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Branching in Polyethylenes. Study by High Resolution Nuclear Magnetic Resonance

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SUMMARY

The values of the CH_3/CH_2 ratios measured from accumulated NMR spectra of polyethylenes samples are in good agreement with those obtained from conventional IR techniques. Because NMR does not require calibration, systematic errors could be less important. Owing to the estimated values of the CH/CH_3 ratios, tetrasubstituted carbon atoms are present in all the high-pressure polyethylene specimens.

INTRODUCTION

The solid-state properties of polyethylenes (PE) are influenced by the presence of alkyl branches. Up to now, IR techniques have always been used in the determination of the CH_3/CH_2 ratios. According to Roedle [1], an intermolecular hydrogen-transfer mechanism (back-bitting) is

Table 1. Experimental Results of Some Polyethylene Specimens

Sample	MA2004[b]	MA2004 (SH)	MA2004[b] (IH)	MA0402[b]	MA0421[b]	MG0426[b]	PH[c]
Catalyst	Rad.[g]	Rad.[g]	Rad.[g]	Rad.[g]	Rad.[g]	Ziegler	Phillips
Pressure[f]	HP	HP	HP	HP	HP	LP	LP
Density[d] (g/cm^3)	0.9174	–	–	0.9204	0.9251	0.9821	0.9733
$\overline{M_n}$(GPC)[a]	8.9×10^3	6.1×10^3 [e]	–	13×10^3	11.2×10^3	7.6×10^3	6.6×10^3
$\frac{\overline{M_n}}{\overline{M_w}}$(GPC)[a]	8.77	–	–	10.6	5.9	8.1	12.9
Intrinsic viscosity (dl/g)	0.96	–	–	1.41	1.11	1.43	2.38
CH_3/CH_2 (IR)	3.8×10^{-2}	–	3.4×10^{-2}	3.6×10^{-2}	2.8×10^{-2}	10^{-2}	10^{-2}
CH_3/CH_2 (NMR)	3.1×10^{-2}	4×10^{-2}	2.7×10^{-2}	3.2×10^{-2}	2.5×10^{-2}	4×10^{-3}	–
CH/CH_3 (NMR)	4.7×10^{-1}	5.2×10^{-1}	2.8×10^{-1}	2.5×10^{-1}	2.7×10^{-1}	–	–

[a] $\overline{M}_n$ and $\overline{M_w}$ obtained using Waters Polystyrene standards (Q = 11).

[b] PE specimens made by Ethylene-Plastique.

[c] PE specimens made by BP Chemicals.

[d] Density measured at 23°C for PE specimens annealed at 150°C during 1 hr and cooled at a rate of 5°C/hr.

[e] $\overline{M}_n$ from vapor pressure osmometry in toluene solvent (Mechrolab 301).

[f] HP: high pressure. LP: low pressure.

[g] Rad: radical polymerization.

responsible for the presence of butyl branches in free-radical PE polymerized under high pressure (HP-PE). From IR, irradiation, and mass spectrometry analysis of PE and deuterated model compounds, Willbourn [2] concluded that the branches are probably ethyls and butyls.

The present study is concerned with the high-resolution nuclear magnetic resonance (HR-NMR) analysis of different PE. Theoretically, an enhanced signal/noise ratio by NMR spectrum accumulation allows quantitative determinations of methine, methylene, and methyl protons, hence the CH_3/CH_2 ratios. In this work, only the numbers of branches were estimated, not their length.

EXPERIMENTAL

Materials

All the PE samples used here are commercially available polymers made by Ethylene-Plastique and BP Chemicals. Table 1 gives details about these polymers.

NMR Analysis

The PE specimens were dissolved in o-dichlorobenzene (ODCB) and filtered at 130°C in order to avoid any undesirable fractionation. The NMR spectra were recorded using a Varian DA-60-IL Spectrometer and a Jeol JR-Al Spectrum Accumulator. (Solution of 5% PE in ODCB; temperature, 130°C; internal reference, one of the most intense line of ODCB; frequency measurements based on the hexamethyldisiloxane singlet at 9.91 τ.)

Because of the weakness of the methyl and methine resonances compared to the methylene ones, all the accumulated spectra were recorded in two steps. At first the CH_3/CH_2 ratio is obtained, and in the second step the CH/CH_3 ratio. In spite of the high temperature (130°C), the resolution was not sufficient to allow direct integration of the spectra. All the intensity measurements were achieved by planimetry after a visual estimation of the overlapping resonances. Nonetheless, in the case of the methine resonances, the estimation of the CH/CH_3 is not very accurate.

IR Analysis

The IR instrument used in this study was a Beckmann IR-10 Spectrometer. The spectra were recorded with PE specimens melted at 150°C.

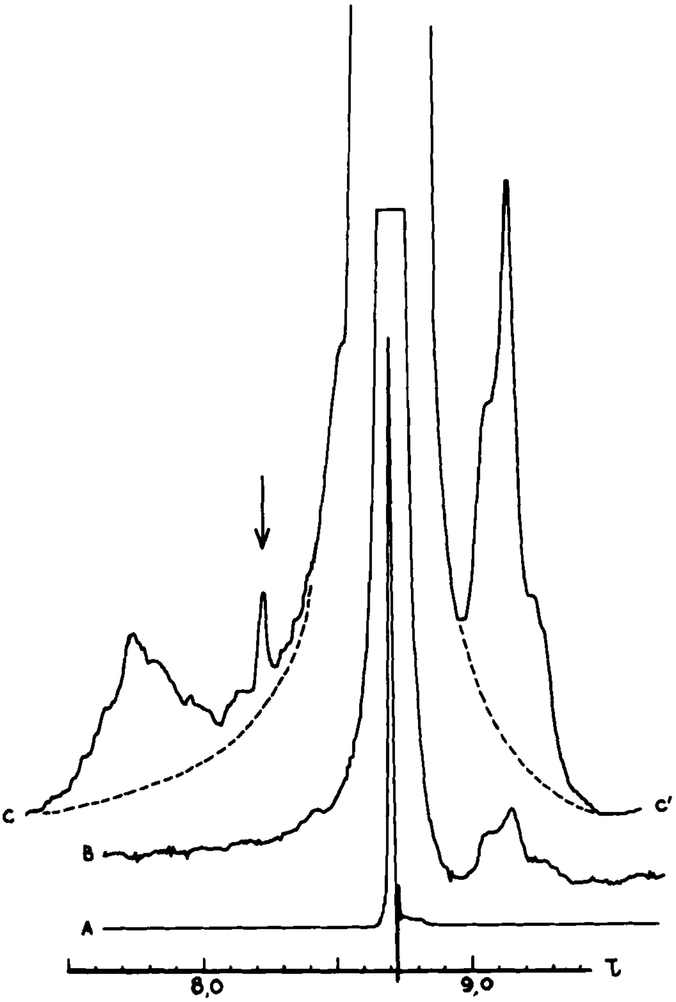

Fig. 1. NMR spectra of a high-pressure polyethylene. (A) Single scan spectrum. (B) Accumulated NMR spectrum; methylene and methyl resonances. (C, C′) Accumulated NMR spectrum; methine (C) and methyl (C′) resonances (the actual intensity of C′ has been reduced four times). The arrow indicates a nonidentified impurity.

Optical density measurements were calculated from the two IR bands at 1366 and 1378 cm^{-1} (Fig. 2). The actual CH_3/CH_2 ratios were determined using a calibration curve obtained from linear hydrocarbons [3].

We also used gel permeation chromatography (GPC) (Waters Associates instrument; solvent, 1,2,4-trichlorobenzene at 135°C) and viscometry (Ubbelhode; solvent, decalin at 135°C). Differential scanning calorimetric analysis were carried out using a CPC 600 (C.E.A. Patent) instrument.

RESULTS AND DISCUSSION

In the single scan NMR spectrum of PE, only the methylene resonances could be observed at 8.75 τ (Fig. 1A). After accumulation, the spectrum of the methyl protons (158 scans) appears as a triplet centered at 9.15 τ (Fig. 1B), while the methine resonances are an unresolved broad absorption near 8.2-8.3 τ. The dome centered at 7.8 τ is mainly due to ^{13}C satellite from methylene protons (256 scans, Fig. 1C).

In the estimation of the CH/CH_3 ratios (Spectra C and C′, Fig. 1), $^{13}C-H$ satellites from methylene groups, located at approximately 1 ppm from each side of the main peak, have been taken into account (intensity of the two satellites = 1.1% of the main peak). The intensity of Spectrum C (Fig. 1C) is in fact the sum of the intensities of the methine protons and 0.55% of the methylene protons. Hexamethyldisiloxane was not used as an internal reference, so there was no perturbation from ^{13}C satellite in the methyl resonances. Finally, the contribution of the ^{13}C satellite from methyl groups to the intensity of the methylene resonances is negligible.

The values of the CH_3/CH_2 ratios are listed in Table 1; there is rather good agreement between IR (Fig. 2) and NMR techniques. Methyl groups from branches are in greater quantity in the HP-PE specimens. It is interesting to note that no methyl group could be detected in the Ziegler sample MA 0426 by IR analysis, while by NMR the CH_3/CH_2 ratio was found to be about 4×10^{-3}. Vinyl absorption bands were only observed by IR (at 910 and 990 cm^{-1}) in the Phillips specimen.

The highest melting point of HP-PE MA 2004 is about 106°C. After refluxing in boiling hexane (under inert N_2 atmosphere for 48 hr at 68°C), a soluble fraction of PE (~10%) was separated ($\bar{M}_n = 6.1 \times 10^3$, by vapor pressure osmometry). After the same thermal history (sample annealed at 82°C for 90 min), the differential scanning calorimetric analysis (DSC) trace of the soluble fraction (SH) (Fig. 3B) differs from the one of the insoluble fraction IH (Fig. 3A). Under the same conditions the DSC trace

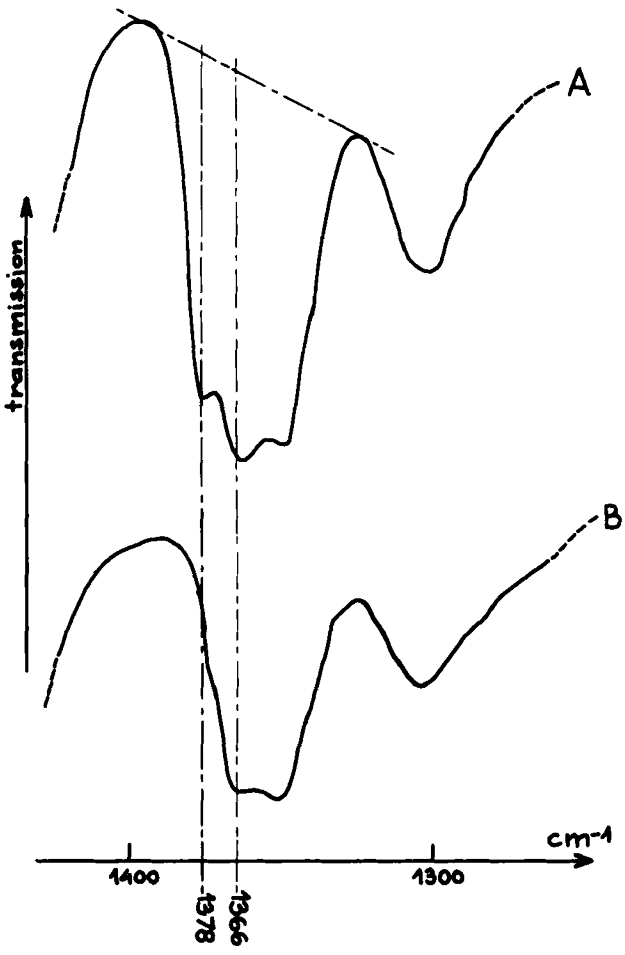

Fig. 2. IR spectra of polyethylene samples melted at 150°C. (A) High-pressure polyethylene. (B) Phillips specimen.

of the IH fraction is not very different from that of the initial MA 2004, while the DSC trace of the SH fraction is less resolved. At 97°C, only 30-35% of IH have been melted, and the percentage of melt polymer reached 50-55% for SH (estimation by planimetry measurements.)

From NMR analysis, the SH fraction does contain more methyl groups than both the initial polymer and the IH fraction (Table 1).

A survey of the estimated values of the CH/CH_3 ratios (Table 1) shows

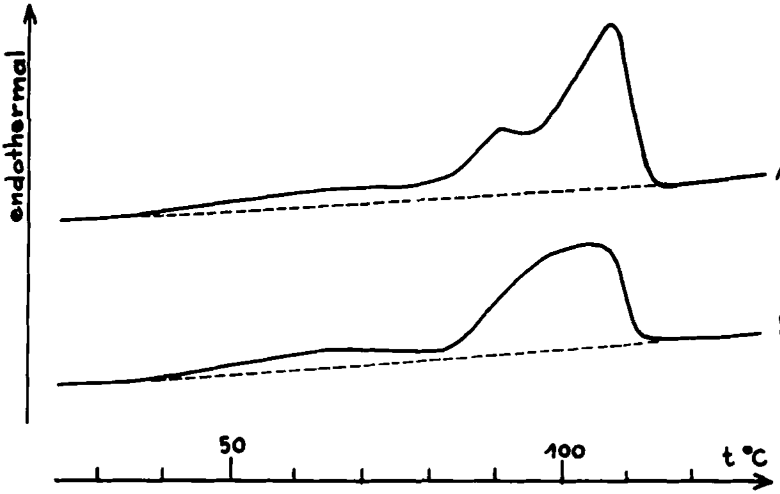

Fig. 3. Differential scanning calorimetric analysis traces of high-pressure polyethylene MA 2004 after being annealed at 82°C for 90 min. (A) Insoluble fraction in boiling hexane (IH). (B) Soluble fraction in boiling hexane (SH).

that, for all HP-PE specimens, these values are lower than unity. About 50-70% of the methine groups (these values could be overestimated) have lost their protons by hydrogen transfer during the polymerization process, and the corresponding carbon atoms are tetrasubstituted. In the case of the two fractionated sample, the SH fraction contains more methine and methyl groups, and the IH fraction is richer in tetrasubstituted carbon atoms. It is possible that the presence of quaternary carbon atoms could also favor the insolubility and the crystallinity of the IH fraction. Actually, for the same number of branches per polymer chain, the number-average sequence length of linear sequences is greater when a part of the branched units of the chain has two branches instead of one.

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