

# Characterization and Microstructure Study of Low-Density Polyethylene by Fourier Transform Infrared Spectroscopy and Temperature Rising Elution Fractionation

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**ABSTRACT:** Infrared spectroscopy is a powerful technique for studying the microstructure and determining the short-chain branch distribution of polyethylene. In this work, the types and amounts of short-chain branches in low-density polyethylene were investigated with Fourier transform infrared spectroscopy, and a new and simple method for the determination of butyl short branches was discovered. The amount of each unsaturated species in low-density polyethylene was also determined with Fourier transform infrared after the bromination of sam-

ples. Furthermore, the resin was fractionated by preparative temperature rising elution fractionation, and the branch distribution and melting endotherm of each fraction were analyzed with attenuated total reflectance/Fourier transform infrared and differential scanning calorimetry. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3492–3501, 2008

**Key words:** microstructure; polyethylene (PE); FTIR; fractionation of polymers

## INTRODUCTION

Of synthetic macromolecules used today, polyethylene is produced in the largest volume, and it is the fastest growing petrochemical market in the world,<sup>1</sup> so considerable research has been focused on the structure–property relationship of ethylene-based polymers since their commercial inception in the 1930s.<sup>2</sup> Branching in polyolefins has been examined for more than 60 years because of its ultimate effect on the behavior of resins. The short-chain branch distribution (SCBD) in low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) is a fundamental structural parameter that, together with the molecular weight distribution, defines the potential performance of resins. In LDPE, however, SCBD is more complex because short-chain branches (SCB) are produced by intramolecular chain transfer or backbiting of the growing radical,<sup>3</sup> whereas in LLDPE, SCB are introduced into the backbone by the copolymerization of ethylene with  $\alpha$ -olefins; this makes it possible to introduce certain select types of SCB into LLDPE.<sup>4</sup>

A variety of techniques have been used to measure SCB and their distribution in LDPE, such as infrared (IR) spectroscopy,<sup>5–8</sup> <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy,<sup>9,10</sup> pyrolysis hydrogenation/gas chromatography,<sup>11,12</sup> and  $\gamma$ -radiolysis.<sup>13</sup> Among these methods, only spectroscopic methods have provide direct measurements of SCB, and IR spectroscopy has attracted more attention because of its simplicity, speed, and low equipment cost. In fact, the IR spectra of different types of polyethylene have been studied in greater detail than those of other polymers.<sup>14</sup> Many studies have been conducted to evaluate the branch types and contents in LDPE by IR spectroscopy, focusing on the methyl deformation band (symmetric) around 1377 cm<sup>-1</sup>, the methyl rocking band region between 1200 and 800 cm<sup>-1</sup>, and the methylene rocking region between 770 and 720 cm<sup>-1</sup>.<sup>15</sup>

Furthermore, in recent years, fractionation methods such as temperature rising elution fractionation (TREF)<sup>16</sup> and crystallization analysis fractionation<sup>17</sup> have also used for the determination of SCBD in semi-crystalline polymers. TREF is a very powerful technique for studying the compositional heterogeneity in polyolefins and has earned great success in the determination of the microstructure of polyethylene because this type of fractionation is based on crystallizability, which has been shown to be influenced mainly by the degree of branching and comonomer content (if it exists).<sup>18</sup>

In this study, Fourier transform infrared (FTIR) spectroscopy was used to characterize the microstructure of LDPE, including the determination of CH<sub>3</sub> per 100 carbon atoms and the amounts and types of unsaturated species per molecule. We also report a novel and rapid method for the determination of butyl short branches in LDPE. Furthermore, the resin was fractionated by TREF,

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**TABLE I**  
Some Physical Properties and the Molecular Weights of the Polyethylene Resins

Characteristic	Test method	Resin		
		LDPE	HDPE	LLDPE
Melt flow index (g/10 min)	ASTM D 1238	1.7–2.3	8.0	0.8–1.0
Density (g/cm <sup>3</sup> )	ASTM D 1505	0.918–0.922	0.964	0.919–0.921
Elongation at break in the machine direction (%)	ASTM D 882	330	—	620
Elongation at break in the transverse direction (%)	ASTM D 882	600	650	840
Tensile strength at break in the machine direction (MPa)	ASTM D 882	16	—	32
Vicat softening point (°C)	ASTM D 1525	92–96	128	—
ESCR, F50 (h)	ASTM D 1693	—	3	—
$M_w^a$	—	196,900	67,500	154,900
$M_n^a$	—	19,000	14,000	24,100
Molecular weight distribution mode <sup>a</sup>	—	Unimodal	Unimodal	Unimodal

$M_n$ , number-average molecular weight;  $M_w$ , weight-average molecular weight; ESCR, F50, environmental stress-crack resistance (50% failure).

<sup>a</sup> By GPC.

and each fraction was analyzed with differential scanning calorimetry (DSC) and attenuated total reflectance/Fourier transform infrared (ATR–FTIR) spectroscopy.

## EXPERIMENTAL

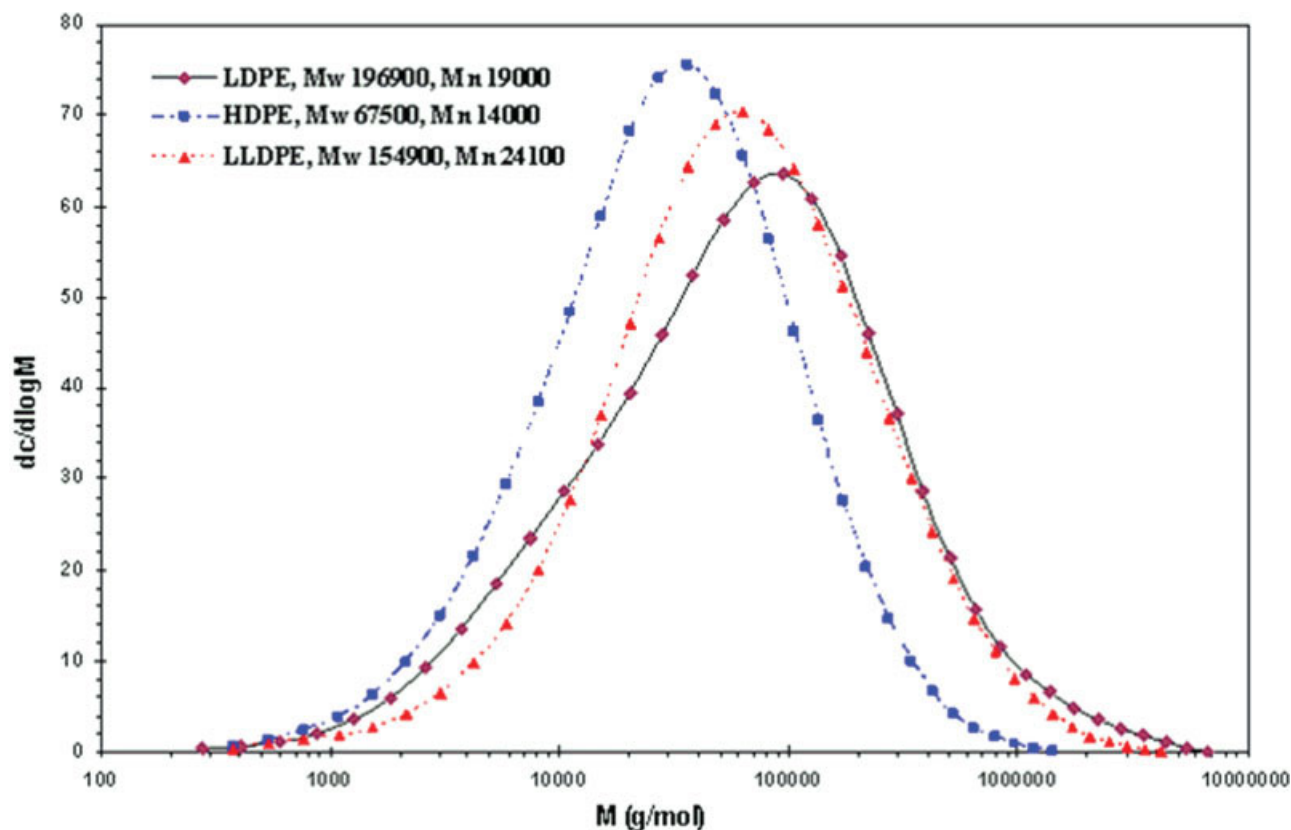
### Materials

Polyethylene samples used in this study were commercial LDPE (grade LF0200), high-density polyeth-

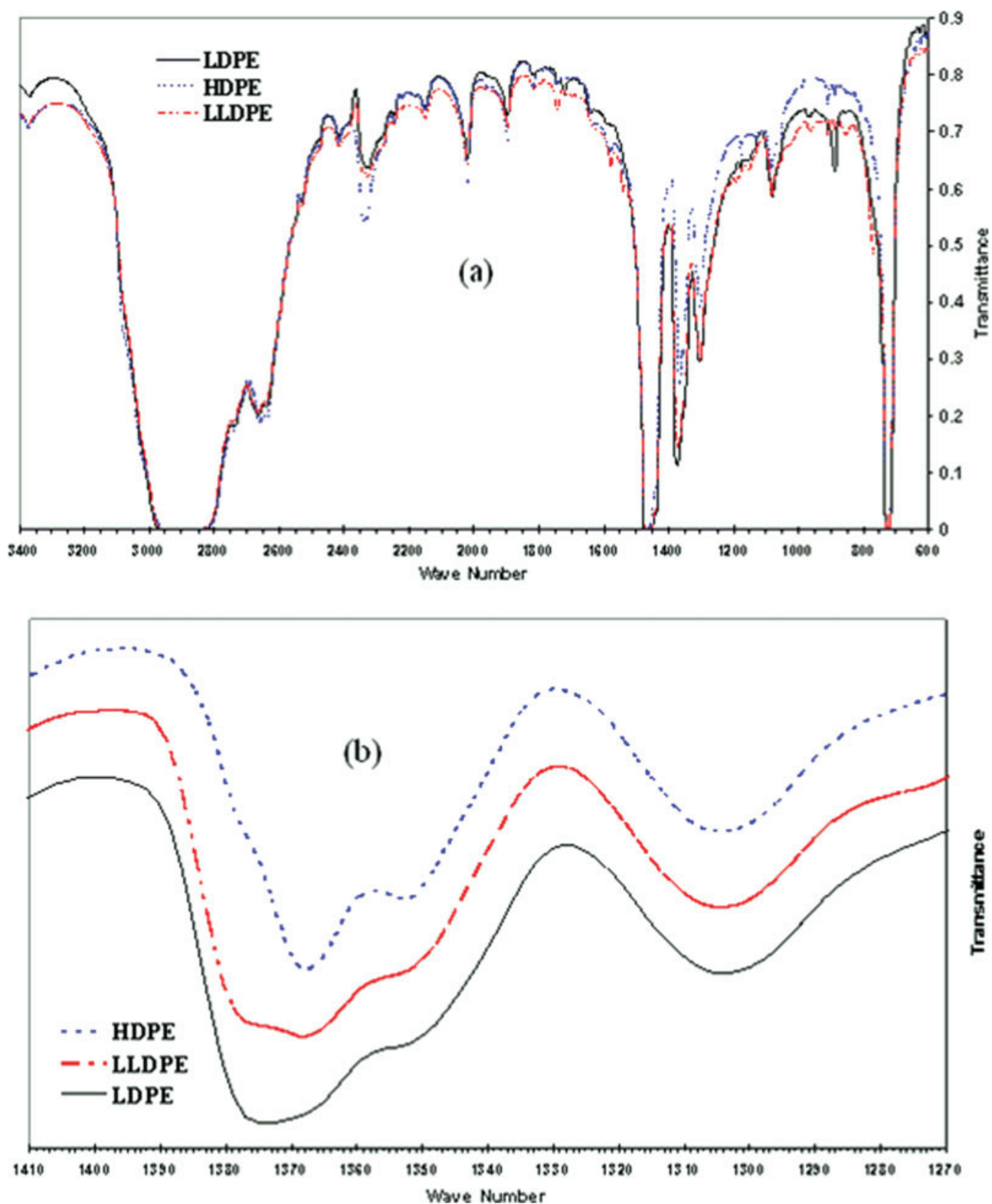
ylene (HDPE; grade M80064), and LLDPE (grade AA0209). All resins were analyzed as received without additive separation. HDPE and LLDPE were used for IR comparison and spectral compensation.

### Preparative TREF

Preparative TREF was performed on a column (inner diameter = 400 × 16 mm) packed with glass beads (1.0 mm) as supports. A modified column was



**Figure 1** GPC chromatograms of LDPE, HDPE, and LLDPE (trichlorobenzene, 140°C;  $M_w$ , weight-average molecular weight;  $M_n$ , number-average molecular weight; C, concentration; M, molecular weight). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** Comparison of FTIR spectra of LDPE, HDPE, and LLDPE: (a) full range and (b) methyl deformation band region. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

designed to ensure precise temperature control of the column and elution solvent. The polymer was dissolved in xylene (containing 0.1% Irganox 1010) at a concentration of about 0.015 g/mL at 120°C and

then loaded into a column preheated to 120°C. The column was subsequently cooled to room temperature at 2°C/h and kept at 25°C for 10 h. Then, the column was heated at a rate of 10°C/h to the upper

**TABLE II**  
Absorbances of the Reference Films for Methyl ( $A_{1377}$ ) and Methylene ( $A_{1304}$ ) and Absorptivity due to the Methyl Band

Film no.	$A_{1304}$	$A_{1377}$	$A_{1377}$ (due to the methyl group)	$K'_{1377}$ ( $\text{cm}^2/\text{g}$ )
1	0.1544	0.2341	0.1569	5.664
2	0.1510	0.1910	0.1152	5.847
3	0.0934	0.1163	0.0696	6.203
4	0.03025	0.0410	0.0258	5.722

temperature of the desired range, and 100 mL of xylene was pumped through the column at 10 mL/min after 30 min passed for equilibrium at the elution temperature. Fractions collected at 40, 50, 60, 65, 70, 75, 80, and 100°C were precipitated by the addition of 100 mL of methanol, filtered, washed with acetone, and vacuum-dried at 60°C until a constant weight was achieved.

### Characterization

Gel permeation chromatography (GPC) analysis of the whole polymer was made on a Waters Milford MA 2000 high-temperature GPC instrument (Milford, MA) with trichlorobenzene at 140°C.

IR spectra were acquired with a Bruker Equinox 55 FTIR spectrophotometer (Ettlingen, Germany) equipped with a deuterated triglycine sulfate detector (which is very suitable for quantitative analysis) and a Golden Gate micro-ATR instrument. Samples were prepared for FTIR spectroscopy as follows: an appropriate amount of the polymer was hot-pressed between aluminum foil at 170°C for approximately 90 s at 30,000 lb, immediately removed from the press, and shock-cooled with a slurry of ice and water. Annealed samples were prepared in the oven at 100°C for 24 h. Samples were examined by micro-ATR-FTIR without preparation. Band position measurements were obtained with Opus software.

DSC measurements for the whole polymer and its fractions were made on a TA DSC Q100 V9.0 (New Castle, DE) equipped with thermal analysis data acquisition software. Polymer samples (ca. 5 mg) were sealed in standard aluminum pans. First, each sample was melted by the temperature being raised to 160°C, and it was kept there for 10 min to ensure complete melting and to remove the thermal history. The sample was then cooled to room temperature at

the cooling rate of +5°C/min. After this, the melting endotherm was recorded by the heating of the sample directly to 160°C at a heating rate of +5°C/min.

Some important mechanical and physical properties of the resins (see Table I) were measured according to American Society for Testing and Materials procedures.

Density measurements of the whole polymer and polymer films were carried out with a Ceast densitometer (Pianezza, Italy) according to ASTM D 1505-92.

## RESULTS AND DISCUSSION

### Qualitative analysis

LDPE (grade LF0200) was made with an autoclave reactor and had a high molecular weight with a broad molecular weight distribution according to its GPC chromatogram (Fig. 1). The GPC chromatograms of HDPE and LLDPE are also shown in Figure 1.

Some physical properties of LDPE (grade LF0200), HDPE (grade M80064), and LLDPE (grade AA0209) are listed in Table I.

Figure 2 shows the FTIR spectrum of the LDPE film versus those of HDPE and the LLDPE.

These three polymers have similar structures, and their differences arise mainly from SCBs in each resin. As shown in Figure 2, it is possible to distinguish between LDPE, HDPE, and LLDPE by their IR spectra.<sup>19</sup>

The IR spectrum of LDPE shows a methylene rocking mode at 720/730  $\text{cm}^{-1}$ , a methyl rocking band at 894.5  $\text{cm}^{-1}$  (arising from butyl short branches), methylene wagging in the amorphous region at 1305 and 1353  $\text{cm}^{-1}$ , a methyl deformation band (bending mode) at about 1380  $\text{cm}^{-1}$ , and a methylene deformation band at about 1460  $\text{cm}^{-1}$ .

### Quantitative analysis

For the quantitative determination of SCB in LDPE, we used the ASTM D 2238-92 test method.<sup>20</sup> Four suitable films of HDPE as a reference polyethylene with different thicknesses were prepared, and self-compensated spectra of these films with a fairly annealed film of HDPE were recorded. Data are given in Table II:  $K'_{1377}$  is the absorptivity for the

**TABLE III**  
FTIR Data for the Sample Film Compensated with the HDPE Reference Film

Thickness of the sample film (cm)	Density of the sample film ( $\text{g}/\text{cm}^3$ )	$A_{1377}$ (due to methyl)		$A_{1377}$ (due to methyl) + $A_{1377}$ (due to methyl) in the reference film	$K'_{1377}$ for LF0200 ( $\text{cm}^2/\text{g}$ )	
		$A_{1304}$	$A_{1377}$			
0.0208	0.933	0.1546	0.5872	0.5099	0.5357	27.60

TABLE IV  
FTIR Data for the Sample Film Compensated with the HDPE Reference Film

Cell thickness (cm)	Density of <i>n</i> -cetane (g/cm <sup>3</sup> )	$A_{1304}$	$A_{1377}$	$A_{1377}$ (due to methyl)	$K'_{1377}$ for <i>n</i> -cetane (cm <sup>2</sup> /g)	$f_{1377}$
0.0234	0.773	0.338	1.483	1.314	72.6	0.172

methyl group, and  $A_{1377}$ (due to the methyl group) is the absorbance with perfect compensation of the amorphous band. The latter was calculated according to the following equation:

$$A_{1377}(\text{due to methyl group}) = A_{1377} - 0.5A_{1304}$$

After calibration of the data for the reference polyethylene, a few films of LDPE with thicknesses near 0.03 cm were prepared; compensated spectra were recorded by the placement of the sample film in the sample beam of the spectrophotometer and a reference film of HDPE in the reference beam, and  $A_{1377}$  due to the methyl group was calculated (Table III).

To convert absorptivity data into methyl groups, the conversion factor  $f_{1377}$  must be used. This factor can be derived from spectra of standard reference samples such as homopolymers of 1-olefins and/or paraffins. *n*-Hexadecane (*n*-cetane) was used in a

NaCl cell with a known thickness to determine  $f_{1377}$  according to the following equation:<sup>20</sup>

$$f_{1377} = (114/K'_{1377} \text{ for } n - \text{hexadecane}) \times 0.110$$

Data calculated according to this equation are given in Table IV.

Methyl groups per 100 carbon atoms can be obtained by the multiplication of the conversion factor in absorptivity due to methyl groups ( $K'_{1377}$ ). For LDPE, this value is 4.75; this means that it has 4.75 SCB per 100 carbon atoms.

#### Determination of butyl branches in the resin

Unfortunately, the absorption at 894.5 cm<sup>-1</sup>, arising as a result of butyl branches, is highly covered by vinylidene and vinyl unsaturation bands at 888 and 910 cm<sup>-1</sup>, respectively, so any quantitative use of

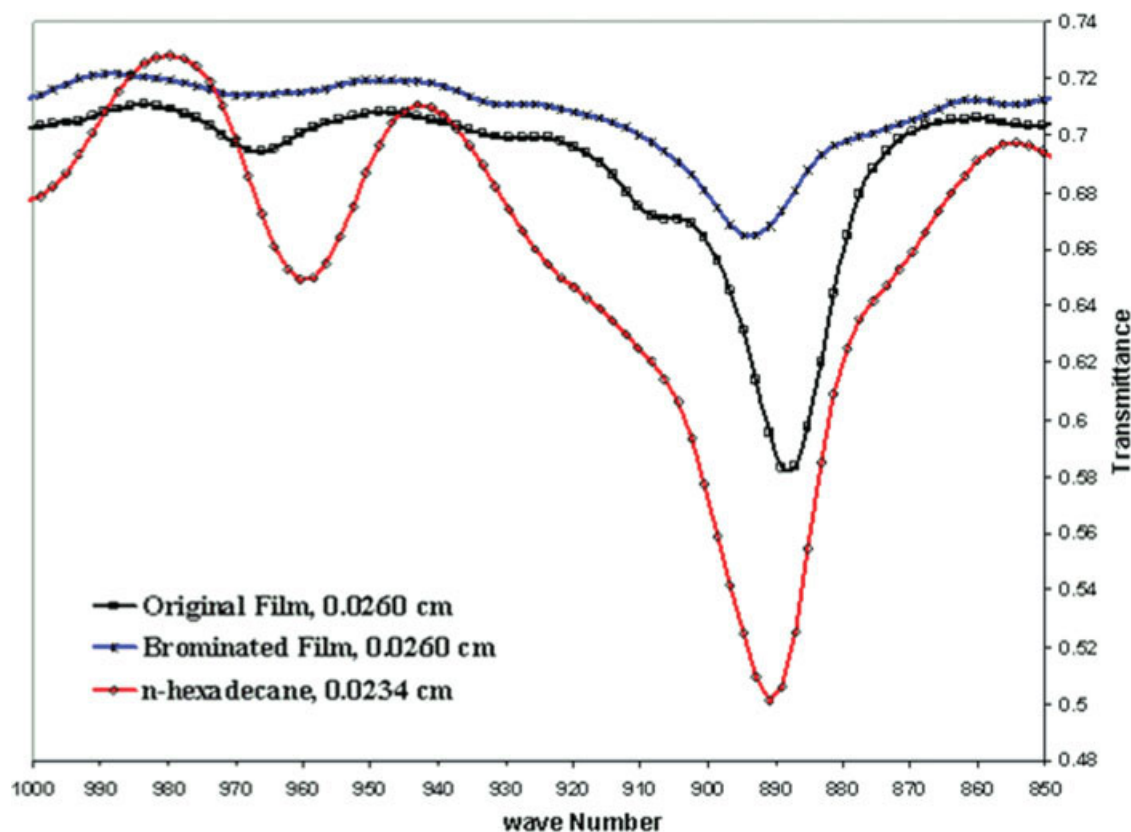


Figure 3 FTIR spectra of an LDPE film before and after bromination and *n*-hexadecane (NaCl cell) in the methyl rocking region. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE V  
FTIR Data for *n*-Hexadecane and an LDPE Film for Butyl Branch Determination

Sample	Thickness (cm)	Density (g/cm <sup>3</sup> )	$A_{894.5}$	$K'_{894.5}$ (cm <sup>2</sup> /g)	$f_{894.5}$	Butyl branches/100 carbon atoms
<i>n</i> -Hexadecane	0.0234	0.773	0.1816	10.04	1.245	12.5
LDPE film	0.0260	0.930	0.0325	1.34	1.245	1.668

this band can be made only after the resolution of these interferences. This can be done by hydrogenation<sup>21</sup> or by bromination,<sup>22</sup> which eliminates double bonds in the resin. Hydrogenation converts the vinyl and vinylidene unsaturations into more methyl groups and takes place under more severe conditions. Bromination, however, is more suitable and occurs under mild conditions without any effect on the branch content.<sup>23</sup>

One suitable film of LDPE with a known density and thickness was placed in a 5 vol % solution of bromine in carbon tetrachloride for 12 h with agitation and then was washed in carbon tetrachloride and dried in an oven.<sup>23</sup> Figure 3 shows the FTIR spectra of the original and brominated films. Unsaturation bands at 888 and 910 cm<sup>-1</sup> were completely eliminated, and only a butyl absorption band remained at 894.5 cm<sup>-1</sup>. This resolved band could be used for the quantitative determination of butyl short branches in LDPE. For this purpose, we used a new method that relies on the ASTM 2238-92 test method and uses *n*-hexadecane as a standard. First,  $K'_{894.5}$  for *n*-hexadecane was determined by its absorbance at 894.5 cm<sup>-1</sup> (Fig. 3), and then the conversion factor  $f_{894.5}$ , which converts absorptivity data to butyl groups per 100 carbon atoms, was calculated. Because *n*-hexadecane has 12.5 butyl branches per 100 carbons, this was accomplished easily. Data for *n*-hexadecane and LDPE film are given in Table V. For polyethylene, one can calculate butyl branches per 100 carbon atoms by  $K'_{894.5} \times f_{894.5}$ . This value was 1.668 for the LDPE sample used in this study.

Because SCB in LDPE, created by backbiting, which is a statistical phenomenon, they are statistically distributed through the resin with various lengths, and the percentage of each SCB in commercial LDPE is approximately constant. The percentages of branches in LDPE are given in Table VI. They were determined by NMR studies of some commercial LDPEs.<sup>4</sup>

According to these values, in LDPE (grade LF0200), butyl short branches per 100 carbon atoms must be

4.75 (Total short branches)

$$\times 0.3575 \text{ (Butyl branch fraction in LDPE)} = 1.69$$

This is in good agreement with the method introduced here.

#### Determination of unsaturation in LDPE

Three major characteristic IR bands that exist in polyethylene due to unsaturation are a vinylidene unsaturation at 888 cm<sup>-1</sup>, a vinyl unsaturation at 910 cm<sup>-1</sup>, and a trans substituted double bond at 964 cm<sup>-1</sup>.<sup>24</sup> As mentioned earlier, bands at 888 and 910 cm<sup>-1</sup> are in severe interference with the band at 894.5 cm<sup>-1</sup> due to butyl short branches. To resolve this interference, the resin can be brominated (as discussed previously), and then the spectrum of the brominated polymer can be subtracted from the spectrum of the original polymer. In the brominated polymer, the bands at 888 and 910 cm<sup>-1</sup> were deleted, and only the butyl band at 894.5 cm<sup>-1</sup> was present. After subtraction, the resolved bands at 888 and 910 cm<sup>-1</sup> were obtained (Fig. 4), and the calculation of each double bond was performed with the Beer-Lambert law and molar extinction coefficient value for each absorbance.<sup>23,24</sup> Table VII shows the data and total double bonds per molecule of LDPE.

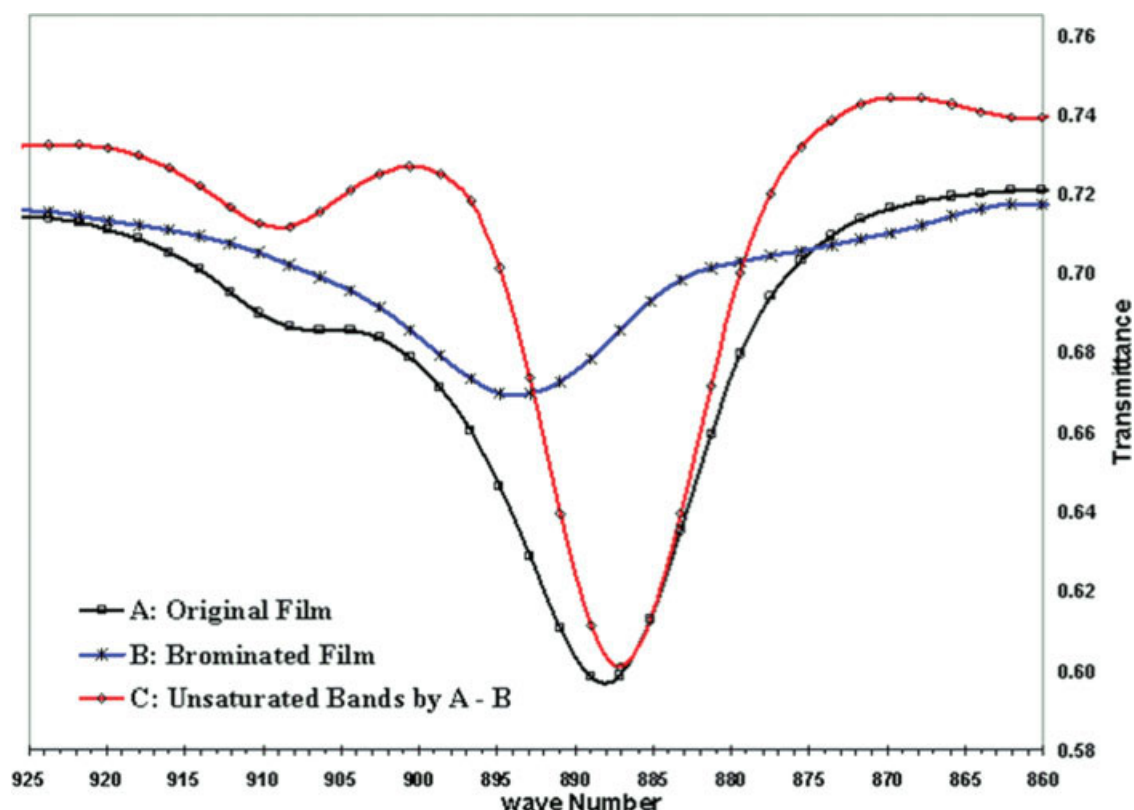
For vinyl groups at 910 cm<sup>-1</sup>, an independent determination exists that gives vinyls per 1000 carbon atoms as follows:<sup>25</sup>

$$\text{Vinyls per 1000 carbon atoms} = 1.22 \times A_{910}/10t$$

where  $A_{910}$  and  $t$  are the absorption at 910 cm<sup>-1</sup> and the film thickness (cm), respectively. According to

TABLE VI  
Percentages of Different Short Branches in Some Commercial LDPEs

Sample	Total CH <sub>3</sub> /1000 carbon atoms	Methyl (%)	Ethyl (%)	Propyl (%)	<i>n</i> -Butyl (%)	<i>n</i> -Pentyl (%)	Longer than <i>n</i> -hexyl (%)
LDPE A	19.9	2	32	2	37	13	14
LDPE B	24.9	2	37	2	34	11	14
LDPE C	17.3	3	31	2	37	13	14
LDPE D	6.7	2	34	3	35	11	15
Mean value		2.25	33.5	2.25	35.75	12	14.25



**Figure 4** FTIR spectra of an LDPE film before and after bromination and a subtracted spectrum showing resolved unsaturation bands at 888 and 910  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

this equation, the number of vinyl groups in the LDPE (grade LF0200) sample was 0.03561 per 1000 carbon atoms. This is equal to 0.0483 vinyl groups per molecule, which is in good agreement with the Beer-Lambert calculation in Table VII (the number-average molecular weight of LF0200 was 19,000 g/mol, as determined by GPC).

### Preparative TREF analysis

Preparative TREF was used to fractionate LDPE into 7 fractions at 40, 50, 60, 65, 70, 75, 80, and 100°C. Each fraction was weighed and analyzed by ATR-FTIR and DSC (the fraction at 100°C had no polymer

after precipitation). Data are given in Table VIII, and Figure 5 shows the TREF plots.

### ATR-FTIR analysis of the fractions

Because the isolated fractions were so small, the micro-ATR technique was used for IR analysis. ATR-FTIR spectra of the fractions and methyl deformation bands of the fractions at 1377  $\text{cm}^{-1}$  can be observed in Figures 6 and 7, respectively, which present collections of IR spectra of the fractions.

As shown in the IR spectra of the fractions, the absorption bands at 1377  $\text{cm}^{-1}$  increased with the elution temperature in TREF decreasing. This means

**TABLE VII**  
IR Data for Each Type of Unsaturation in LDPE (Grade LF0200)

Film thickness (cm)	Density of the film ( $\text{g}/\text{cm}^3$ )	Wave number ( $\text{cm}^{-1}$ )	Unsaturation type	Absorbance	Molar extinction coefficient ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	Double-bond content (mol/L)	Double bonds per molecule
0.0260	0.930	888	$\text{RR}'\text{C}=\text{CH}_2$	0.0619	131	0.0182	0.3727
0.0260	0.930	910	$\text{R}-\text{CH}=\text{CH}_2$	0.00759	121	0.00241	0.0494
0.0260	0.930	964	$\text{R}-\text{CH}=\text{CH}-\text{R}$ (trans only)	0.0100	85.4	0.00450	0.0921
					Total	0.02511	0.5142

**TABLE VIII**  
DSC Melting Characteristics of the Fractions and Whole Polymer

Sample	Elution temperature (°C)	Weight fraction (g)	Melting temperature (°C)		$\Delta H_f(T_m)^a$ (J/g)	Crystallinity (%) <sup>b</sup>
			Peak	Shoulder		
Whole	—	—	110.3	—	102.5	35
Fr 1	25–40	0.0160	104.3	92.9	147.2 <sup>c</sup>	—
Fr 2	40–50	0.0338	105.7	98.1	129.0 <sup>c</sup>	—
Fr 3	50–60	0.0545	104.6	—	124.6	43
Fr 4	60–65	0.0538	107.6	—	132.4	46
Fr 5	65–70	0.1099	112.4	108.3	113.8 <sup>c</sup>	—
Fr 6	70–75	0.0670	112	—	133.9	46.5
Fr 7	75–80	0.0311	114.5	—	146.9	51
—	80–100	0.0000	—	—	—	—

<sup>a</sup>  $\Delta H_f(T_m)$ , enthalpy of fusion in melting point.

<sup>b</sup> By DSC.

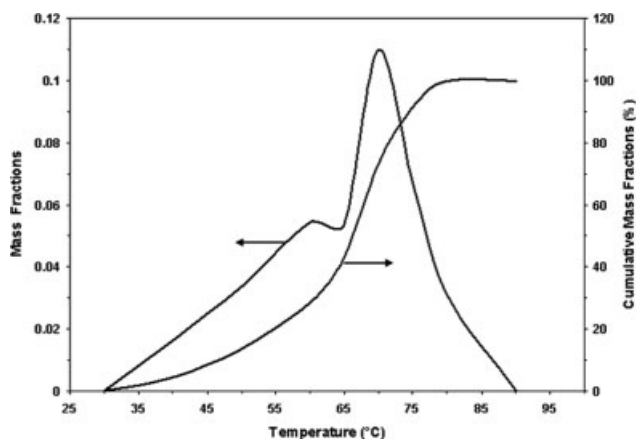
<sup>c</sup> Total value for two peaks.

that the fractions eluted from the column at low temperatures had more SCBs. A plot of the branch content as a function of the elution temperature shows a linear relationship (Fig. 8).

#### Thermal analysis of the fractions

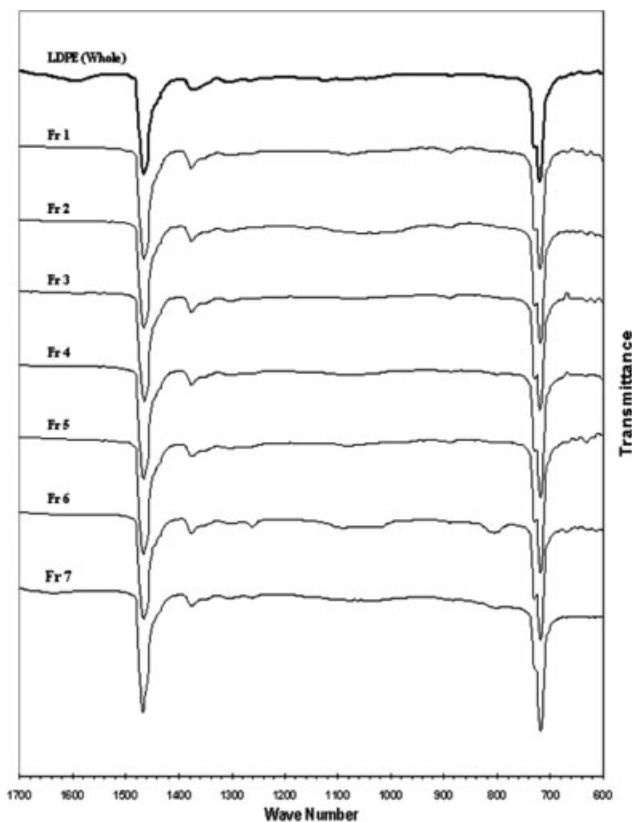
As we know, the morphology and consequently thermal behavior of each fraction are related to the thermal history and molecular heterogeneity, such as the types, amounts, and distributions of branches. Thus, to verify the chain structures of different fractions, a thermal analysis of annealed samples was also conducted. Good annealing of the samples ensured that chains with different SCB contents formed lamellae of different thicknesses, and so the DSC melting curves reflected their presence.

Table VIII shows the melting characteristics of the fractions and whole polymer, as measured by DSC, and Figure 9 shows the melting endotherms of the fractions.



**Figure 5** TREF mass and cumulative mass plots for LDPE fractions.

Fraction 1 (Fr 1) shows two broad peaks with melting points of 92.9 and 104.3°C. The broader endotherm, which shows melting about 18°C below the melting point of the resin, can be attributed to waxy and highly branched low-molecular-weight species formed during the high-pressure process of LDPE production. The waxy appearance of the



**Figure 6** ATR-FTIR spectra of TREF fractions (Fr 1, 40°C fraction; Fr 2, 50°C fraction; Fr 3, 60°C fraction; Fr 4, 65°C fraction; Fr 5, 70°C fraction; Fr 6, 75°C fraction; and Fr 7, 80°C fraction).



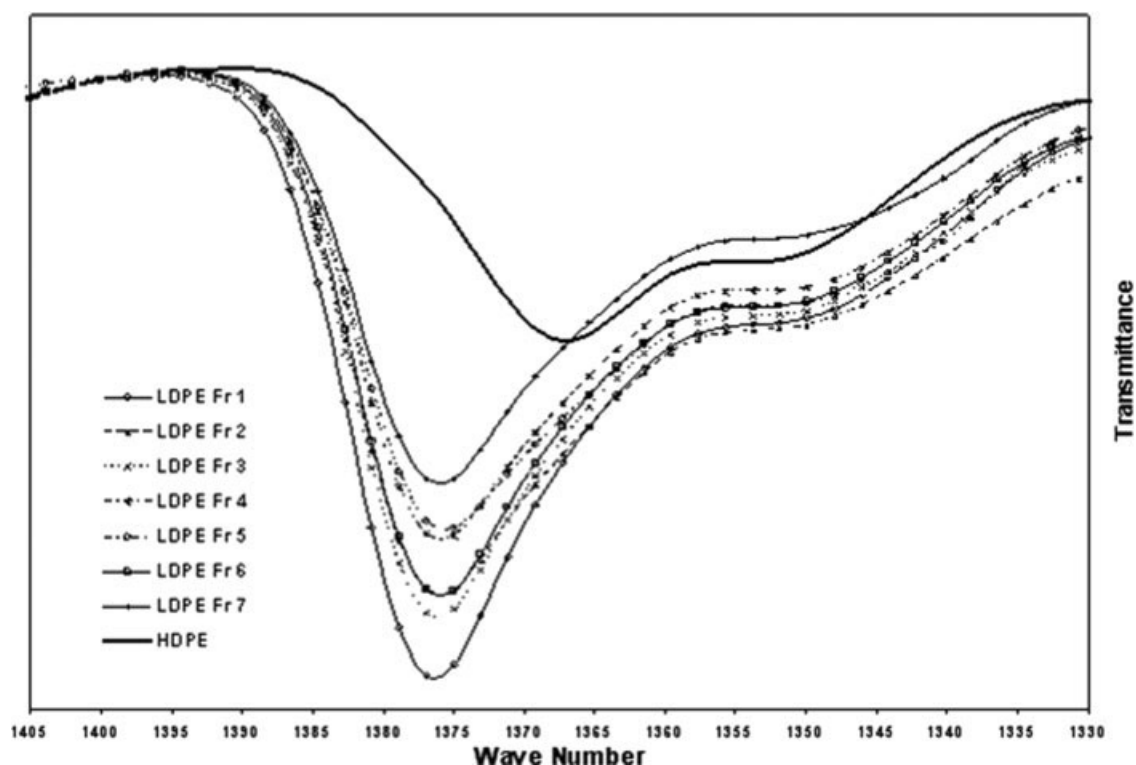


Figure 7 ATR-FTIR spectra of TREF fractions in the methyl deformation band.

LDPE surface is a direct result of the existence of these moieties. The other part of Fr 1 has a melting temperature  $6^{\circ}\text{C}$  below the melting point of the resin, and this means that it is highly branched LDPE because it is the first fraction eluted from the column at  $40^{\circ}\text{C}$ .

The DSC curves of Fr 2 and Fr 3 are similar to that of Fr 1, but the waxy amounts of these fractions (the shoulders) are lower than that of Fr 1. These

lower temperature melting tails of the fractions are due to thinner lamellae or crystals having more internal crystallographic imperfection.

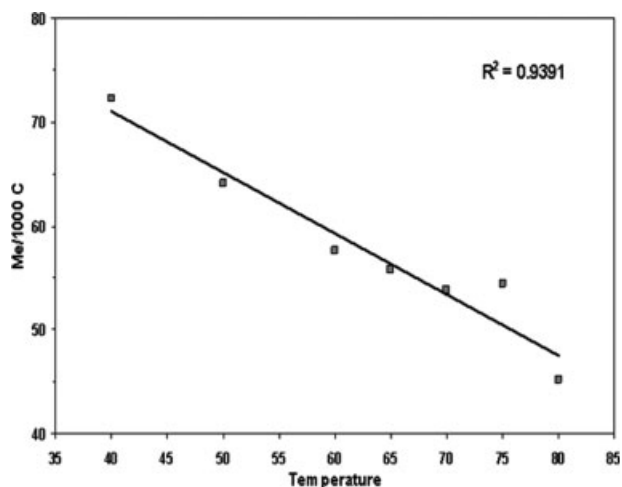


Figure 8 Plot of the branch content versus the elution temperature for LDPE fractions, Me is methyl group.

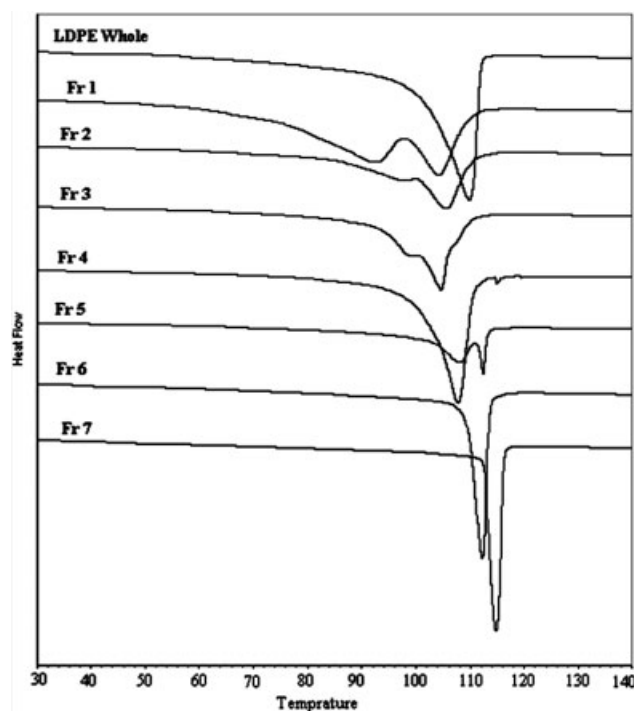


Figure 9 DSC melting endotherms of LDPE and its fractions at a heating rate of  $+5^{\circ}\text{C}/\text{min}$ .

The DSC endotherm of Fr 4, eluted at 65°C, is very similar to the whole resin endotherm. Its melting peak does not show a shoulder similar to that of previous fractions. Although this fraction has a rather high SCB content (56 CH<sub>3</sub> per 1000 carbon atoms), the SCB distribution is narrow. Fr 5 is the largest fraction eluted from the column at 70°C. Its melting curve has two major peaks. The broader peak belongs to polyethylene with a melting point of 108.3°C, and the narrower is related to polyethylene with a melting point of 112.4°C. As for the melting points of these peaks, the first one can be attributed to Fr 4, and the second can be attributed to Fr 6.

Fr 6 and Fr 7 show strong melting peaks at 112 and 114.5°C, respectively. The sharper melting peaks observed at higher melting temperatures are attributable to the presence of the thicker lamellae and show that these fractions have few side chain branches and a high degree of crystallinity (Table VIII). However, the melting point of Fr 7 shows that this fraction (which is the most crystalline portion of the resin) is also LDPE because it contains a valuable amount of SCBs, which inhibit crystallization, whereas HDPE has crystals that melt at about 133°C.

### CONCLUSIONS

This study shows that LDPE (grade LF0200) is a high-molecular-weight resin with a considerable number of SCBs, as calculated by FTIR spectroscopy. Butyl short branches in the resin were also determined by a new method using the methyl rocking band at 894.5 cm<sup>-1</sup> after bromination of the resin. FTIR spectroscopy was also used for the quantitative determination of all types of double bonds in the resin and revealed that it contains 0.5 double bonds per molecule. Double bonds in polyethylene are very important for kinetic studies and can affect the chemical resistance of the resin.

To fractionate the polymer according to its SCB content, TREF was used, and LDPE was fractionated into seven fractions. The complete characterization of the fractions with DSC and ATR-FTIR showed that the SCB frequency decreased and the crystallinity increased as a function of an increasing TREF elution temperature. Low-temperature fractions had tails related to waxy moieties in LDPE. The melting temperature of the fractions increased with increas-

ing elution temperature, and endotherms were sharper in high-temperature fractions. These results show that low-temperature fractions have thinner lamellae or crystals with structural defects, and high-temperature fractions have thicker lamellae; this is a direct result of the SCB content of the fractions.

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