

Thermal Fractionation and Identification of Low-Density Polyethylenes

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SYNOPSIS

In the present publication, a method to identify and distinguish between different types of low-density polyethylene based on thermal fractionation and FTIR analysis is described. It was shown that during thermal fractionation four to seven endothermic peaks are obtained as opposed to one or two peaks obtained during regular differential scanning calorimetric analysis. The ratio between band heights at 1368 and 1376 cm^{-1} was found to represent the length of the side chain (branch). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyethylene (PE), low-density polyethylene (LDPE), medium-density polyethylene (MDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) are widely used today in different packaging applications in the form of flexible films and laminates for bags and as semirigid and rigid containers as well as in pipe extrusion and injection molding of different items. Whereas LDPE, MDPE, and HDPE are homopolymers, LLDPE is the common name for copolymers of ethylene with small amounts of the alpha-olefins: butene (Union Carbide), hexene (DuPont), and octene (Dow Chemical). Thus, LLDPE actually represents three families of polymers where the grades in each family differ in molecular weight (MW) average and in molecular weight distribution (MWD) and the three families differ in the comonomer and therefore also in the properties. A schematic description of the structure of the three main polyethylene types was given by Miltz.¹ The use of LLDPE, which is the most recently developed and applied among the polyethylenes, expanded very rapidly in the 1980s as a single polymer and as a blend with other polyethylenes, primarily LDPE, in film manufacturing.

The LLDPEs, in general, have better mechanical properties than those of LDPE,^{2,3} but their melt vis-

cosity is higher (and are therefore more difficult to process), are more difficult to orient, and have poorer optical properties and inherent cling characteristics (a property important for stretch films).⁴ Blends of LLDPE and LDPE provide properties that could be better tailored for specific applications than for each polymer separately. The type of LLDPE used in films affects their properties as was demonstrated by different researchers.^{5,6} Since film manufacturers do not necessarily reveal the composition of commercial films, the ability to identify the type of LLDPE used in different films (applied in packaging and agriculture) is valuable. The melting range of LLDPE is reported, in the scientific and technical literature, to be in the range of 115–130°C compared to 105–115°C of LDPE¹ and the endotherms of melting of each polymer, as measured by differential thermal calorimetry (DSC), was generally reported to comprise one or two peaks.^{5,7-9}

Because of the similarity in structure, it is difficult to identify the type of LLDPE and no simple method for such an identification was found in the scientific literature. The present publication describes the thermal fractionation of LDPEs and a method for identification of the different LLDPEs.

EXPERIMENTAL

Materials

The structure and properties of the LDPE studied in the present work was previously described^{10,11} and

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was designated as grade PE-A. Three LLDPE of the butene type, two of the hexane type, and five of the octene type were studied and are designated as B-1, B-2, B-3, H-1, H-2, O-1, O-2, O-3, O-4, and O-5, respectively. Some identifying properties of these polymers are summarized in Table I.

Methods

Initial DSC Analysis

In the initial set of experiments, the PEs were heated in the DSC (DuPont Model 2000) instrument at a rate of 10°C/min from room temperature to 200°C (to obtain the first endotherm), then cooled at the same rate to 30°C (to obtain the exotherm) and heated again at the same rate to 200°C to obtain the second endotherm. This procedure was followed in order to equate the thermal history of the different samples.

Thermal Fractionation

The polymer samples were heated in the DSC instrument from room temperature to 130°C at a rate of 10°C, maintained at this temperature for 30 min, and then successively cooled by 5°C at a rate of 1°C/min and maintained at each temperature for 30 min.

Table I Characteristics of the Studied LDPEs and LLDPEs

Polymer	Density (g/cc)	Melt Flow Index (g/10 min)
LDPE (PE-A)	0.923	0.25
B-1	0.917	2.69
B-2	0.920	0.90
B-3	0.918	1.0
H-1	0.918	0.90
H-2	0.918	0.92
O-1	0.919	0.96
O-2	0.917	2.10
O-3	0.923	0.68
O-4	0.920	1.0
O-5	0.912	1.1

Thus, the sample was kept at each of the following temperatures: 130, 125, 120, 115, 110, 105, 100, 95, and 90°C for 30 min and then cooled to 30°C at a rate of 10°C/min. The sample was then heated again to 200°C at a rate of 10°C/min to obtain the second endotherm during which several peaks (fractionation method) were obtained for each sample. This is, in principle, a similar method to the "stepwise isothermal segregation technique (SITS)" described

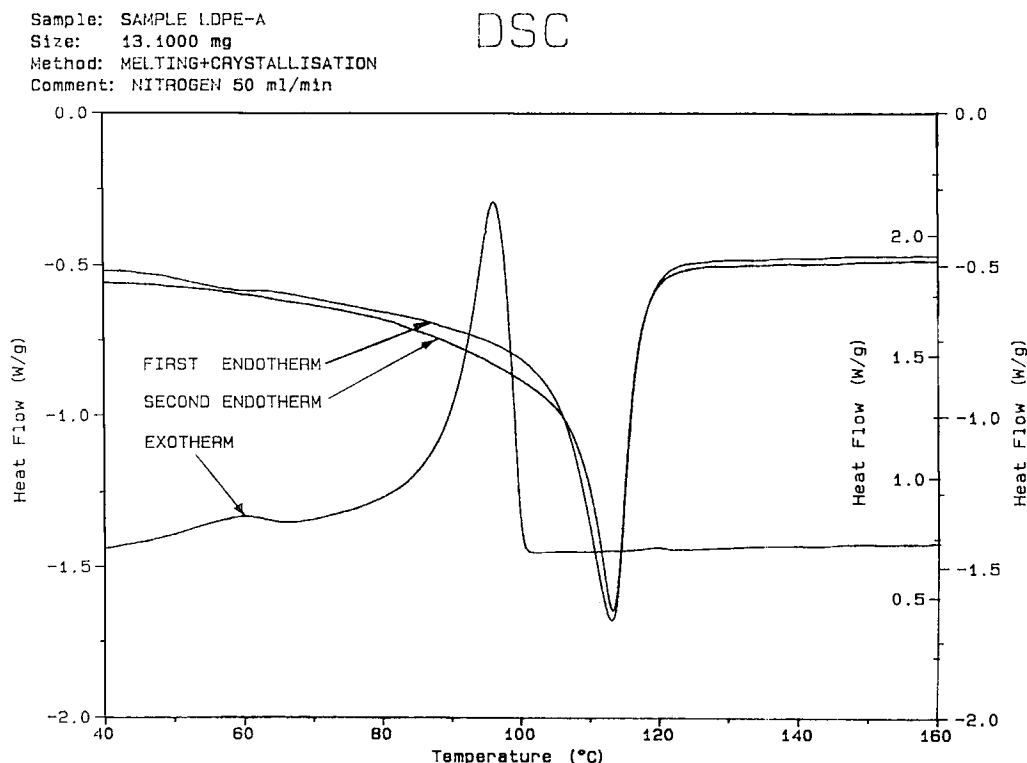


Figure 1 First endotherm and exotherm and second endotherm of LDPE : PE-A.

Sample: SAMPLE O-1
 Size: 7.4000 mg
 Method: MELTING+CRYSTALLISATION
 Comment: NITROGEN 50 ml/min

DSC

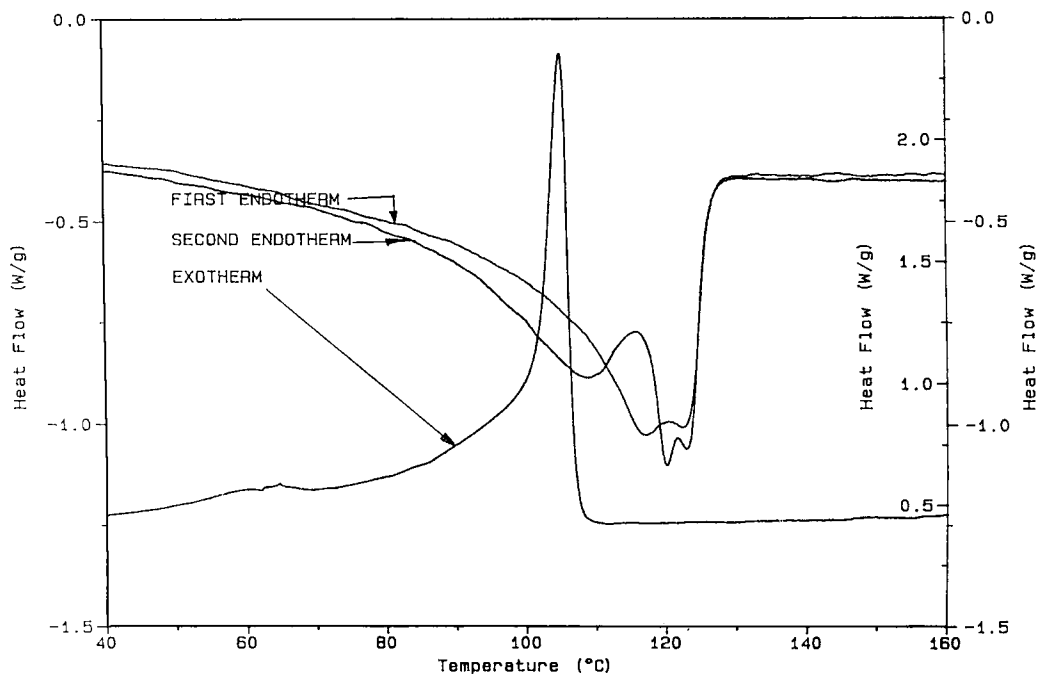


Figure 2 First endotherm and exotherm and second endotherm of LLDPE : O-1.

Sample: SAMPLE LDPE-A
 Size: 6.1000 mg
 Method: ISOTHERMAL METHOD
 Comment: NITROGEN 50ml/min

DSC

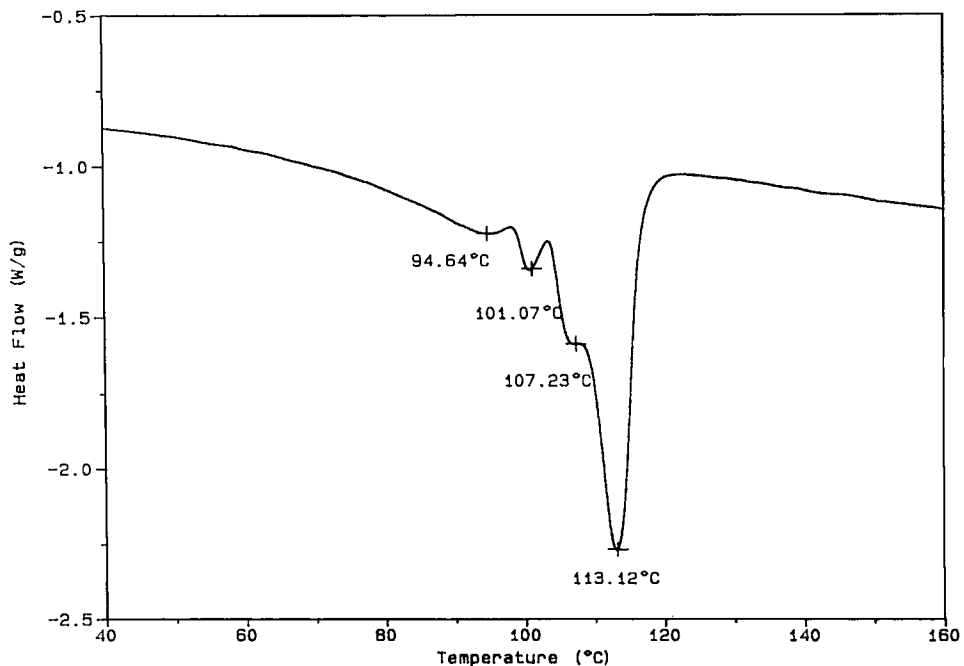


Figure 3 Endotherm of sample PE-A obtained during the thermal fractionation.

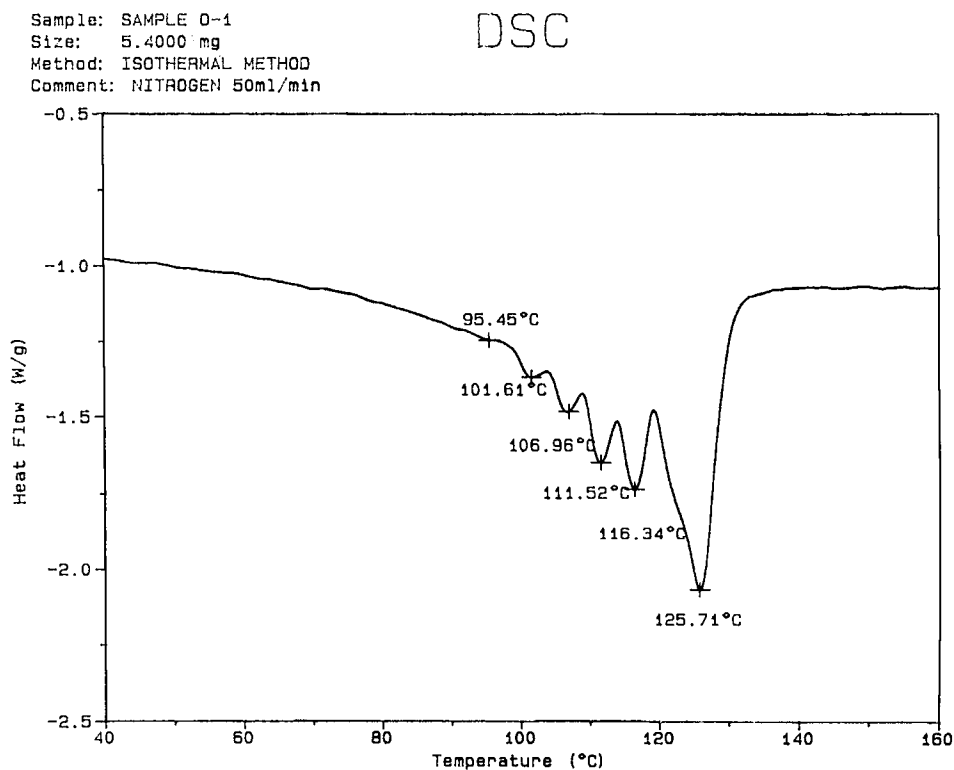


Figure 4 Endotherm of sample O-1 obtained during the thermal fractionation.

by Kamiya et al.¹² The only details, however, given in that reference is that "the sample was melted at 200°C and subjected to isothermal crystallization at intervals of 5°C over its melting range and its melting behavior was analyzed at a temperature rising rate of 5°C/min after the sample was cooled to room temperature."

Infrared (FTIR) Analysis

Films of the different samples were prepared from the pellets by compression molding. The FTIR spectra of the films were obtained in an FTIR spectrophotometer (Perkin-Elmer Model 16 PC) in the range of 400–4000 cm^{-1} .

RESULTS AND DISCUSSION

Figures 1 and 2 represent the first and second endotherms as well as the exotherms for the LDPE (PE-A) and one representative LLDPE (O-1), respectively. In most of the literature, it is claimed that polyethylenes demonstrate one melting peak when heated in the DSC. The normal heating rates during these experiments are 10 or 20°C/min. From Figures 1 and 3, it can be seen that during normal

heating or cooling in the DSC really only one or two peaks are obtained as was also claimed in the literature.^{5,7-9} Similar endotherms and exotherms were obtained for the other octene as well as for the hexene- and butene-type copolymers.

Figures 3 and 4, represent the respective endotherms of the same samples that were heated in the DSC according to the fractionation method described in the Experimental section. It can be seen that for the LDPE four peaks and for the LLDPE six to seven peaks were obtained in the temperature range of 92–130°C. These peaks represent the melting, at different temperatures, of different zones in the polymer, probably differing in molecular weight and molecular weight distribution, configuration, and distribution of side branches, all of which may affect the crystalline structure or size of crystallites. Kamiya et al.¹² compared the temperature rising elution fractionation (TREF) and the SIST methods to study the comonomer distribution in narrow fractions of LDPE. They found that beyond a molecular weight average (M_w) of 10,000 the effect of end-group crystallization was molecular weight-independent. They also found differences in the DSC endotherms, including the number of peaks, obtained by the SIST method between fractions containing low and high concentrations of comonomers.

Table II Melting Peaks of the Different LDPE Polymers

Polymer	Melting Peaks (°C)							
	MP1	MP2	MP3	MP4	MP5	MP6	MP7	MP8
PE-A	95.2	100.0	106.0	—	114.0	—	—	—
B-1	92.4	99.7	104.6	109.3	114.2	—	124.0	—
B-2	92.9	100.5	105.4	110.0	115.4	—	126.7	—
B-3	92.5	100.0	104.9	110.0	115.1	—	126.1	—
H-1	95.7	100.8	105.6	110.4	115.7	121.4	—	130.2
H-2	94.3	100.4	105.2	110.2	115.5	121.0	—	129.0
O-1	94.8	100.7	105.7	110.7	115.7	—	124.6	—
O-2	94.5	100.7	105.6	110.4	115.3	—	126.0	—
O-3	98.7	101.5	106.6	111.3	116.3	—	125.7	—
O-4	93.8	99.8	104.8	109.8	114.8	—	124.8	—
O-5	93.6	100.4	105.3	110.1	114.7	—	125.1	—

They found, however, no differences between polymers with different comonomers in fractions containing high comonomer concentrations. Our study was carried out with whole LLDPEs and not with fractions. We found that the number and position of the peaks in the DSC endotherms obtained during the fractionation method outlined in the Experimental section depended on the type of comonomer in the polymer.

It is not difficult, of course, to distinguish between LDPE and LLDPE as the highest melting peak of

the former is at a temperature below 115°C compared to 124°C and above for the latter. However, no method was found in the scientific and technical literature that enables one to identify and distinguish between the different types of LLDPE, as was stated in the Introduction.

In Table II, the temperatures of the different peaks of the polymers are summarized. From this table, it can be seen that while the hexene-type polymers have peaks in the range of 120–123 and 129–132°C these peaks are absent in the butene-

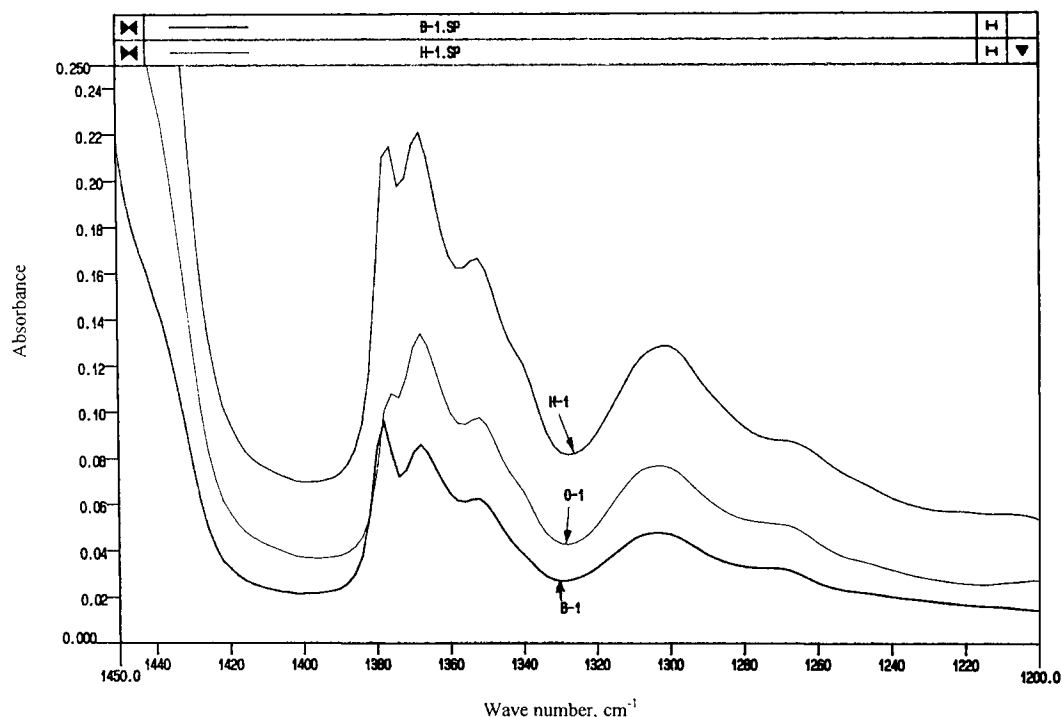


Figure 5 FTIR spectra of samples B-1, H-1, and O-1 in the range of 1200–1450 cm^{-1} .

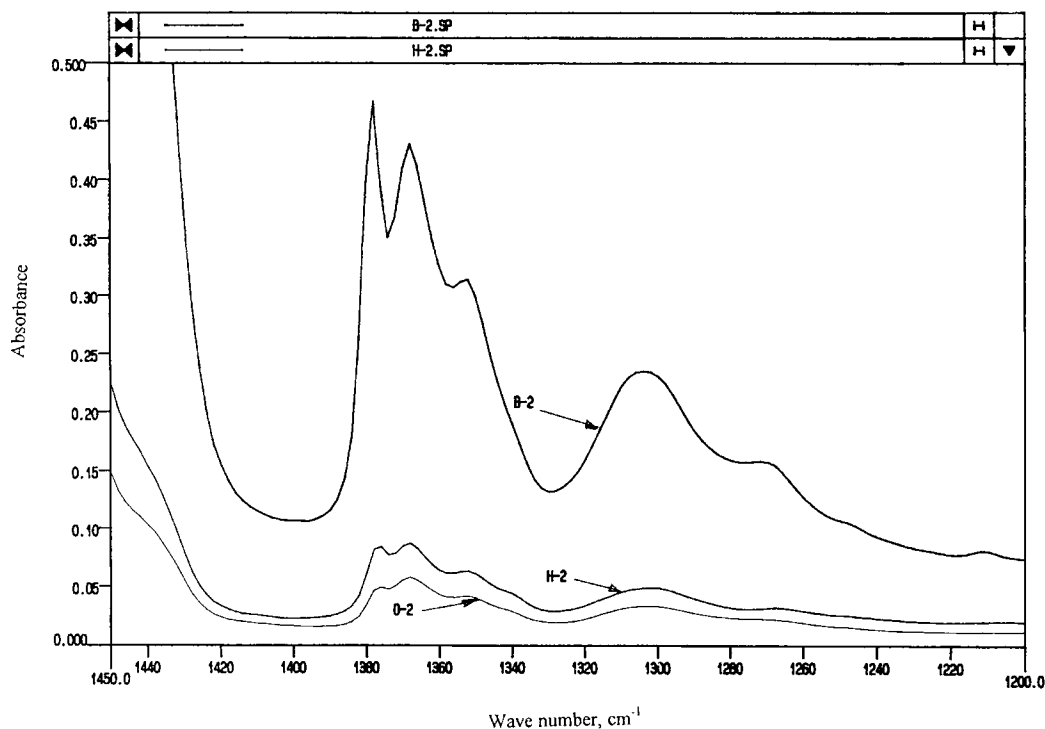


Figure 6 FTIR spectra of samples B-2, H-2, and O-2 in the range of 1200–1450 cm^{-1} .

and octene-type polymers. On the other hand, the two latter groups have peaks in the range of 124–127°C which are absent in the hexene-type copolymers. This difference enables one to differentiate the hexene-type polymers from the octene- and butene-type ones but does not enable one to differentiate between the two latter types. From Table II, it can also be seen that the lowest peak in the butene-type polymers was at a temperature below 93°C while the equivalent peak in the hexene and octene types was above this temperature. This difference gives some indication of the possibility to differentiate between the butene and the other two types of LLDPEs, but it is not large enough, however, to draw a definite conclusion.

As was pointed out in the Experimental section, FTIR spectra of the polymers were run in the range of 400–4000 cm^{-1} . When inspecting these spectra in the broad range, no difference could be found between the different polymer types in most of the range except of the 1300–1400 cm^{-1} .

In both Figures 5 and 6, the FTIR spectra for one butene-, one hexene-, and one octene-type LLDPE is shown in the range of 1200–1450 cm^{-1} . It can be seen that the relative height of the bands at 1368 and 1376 cm^{-1} changes progressively when going from the octene- to the hexene- to the butene-type copolymers. The band at 1368 cm^{-1} is attributed to the absorption of methylene groups (also known in the literature as $-\text{CH}_2-$ wagging bands,¹³) whereas bands in the range of 1376–1379 cm^{-1} are attributed to the absorption of the methyl group. Thus, the ratio between these two bands represents the length of the side chain (branch). In Table III, the ratios between the two band heights are summarized for the three polymer types. It can be seen that this ratio changes from about 1.35 to about 1.06 to about 0.93 when going from the octene to the hexene to the butene types, respectively. In Figure 7, the above-mentioned ratios are plotted as a function of the comonomer side chain length. It can be seen that an almost linear relationship exists be-

Table III Ratios Between Bands at 1368 and 1376 cm^{-1} for the LLDPEs

Polymer	O-1	O-2	H-1	H-2	B-1	B-2
Ratio	1.42	1.29	1.08	1.04	0.96	0.89

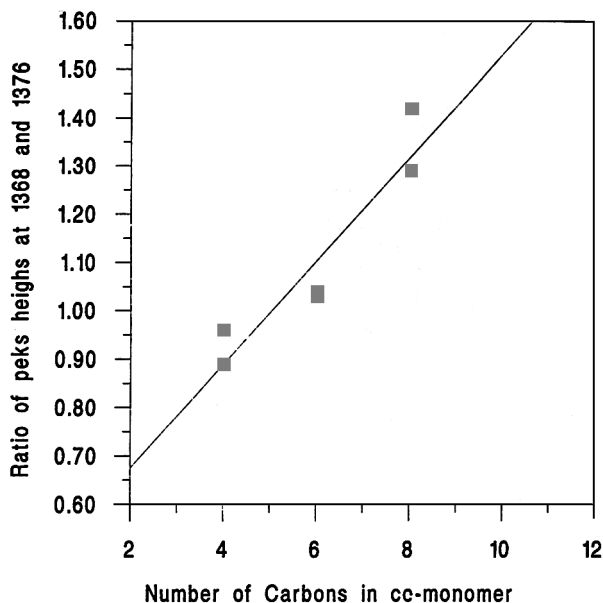


Figure 7 Relationship between the ratio of band heights at 1368 and 1376 cm^{-1} and the number of carbon atoms in the comonomer chain.

tween the ratio of the above-mentioned band heights and the length of the side chain in the comonomer. It can be concluded that fractionation, as described in the present publication, together with IR analysis can be used to identify and distinguish between the different types of LLDPE.

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