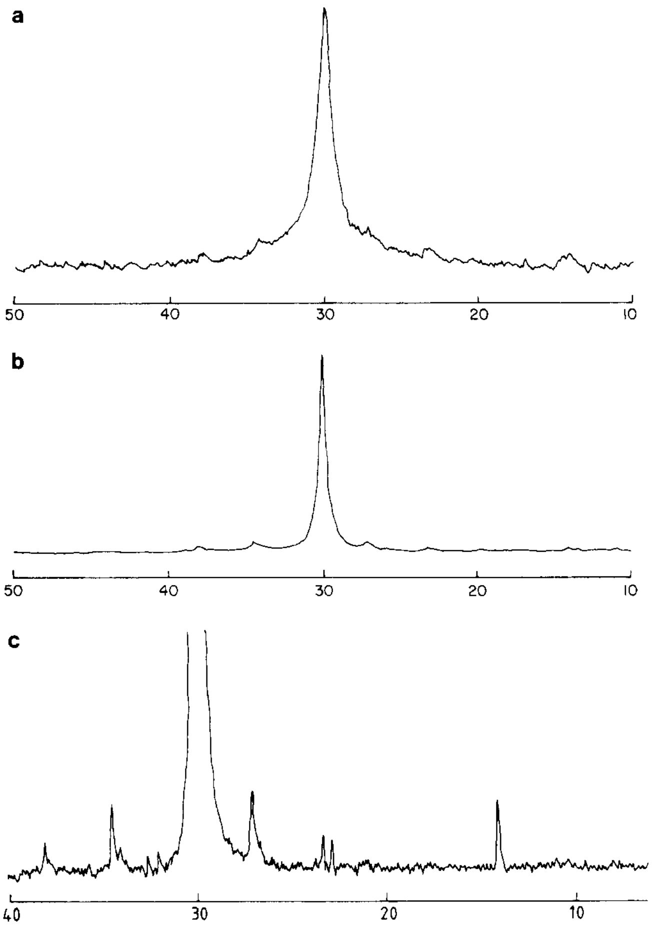
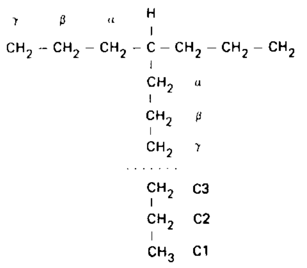


Figure 2 Effect of temperature on the ^{13}C n.m.r. spectra: (a) 80°C; (b) 120°C; (c) 140°C

Table 3 Integrals of absorption bands at different temperatures (given as a percentage of main-chain carbon atoms)

Temperature (°C)	Absorption band (ppm shift from TMS) 38.0	34.5	30.1	27.2	23.2	17.0	14.1
140	0.8	1.6	93.6	2.7	0.5	0	0.9
120	2.1	5.4	84.8	53	1.8	0	0.7
110	2.3	4.9	85.6	1.8	3.4	0	2.0
80	2.4	4.9	86.2	0	5.2	0.8	3.3

labelled according to the nomenclature of Carman and Wilkes[8]



Molten polymer had a shorter T_1 than in solution (see *Table 4*), implying a strong effect of the solvent on chain configuration and molecular relaxations. Comparison is made between molten and solution samples along with the slack variables given in *Tables 5* and *6*. The quality of the spectra are substantially improved, producing lower slack variables with the experiment on molten material.

Very good agreement was observed between i.r. spectroscopic analysis of LLDPEs, containing only one type of branch, and the ^{13}C n.m.r. simplex analysis on molten materials (*Table 7*). We consider this superior to previous methods involving matrix inversion without introducing slack variables.

CONCLUSIONS

The simplex method has been used to determine the ^{13}C n.m.r. spectra of LDPE, with distinct advantages over the conventional inversion of matrix method once the latter leads to unacceptable results. Higher signal to noise ratios than those quoted in this paper are achieved in typical 'state-of-the-art' solution work[9], though only after longer pulse intervals and a larger number of scans. Increased speed of determination reduces risks of thermal degradation and machine drift.

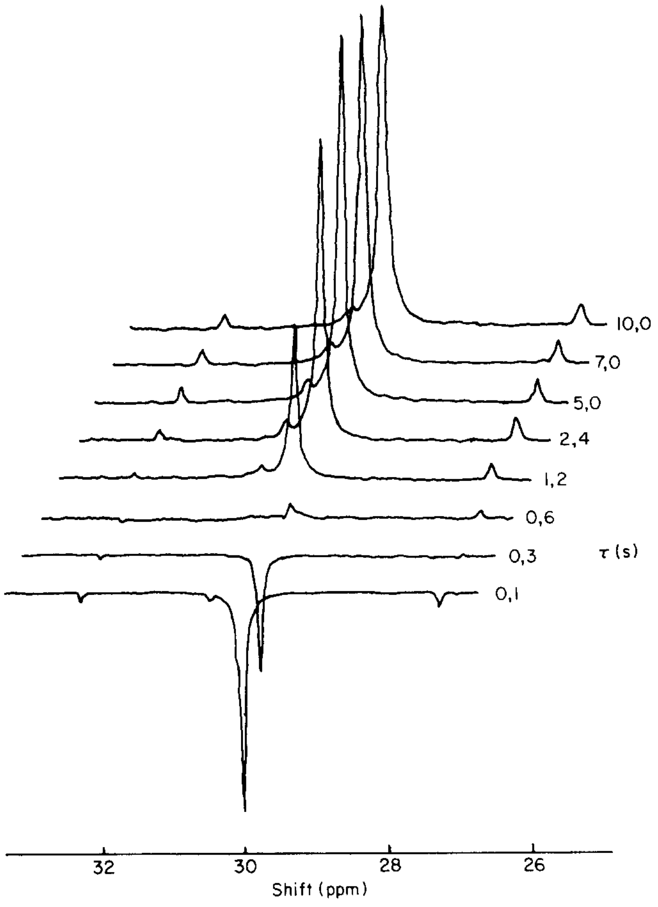


Figure 3 Fast inversion-recovery experiment, D1

Table 4 Spin relaxation times (in seconds) of carbon atoms round the ethyl and hexyl branch for (a) molten PE at 140°C, (b) PE in solution (trichlorobenzene 40% w/v, 67.91 MHz, 118°C)

	(a) Ethyl (S6)	Hexyl/ long-chain (D1)	(b) Ethyl (LDPE)	Hexyl/ long-chain (LDPE)
main chain	1.02–1.32		2.0	
branch carbon	0.68	0.53	2.3	1.2
Cα	0.74	0.48	1.3	1.0
Cβ	1.07	0.58	1.4	1.3
Cγ	–	0.82	–	–
C3	–	1.34	–	–
C2	0.88	1.56	1.3	3.7
C1	3.05	1.87	5.1	7.1

Table 5 Melt studies at 140°C

	Branch concentration			
Samples	Ethyl	Butyl	Amyl	⩾Hexyl
S1	13.1	–	–	–
S4	14.7	–	–	–
S5	12.3	–	1.2	–
S7	–	–	–	–
D1	–	–	–	17.8
D2	–	–	–	16.4
BX2	3.0	10.5	3.8	5.4
BX3	1.1	5.3	1.9	3.5
BX4	–	4.7	1.4	2.3

Pre-pulse delay, 10 μs
Post-pulse delay, 10 s
Dwell time 20 μs
Data size, 8 kbyte to 32 kbyte
Spectral width 25 000 Hz
Sample preparation: molten polymer
Temperature, 140°C
Pulse angle, 55°
Number of scans, 400–1000
Pulse width, 10 μs

Table 6 Solution studies

	Degrees of branching per 1000 main chain carbon atoms			
Sample	n-Ethyl	n-Butyl	n-Amyl	⩾n-Hexyl
S1	14.4	–	–	–
S2	18.6	–	–	–
S3	15.2	–	–	–
S4	17.4	–	–	–
S5	10.5	–	–	–
S6	3.7	–	–	–
S7	0.8	–	–	–
D1	–	–	–	14.3
D2	–	–	–	16.1
BX1	0.7	13.1	2.9	2.2
BX2	1.1	7.0	1.7	2.8
BX3	1.3	10.3	1.3	4.5
BX4	1.3	4.0	0.5	1.4

Temperature, 95°C
Pulse angle, 60°
Sample: 20% (w/v) of polymer in $CD_3C_6D_5$
Number of scans, 1800
Pulse interval, 15 s
Pulse width, 10 μs
Number of data points, 3200
Spectral width, 25 000 Hz

Table 7 Comparison of i.r. and ^{13}C n.m.r.

	Total branches per 1000 main-chain carbon atoms			
Sample	^{13}C n.m.r. solution	^{13}C n.m.r. molten	i.r.	Branch type
L1		18.8	18.9	Ethyl
L2		22.3	20.2	Ethyl
L3		16.1	15.0	Ethyl
S1	14.4	13.1	13.7	Ethyl
S4	17.4	14.7	16.3	Ethyl
S5	10.5	12.3	11.6	Ethyl
S7	0.8	0.0	1.7	Ethyl
D1	13.8	14.3	14.1	n-Hexyl
D2	16.1	16.4	14.0	n-Hexyl

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