

Determination of Total Short-Chain Branching in Polyethylenes by Computerized Data Processing of Infrared Spectra

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Synopsis

A computer method is described to determine the short-chain branching of polyethylene from IR spectroscopic data. The shape of the band at 1378 cm^{-1} (characteristic to the methyl side groups) was calculated by using first a deconvolution procedure (Ishige method) for the envelope curve of the overlapping peaks in the region of $1300\text{--}1400\text{ cm}^{-1}$, followed by a convolution calculus applied only to the deconvoluted points of the peak in question. The results were in good agreement with values determined by Willbourn's compensation method.

INTRODUCTION

A considerable number of reports¹⁻⁶ have been published about the IR investigations of polyethylenes including their products manufactured by a wide variety of techniques. The absorption bands of methyl groups were identified, and, after that, they were utilized for determination of short-chain branches.⁷⁻¹⁰

Mainly the intensity changes of the band at 1378 cm^{-1} were objected in the studies using different methods.¹¹⁻¹³ Elliott¹⁴ and others found that side chains oriented parallel to the main polymer chain comprised not less than four carbon atoms. Some other authors,¹⁵ however, conducted polarized infrared spectroscopic investigations and concluded that the branched side chains were quite variable in length. They established experimentally that the number of branches containing four or less carbon atoms was generally identical to that of the longer branches.

For a more accurate evaluation of the measurements, Buckley and Cross¹⁶ and Willbourn¹¹ prepared polymethylene by copolymerization of ethane with diazomethane. Although the copolymer synthesized in this way had a higher degree of crystallinity than a polyethylene containing the same amount of methyl groups, it had no influence on the experimental results.⁸

The same authors¹⁷ also prepared polymethylenes comprising side chains with lengths of amyl to *n*-undecyl. It was established that the side chains of polyethylene might be longer than a methyl group but inevitably shorter than an *n*-undecyl chain.¹⁸ It seems to be supported by the fact that pyrolysis products of electron irradiated polyethylene samples consist mainly of C_2H_6 and C_4H_{10} groups.^{19,20} In addition, it was evidenced by several authors^{21,22,11} that branches included C_2 and C_4 hydrocarbons.

There is a rather serious controversy in the literature dealing with the determination of short-chain branching. It might be explained by the fact that the

extinction coefficient of the $\delta_s(\text{CH}_3)$ vibration is dependent on the length of the side groups.^{23,24}

The extinction coefficients of the CH_3 deformation vibrations of short-chain branches in saturated polymeric hydrocarbons was determined by Reding and Lovell²³ and Müller et al.^{25,26} in dependence on the length of side chains in model substances. The number of CH_2 groups arranged between the main chain and the methyl group of alkyl branches affects the intensity of the absorption at 1378 cm^{-1} .

It was shown^{23,25,26} that the extinction coefficient depends also on the degree of crystallinity.

It should be noted, however, that the accurate quantitative analysis also meets with technical difficulties, since at $1400\text{--}1300\text{ cm}^{-1}$ the absorption bands of crystalline structures are also located. Thus, the individual bands are combined at some frequencies, resulting in the appearance of the absorption of methyl groups at 1378 cm^{-1} (characterizing the degree of branching) only as a shoulder; therefore, the overlapping peaks have to be separated. Since Willbourn's compensation method¹¹ is a very tiresome and lengthy procedure, attempts^{26,27} were made to solve the problem by mathematical means.

The aim of this paper is to present a calculation method by the help of which the compensation can be avoided and so the whole procedure becomes faster.

EXPERIMENTAL

Materials. Polyethylene samples obtained by various technologies at different parameters were analyzed. Their tradenames were: Epolene C 101, C 13, C 10, N 12; Lupolen KR 1051; Hostalen GC, GF; Hoechst PA 560, PA 130; BASF Wachs 400; and Alkathene HD.

Methods. Polyethylene samples were compression-molded between smooth-heated plates at $135\text{--}140^\circ\text{C}$ into films of $90\text{--}140\text{ }\mu\text{m}$ in thickness.

Infrared spectra were recorded by a Zeiss UR-10 Double-beam Spectrograph. The measuring beam passed through the polyethylene specimens while the compensating beam, if necessary, transmitted a linear polyethylene film.

For all spectra absorbances (ordinate values) belonging to the wave numbers (abscissa) at every 1.25 cm^{-1} were determined in the interval of $1320\text{--}1420\text{ cm}^{-1}$.

Data processing was carried out by a HP 9830B desktop computer. Functions of absorbance per specimen thickness (A/l) against the degree of branching in terms of 1000 carbon atoms ($\text{CH}_3/1000\text{ C}$) were established. Considering their linearity, the equations were formulated by the least squares method.

COMPUTATIONS

In the present paper, only determination of total degree of branching is covered. The principle of the calculation method for determination of the component which is characteristic to the short-chain branching among overlapping bands is as follows: First of all, the spectrum is transformed so that the transformation values characteristic of the individual components (peaks) can be separated from each other. Then the transformed values of the band charac-

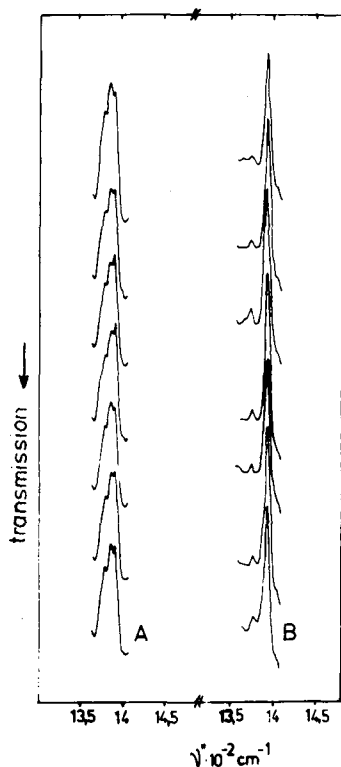


Fig. 1. Noncompensated (A) and compensated (B) spectra of some polyethylene samples in the range of $1350\text{--}1450\text{ cm}^{-1}$.

teristic of branching are selected and retransformed, resulting in the “pure” form of the band wanted.

The advantage of this method is that the errors due to the approximations and assumptions used in the transformation are compensated for by the retransformation when the same errors are involved inversely.

For transformation, the deconvolution procedure was used, i.e., overlapping of bands was regarded only as a band-widening effect caused by the imperfectness of the instrument. It is obviously not a reasonable assumption but permissible since the errors become level during the convolution, corresponding to the inverse transformation.

Deconvolution was performed by the procedure of Ishige et al.²⁸ It was considered the most suitable since, being an iteration technique, it was less sensitive to noise, involved only a few initial limiting conditions, and required relatively short computing time.

The principle of the deconvolution technique is as follows: Let the measured curve be designated by f , the nondistorted (wanted) curve by w , and the operator describing mathematically the band widening effect by $G *$; then the problem is settled:

$$f = G * w \quad (1)$$

As f and $G *$ are known, w can be determined.

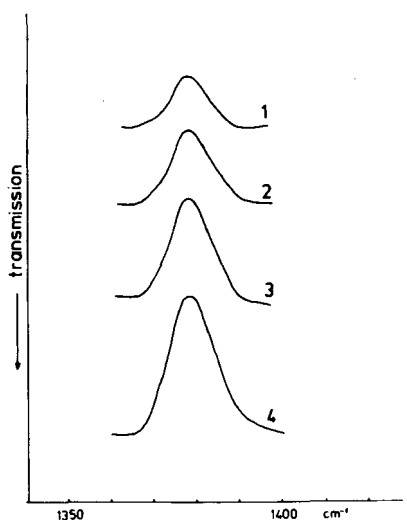


Fig. 2. Compensated IR spectra of polyethylene in the range of 1350–1450 cm^{-1} .

During the calculations, a certain tentative w'_1 function is supposed (normalized to unit area), which can even be the correspondingly normalized original f curve itself; then it is subjected to the operation $G *$, obtaining the function

$$f'_1 = G * w'_1 \quad (2)$$

which is compared to the referring f function by scanning from point to point. Inasmuch as the summarized deviation between the two functions exceeded an arbitrarily defined threshold value, w'_1 would be changed according to the deviation:

$$w'_2 = w'_1 + (f - f'_1) \quad (3)$$

The function w'_2 obtained in this way is then normalized and transformed by the $G *$ operation again into the function

$$f'_2 = G * w'_2 \quad (4)$$

which is compared to function f from point to point. This periodic procedure is continued until the summarized absolute deviations between the measured and the actual calculated function have decreased below the desired value.

During the processing of spectra, the following approximations were introduced:

(a) Operation $G *$ was replaced by a convolution integration:

$$f(\nu) = \int_{-\infty}^{+\infty} g(\nu - y) \cdot w(y) dy \quad (5)$$

where y is an auxiliary integration variable in wave number dimension, ν is the wave number, and $g(y)$ is a function corresponding to the curve of a band undisturbed by the adjacent ones.

(b) The function $g(y)$ was approximated by the spectra compensated with a branchless polyethylene.

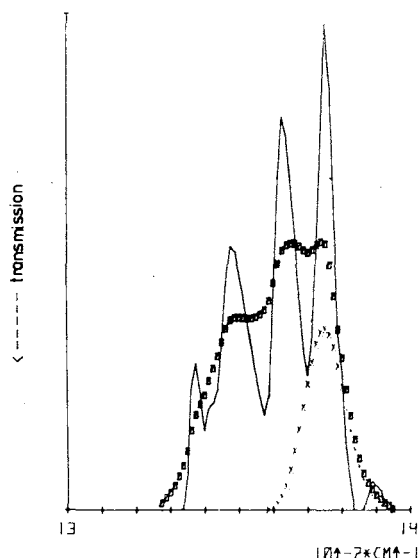


Fig. 3. Original (\square), transformed (—), and retransformed (xxx) IR spectra of LDPE in the range of 1300–1400 cm^{-1} .

(c) The integral was substituted by summation:

$$f_{\nu} = \sum_{y=-a}^{+a} g(\nu - y) \cdot w(y) \quad (6)$$

where $a = 8$ and y has only integer values.

(d) The shape of function g was regarded as constant in the studied range of wave numbers.

RESULTS

Figure 1 shows some noncompensated and compensated spectra of polyethylenes in the range of 1320–1420 cm^{-1} .

It was attempted to establish how much the results were influenced by the shape of the function g , which might depend partly on the intensity of the compensated band and partly on the experimental errors.

In order to determine the function g , four bell-shaped curves obtained by compensation at different intensities (i.e., the band characteristic to branching) were used, as shown in Figure 2.

The bell-shaped curve was then approximated by its 17 equidistant points and the distances (1.25 cm^{-1}) between the adjacent points were regarded as unity for the following treatments.

Several IR spectra of various polyethylenes were processed by the present calculation method. Although the individual bands of curves have not been completely resolved (Fig. 3), they are distinct enough to extrapolate the overlapped part of the wanted "corrected" band with minor error. Thus, the "corrected" (or, in other words, transformed) band can be obtained. Omitting then the other components, the wanted band can directly be set up (calculating f with the knowledge of w and g).

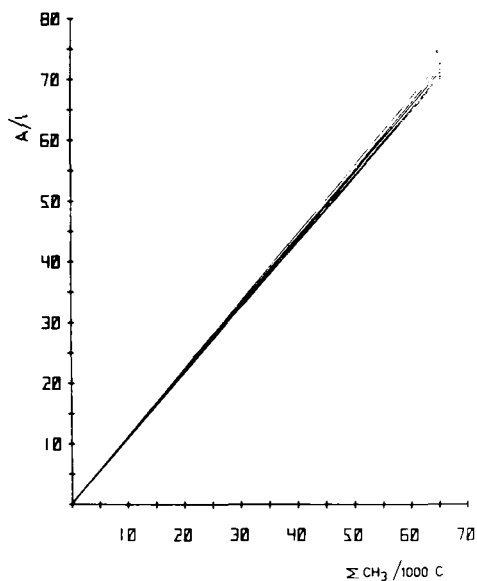


Fig. 4. Changes in the relationship between A/l and $\text{CH}_2/1000 C$ using the "g" functions obtained from different intensity maxima.

Now, since the intensities of individual bands are known for samples of known degree of branching, an absorbance vs. total branching calibration curve was determined which passes to the origin. Slopes of a series of calibrations recorded by using different g functions obtained from compensation curves of different intensities are nearly identical (Fig. 4), i.e., the procedure is practically insensitive to the errors occurring in the determination of the function g . The slope of the straight line obtained by the present method is 1.176. Data for the total branching obtained by different g functions are collected in Table I.

TABLE I
Total Short-Chain Branching of Polyethylenes Using Different g Functions Obtained from Compensated IR Curves of Different Intensities

Sample	Index of curves ^a				From the average of curves
	1	2	3	4	
Lupolen 1810	23.1	22.9	23.2	23.0	23.1
Epolen C 11	8.9	9.0	9.3	8.6	9.2
Hostalen GC	3.2	2.9	3.1	3.0	3.0
Marlex 6015	1.6	1.4	1.5	1.4	1.5
Lupolen 6011	1.1	1.4	1.1	1.1	1.0
Alkathen HD	8.4	8.4	8.3	8.0	8.1
Hostalen GF	6.9	6.0	5.8	5.6	5.7
Hoechst PA 520 ^b					
A					39.0
B					39.6
C					39.0

^a See Figure 2.

^b Films with variable thickness: (A) = 43.8 μm , (B) = 51.0 μm , (C) = 38.9 μm .

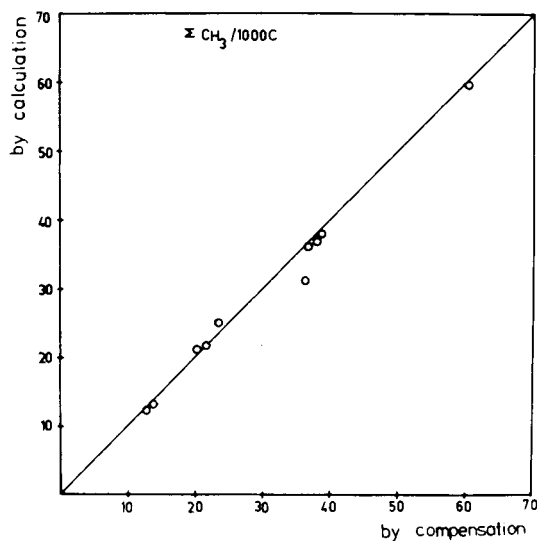


Fig. 5. Comparison between the total degrees of branching when determined by the compensation and by the computer method.

In Figure 5 the compensation technique and the present procedure are matched by the data for total branching of several high and low density polyethylene samples.

The branching frequencies of the sample PE C-28878/0 were determined also by NMR technique.²⁹ The result was 17.4 $\text{CH}_3/1000\text{C}$ which is in good agreement with the 16.9 $\text{CH}_3/1000\text{C}$ value of our measurement.

The presented calculation method for peak resolution is definitely faster than the Willbourn's compensation procedure. It is especially advantageous in the case of low branching concentrations (one to five branching points for 1000 C atoms), where the determination of the correct thickness of the polyethylene films used for compensation is very time-consuming. In the course of compensation the base line is frequently shifted, which produces an additional source of error.

The question remains, however, as to the accuracy of the whole procedure, that is, the determination of the branching frequency where the curve resolution is only one step. A number of authors^{23,25,26} have shown that the extinction coefficient is dependent on the length of the side group as well as on the degree of crystallinity of the sample. So the IR results can not directly be converted to absolute methyl content without knowing the proper extinction coefficients and the proportion of the different kinds of side groups present in a given sample.²⁵

One should take into consideration, however, the following: the dependence of the extinction coefficient on the sample crystallinity is not significant^{23,25}; at the same time, the majority of the branches consists of ethyl and butyl groups and their concentration rate can be determined by other methods.^{25,26}

On the basis of these facts, one may state that the branching frequency of the polyethylenes can be determined by the method presented with reasonable accuracy.

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