

# An Effective Method to Identify the Type and Content of $\alpha$ -Olefin in Polyolefine Copolymer by Fourier Transform Infrared–Differential Scanning Calorimetry

Qing Zhang,<sup>1</sup> Ping Chen,<sup>2</sup> Xiaoli Xie,<sup>1</sup> Xianwu Cao<sup>1</sup>

<sup>1</sup>National Engineering Research Center of Novel Equipment for Polymer Processing, The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China University of Technology, Guangzhou, China

<sup>2</sup>Guangzhou Entry-exit Inspection and Quarantine, Guangzhou, China

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**ABSTRACT:** A new method for identification of ethylene/ $\alpha$ -olefin copolymer was established by Fourier Transform Infrared (FTIR)–Differential Scanning Calorimetry (DSC) in this article. DSC and FTIR spectroscopy techniques were used to analysis the type and content of  $\alpha$ -olefin in polyolefine copolymer. FTIR was available to identify the structures of polyethylene and copolymers of ethylene with different  $\alpha$ -olefins. The type of polyethylene can be determined by the peak position of 1378 and 1369  $\text{cm}^{-1}$ . According to the peak

location of 770, 784, and 895  $\text{cm}^{-1}$ , the type of  $\alpha$ -olefin can also be determined. DSC method was used to decide the position of melting peaks. The quantitative investigation of the content of  $\alpha$ -olefin in polyethylene was calculated by the formula:  $-\ln(\text{CH}_2 \text{ mol fraction}) = -0.331 + 135.5/T_m$ . © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3027–3032, 2009

**Key words:** FTIR-DSC; identification; polyolefine; copolymer;  $\alpha$ -olefin

## INTRODUCTION

Generally, commercial polyethylenes are divided into three grades: high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). HDPE is a linear polyethylene without branching. LDPE is a polyethylene with both short- and long-chain branching. LLDPE is a copolymer of ethylene and  $\alpha$ -olefins: 1-butane, 1-hexane, 1-octane, and 4-methyl-1-pentene, with short chain branching.

The various grades of polyethylene differ in the degree of short- and long-chain branching, as well as the branching distribution. These variations affect the crystallinity, thermal and mechanical properties of the polymer.<sup>1,2</sup> Therefore, the qualitative analysis of short chain branching (SCB) in polyethylene is necessary for the correlation of molecular structure with physical properties. A variety of techniques have been used to identify and quantify the type and composition distribution of comonomer in bulk PE, such as temperature rising elution fractionation,<sup>3,4</sup> nuclear magnetic resonance (NMR),<sup>5,6</sup> Fourier Transform Infrared (FTIR),<sup>7,8</sup> and thermal analysis<sup>9–11</sup> techniques. However, it is often difficult to identify the type and composition of PE blends by a single

analytical instrument, as they have the similar molecular and chemical structures.

Infrared (IR) spectroscopy has been used widely to characterize polymers. The theoretical foundation of qualitative determination and structural analyzing of IR is according to the absorption peak wavelength and number in absorption spectrum. It is determined by molecular structure of extinction substances. By long-term practice, it is found that IR is capable of revealing the related information of most spectrum band and chain structure in PE.

Recently, measurements of the comonomer distribution in branched polyethylene have mostly been performed by using differential scanning calorimetry (DSC) for thermal fractionation. Thermal fractionation is a temperature-dependent segregation process based on recrystallization and reorganization of ethylene sequence from the melt.<sup>12</sup> This technique is based on the analysis of the melting behavior after a suitable thermal treatment, such as stepwise annealing during cooling from the melt. After thermal fractionation, crystals within the sample separate according to the SCB distribution, which determines the lamellar thickness and hence melting temperature. The distribution of lamellar thickness depends on the amount and distribution of the  $\alpha$ -olefin units in the macromolecular chains, provided that the crystallization conditions allow the lamellae to approach equilibrium. Lamella thickness is also related to crystallization conditions. As equilibrium

Correspondence to: Q. Zhang (zhangqing@scut.edu.cn).

lamellae are approached, their melting temperatures approach the copolymer melting temperature defined by Flory.<sup>13</sup> Thermal fractionation has been used to characterize the various types of polyethylenes.<sup>14,15</sup> The procedure enables the fractionation of copolymers according to their composition, which can be seen by the multiplication of the melting peaks on the curves. It can be used as a quantitative analysis to determine branching distribution or methylene sequence length distribution.

For quantitative analysis purposes, an accurate and rapid analytical scheme is needed to identify the type and composition of  $\alpha$ -olefin in PE. The aim of this study was to compare the IR spectroscopy and DSC using thermal fractionation methods regarding their ability to discriminate and assign the class of polyethylene. The ability of the techniques to distinguish the groups of polyethylenes was first investigated using principal component analysis, and then discriminant analysis applied to form a model for assigning unknown samples to their structural class was studied.

## EXPERIMENTAL

### Materials

In this study, there are several polyethylenes in which the types and contents of  $\alpha$ -olefins are not known. They are DF605, DF840, PL1881G, ATTANE 4404G, AFFINITY PL1880, DOWLEX NG 2429G, DOWLEX 2344G, and OCTENE-1 PE. Three types of known samples were used in contrast study. HDPE was supplied by ExxonMobil Chemical Manufacturing, Saudi Arabia. LDPE used was 2426H produced by CNOOC and Shell Petro-Chemical, China. LLDPE DNDA 7042 and 7144 were produced by SINOPEC Maoming Branch. LLDPE DNDA 7145 was provided by Daqing Petrochemical Company, CNPC. The type of  $\alpha$ -olefin in polyethylenes was defined by FTIR, and the content of  $\alpha$ -olefin was measured by DSC.

### Infrared spectroscopy

Samples for FTIR were obtained by hot pressing films at 200°C. The spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer in the range 4000 ~ 400  $\text{cm}^{-1}$ . 32 scans were used for spectral averaging, at a resolution of 2  $\text{cm}^{-1}$ . Blitz and McFadden<sup>8</sup> recommended a thinner specimen (0.1 mm) for FTIR measurements due to the intense absorption of the bands under study. In our study, we have observed strong interference fringes for specimen thickness of 0.1 mm rendering qualitative analysis untenable. Hence, it is desirable to have a film thickness of 0.2–0.3 mm to avoid interference

fringes problems. Band area and position were obtained using standard Nicolet software. The spectra were then converted to absorbance units for data manipulation and analysis.

### Thermal fractionation method

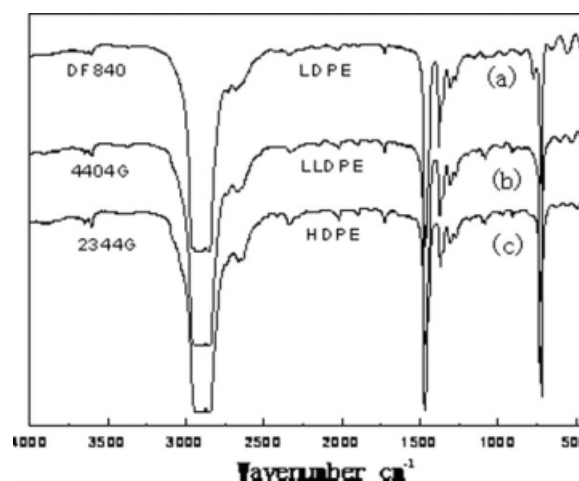
Thermal analysis and thermal fractionation were carried out using the NETZCH DSC 204C. The DSC was operated at ambient temperature mode. Dry nitrogen gas with a flow rate of 20  $\text{mL min}^{-1}$  was purged through sample. The instrument was calibrated with indium and zinc standards. The samples were melted at 170°C and held for 5 min. This procedure was carried out to remove previous thermal history. Each sample was then cooled to 130°C at a rate of 10°C  $\text{min}^{-1}$  and maintained at this temperature for 2 h. The sample was again cooled by 5°C at a rate of 10°C  $\text{min}^{-1}$  and kept at each temperature for 2 h. This procedure was repeated at 5°C intervals to room temperature. The heating scans were obtained by heating the thermal fractionated samples from 30 to 170°C at a heating rate of 5°C  $\text{min}^{-1}$ . A baseline was recorded with empty pans, using identical conditions to the heating scan.

## RESULTS AND DISCUSSION

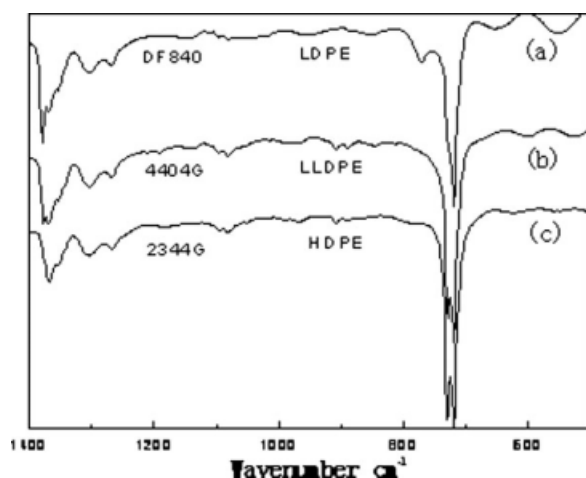
### FTIR characterization

Qualitative analysis of PE by FTIR spectra

Figure 1 shows the typical FTIR spectra of PE copolymers. FTIR is widely used as a rapid analytical tool to identify the type of short chain branching in polyethylenes.<sup>7,8</sup> Ethyl, butyl, and hexyl-type SCB in PEs are readily distinguishable<sup>8</sup> by the region of 1300–1400  $\text{cm}^{-1}$ , 800–1000  $\text{cm}^{-1}$  (the unsaturated



**Figure 1** FTIR spectra of PE copolymer: (a) LDPE DF840; (b) LLDPE 4404G; and (c) HDPE 2344G.



**Figure 2** FTIR spectra of different kinds of PE: (a) LDPE DF840; (b) LLDPE 4404G; and (c) HDPE 2344G.

groups), and 700–900  $\text{cm}^{-1}$  (the branched chains absorption),<sup>16</sup> respectively, as can be seen in Figure 2.

The IR spectra of polyethylenes were found to have significant differences in the 1300–1400  $\text{cm}^{-1}$  region.<sup>11</sup> The ratio of absorptions at 1369  $\text{cm}^{-1}$  (due to methylene group C-H deformation) and 1378  $\text{cm}^{-1}$  (due to the C-H deformation of methyl groups) showed an almost linear relationship between the ratio and length of branching in the copolymer. As the two peaks are so close (overlapping bands at 1369  $\text{cm}^{-1}$  and 1378  $\text{cm}^{-1}$  for some PEs), it is easy to determine the type of PE by comparing the intensity of the spectra.

For comparison, the apparent specific IR spectra of three types of known and unknown polyethylenes are all shown in Figure 3. According to Figure 3, the peak intensity of HDPE at 1378  $\text{cm}^{-1}$  is less than 1369  $\text{cm}^{-1}$ , as to LDPE, the peak intensity at 1378  $\text{cm}^{-1}$  is greater than 1369  $\text{cm}^{-1}$ , and for LLDPE, the peak intensity at 1378  $\text{cm}^{-1}$  is almost equal to 1369  $\text{cm}^{-1}$ .<sup>16</sup> To compare their IR spectrum of three types of known and unknown polyethylenes (Fig. 3), we can distinguish the type of PEs by the two peaks intensity of 1378  $\text{cm}^{-1}$  and 1369  $\text{cm}^{-1}$ . From Figure 3, the type of DF840 could be confirmed as LDPE, and 4404G should be LLDPE, while 2344G is of HDPE.

**Analysis of the type of PE by the absorption peak of unsaturated groups**

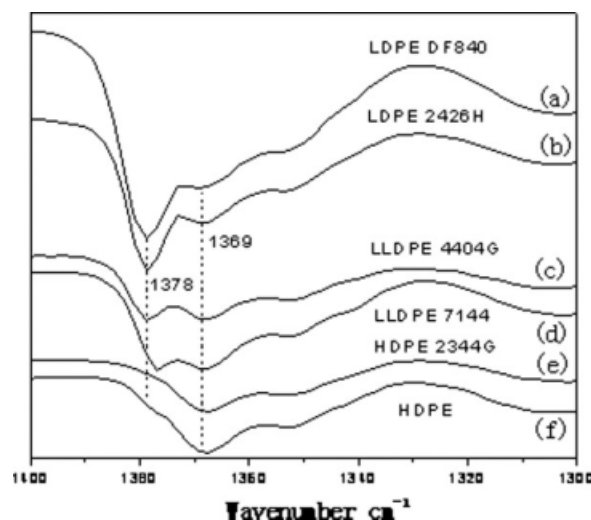
The presence of chain-end unsaturations in commercial PE samples was detected in the FTIR spectra in the bands located at 908 and 888  $\text{cm}^{-1}$ , which are the characteristic vibrations of vinyl end groups. They are the C–H rocking vibration absorption of  $-\text{CH}_2$  in  $\text{RCH}=\text{CH}_2$  and  $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  groups separately. The type of PE can be determined by comparing the intensity of the two peaks. FTIR spectra were consistent

with the presence of terminal double bonds. Because the chain ends or branched chains usually contain double chain bonds, the higher branching degrees of PE, there are more macromolecules at the chain ends. If the possible occurrence of  $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  groups is higher, then the peak intensity of the band at 888  $\text{cm}^{-1}$  shows stronger relativity. The analysis of IR can prove these determinations. As HDPE has essentially no branching, the peak intensity of 908  $\text{cm}^{-1}$  is obviously greater than that of 888  $\text{cm}^{-1}$ . LDPE has many branch chains, which contain several different branch types, including ethyl, butyl, amyl, and longer branches,<sup>8</sup> so the peak intensity of 908  $\text{cm}^{-1}$  is obviously less than that of 888  $\text{cm}^{-1}$  because of its higher branching degree. LLDPE has middle branching degree because it contains a short branch chain; the peak intensity of 908  $\text{cm}^{-1}$  is slightly greater than the band at 888  $\text{cm}^{-1}$ . Chain-end unsaturations were found in all the materials employed here.

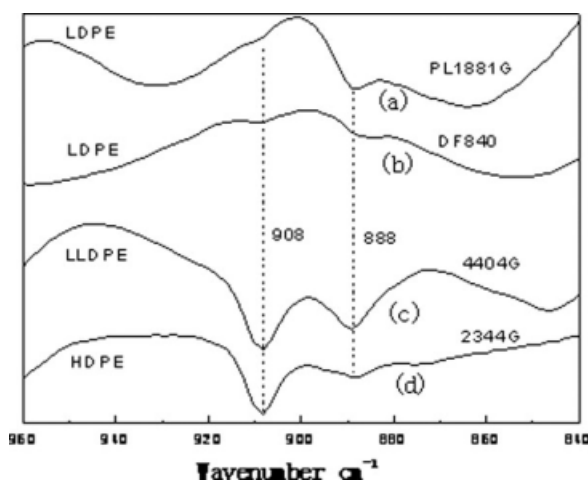
Figure 4 shows four unknown samples of PEs by comparing the peak intensity of 908 and 888  $\text{cm}^{-1}$ , which is in good agreement with the results of Figure 3. The type of PL1881G and DF840 could be LDPE, and 4404G should be LLDPE, while 2344G is of HDPE. Similarly, Figure 5 uses the five known PEs to verify the correctness of this method by comparing the bands located at 908 and 888  $\text{cm}^{-1}$ , which correspond to the vibrations of the unsaturations located at chain ends.<sup>8,17</sup>

**The structure analysis of PE by absorption peak of branched chains**

The weak absorption peak at 700 ~ 900  $\text{cm}^{-1}$  also can characterize the type of polyethylenes. Figure 6 shows a comparison of the FTIR spectra of PEs with different



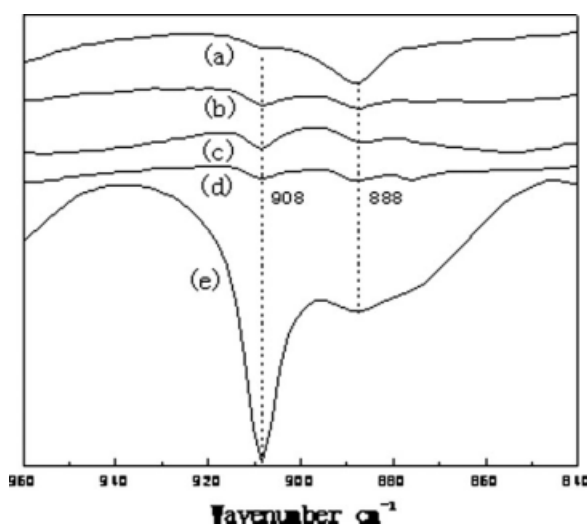
**Figure 3** Characteristic FTIR spectra of different kinds of PE: (a) LDPE DF840; (b) LDPE 2426H; (c) LLDPE 4404G; (d) LLDPE 7144; (e) HDPE 2344G; and (f) HDPE.



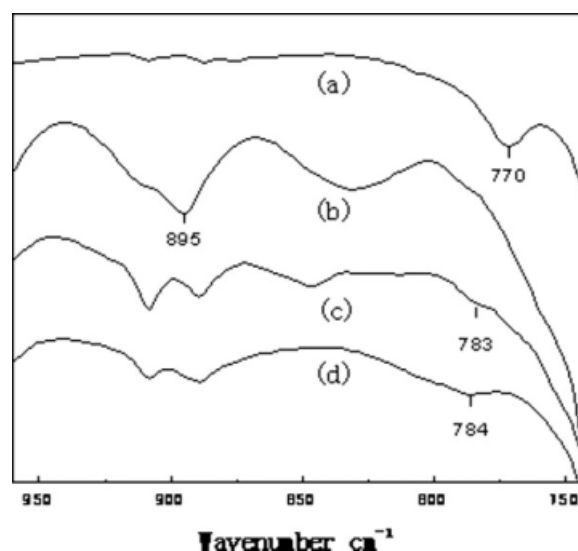
**Figure 4** Comparison of the IR absorption peak of unsaturated groups of PE: (a) LDPE PL1881G; (b) LDPE DF840; (c) LLDPE 4404G; and (d) HDPE 2344G.

$\alpha$ -olefins. The absorption bands at 770, 784, and 895  $\text{cm}^{-1}$  can be used, respectively, to identify butene-1, hexene-1, and octene-1 copolymers.<sup>18</sup> An absorbance band at 770  $\text{cm}^{-1}$  was also used to identify the ethyl branches in butene-1 copolymers. So, LLDPE 7145 contains butene-1, PL1880 with hexene-1, whereas the two samples of 4404G and OCTENE-1 PE have octene-1. Although only a handful of samples were analyzed successfully, we have demonstrated that implementation of the earlier-described techniques to determine the type of polyethylene seems feasible.

The applicability of FTIR spectroscopy method to analyze SCB in PE containing several different branches was quite challenging. It is worth mentioning that C-13 NMR technique is unequivocal for identifying branching type. When dubious results are suspected, C-13 NMR can be applied to confirm



**Figure 5** FTIR absorption peak of unsaturated groups of five known samples: (a) LDPE 2426H; (b) LLDPE 7144; (c) LLDPE 7042; (d) LLDPE 7145; and (e) HDPE.

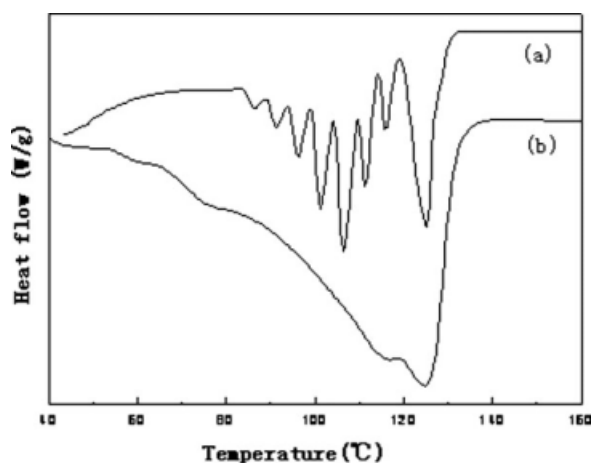


**Figure 6** FTIR spectra absorption peak of branch methylene rocking vibration of PE: (a) LLDPE 7145; (b) PL1880; (c) 4404G; and (d) OCTENE-1 PE.

uncertain identification. C-13 NMR can easily identify amyl or longer branches present only in LDPE. However, C-13 NMR is more time-consuming, requires large quantities of sample, and cannot differentiate terpolymers from copolymers.<sup>18</sup>

#### Thermal fractionation

Thermal fractionation is a temperature-dependent segregation process based on recrystallization of ethylene chains from the melt. As the molten polymer is held at the highest crystallization temperature, the longest ethylene sequence solidifies by chain folding, a preferable configuration to interchain aggregation due to its lower end surface energy. The neighboring sequences can crystallize independently and subsequently melt at temperatures corresponding to their crystal size or lamellae thickness. For illustration, Octene-1 PE was given as an example in Figure 7. At the general cooling rate, different crystal lattices overlap as a result of wide melting peaks [Fig. 7(b)]. Figure 7(a) shows the DSC heating curves after stepwise isothermal crystallization from the melt for Octene-1 PE used in this work. Multiple melting peaks can be seen, which are formed during each step of isothermal crystallization. Each endotherm represents a population of crystals with almost the same thermodynamic stability and the melting temperature, and difference among the endotherms is mainly caused by different crystal sizes.<sup>19</sup> The number and intensity of melting peak in heating curves qualitatively show the difference of the polydispersity of crystalline ethylene sequence length among the samples. The sharper melting peak observed at the higher melting temperature was attributed to the thicker lamellae



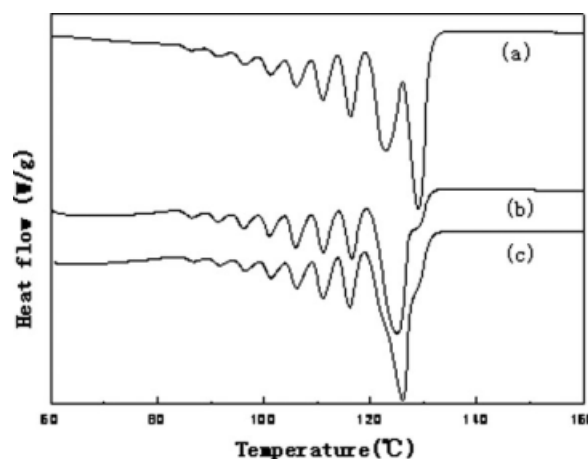
**Figure 7** DSC heating curves of Octene-1 PE: (a) fractionation; and (b) unfractionation.

containing few branches, whereas the broad lower melting endotherm was attributed to thinner lamellae and those containing increasing amounts of branches incorporated in the polymer chain.

The main approach has been employed in the literature to obtain quantitative information from the final melting scan after thermal fractionation. Two calibration steps are required: (1) the melting temperature must be related to ethylene sequence length. (2) the variation of heat of fusing with sequence length level must be adjusted. Several authors<sup>20,21</sup> have reported the calibration curve of the relation between melting point and branching content. The calibration curve proposed by Keating et al.<sup>12</sup> was used in this study to calculate the crystalline ethylene sequence length for each fraction. To estimate the sequence length, we recrystallized the commercially available hydrocarbons with the same program and measured the subsequent melting point. The plot of  $\ln(\text{CH}_2 \text{ mol fraction})$  against  $1/T$  shows a well linearship [eq. (1)], and from this curve, the ethylene sequence length of fractionated ethylene copolymers can be assigned from the melting temperatures of the fractions.<sup>22</sup>

$$-\ln(\text{CH}_2 \text{ mol fraction}) = -0.331 + 135.5/T_m \quad (1)$$

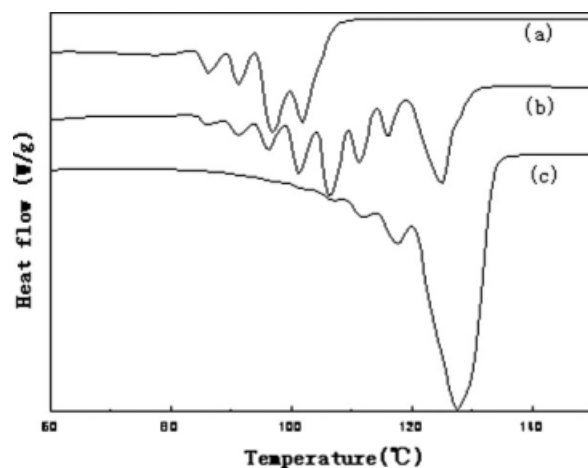
The apparent specific heat curves of certain samples are shown in Figures 8 and 9. Figure 8 shows the final heating DSC scans for three fractionated LLDPEs along with a standard DSC heating run of the copolymers. The fractionated copolymers clearly show a series of melting peaks corresponding to the melting of different mean lamellar thickness crystallites formed and annealed at each  $T_s$  temperature employed. The endotherms of the annealed polymers of PL1881G (LDPE-a), Octene-1 PE (LLDPE-b), and 2344G (HDPE-c) were shown in Figure 9. A greater portion of highly branched molecules can be



**Figure 8** DSC heating curves of three samples of LLDPE: (a) 7144; (b) 7042; and (c) 7145.

seen in the thermograms of the Octene-1 PE with higher comonomer amounts. The thermogram of the copolymer displays eight peaks from 125.2°C to 86.3°C. The heating curves of 2344G was displaced on the heat flow axis for clarity, which showed the polymer to be characterized by a higher portion of less branched segments. Because progressively shorter sequence groups crystallize out at each crystallization stage by successively decreasing crystallization temperatures, the thermogram of PL1881G only presents four peaks. The highest melting temperature is 101.9°C. So, we also can determine the type of polyethylene by comparing the heating curves of copolymers.

The fractionated endothermic curves of ethylene copolymers are compared in Figures 8 and 9. The corresponding melting temperature of six samples were listed in Table I. The content of  $\alpha$ -olefin in copolymers, which were calculated via eq. (1), is listed in Table II. For proving the validity of this calculation



**Figure 9** DSC heating curves of three polyolefins: (a) LDPE PL1881G; (b) LLDPE Octene-1 PE; and (c) HDPE 2344G.

TABLE I  
DSC Melting Points of Polyolefine Copolymers

	Sample	$T_{m1}$ (°C)	$T_{m2}$	$T_{m3}$	$T_{m4}$	$T_{m5}$	$T_{m6}$	$T_{m7}$	$T_{m8}$	$T_{m9}$
Figure 8	LLDPE-a	86.4	91.4	96.5	101.2	106.2	111.0	116.2	122.9	129.1
	LLDPE-b	86.5	91.4	96.1	101.1	105.9	111.1	116.5	125.0	
	LLDPE-c	86.9	91.8	96.5	101.3	106.1	111.2	116.2	126.1	
Figure 9	LDPE-a	86.2	91.3	96.9	101.9					
	LLDPE-b	86.3	91.2	96.0	101.2	106.5	111.2	116.0	125.2	
	HDPE-c	101.5	106.4	112.0	117.7	127.8				

method, LLDPE 7145, PL1881G, Octene-1 PE, and 2344G were detected by C-13 NMR (Varian INOVA 500NB). The results are also displayed in Table II. The comparison shows that the difference between the two methods is about 20%, so it is not significant. Therefore, the calculation method is feasible.

The results correspond well with the microstructure characteristic of polyethylene. The three LLDPE copolymers have the similar content of butane-1 (less than 4%). Generally, the total content of butene-1 is less than 8% in industry. Considering measurement error in both the technical condition (instrument, analytical apparatus) and the complex reaction of copolymerization, the actual content of butene-1 should be less than 8%. These results are consistent with the data indicated in the commercial product. HDPE has essentially less branching and has the lowest content of  $\alpha$ -olefin. LDPE has the highest content of  $\alpha$ -olefin among the three copolymers.

## CONCLUSIONS

In this article, copolymers of ethylene with  $\alpha$ -olefin was studied by FTIR and DSC techniques. The type of polyolefine can be qualitatively analyzed by FTIR spectroscopy. Different typologic polyolefines showed distinct characteristic absorbance peak of FTIR. By comparing the methyl deformation band position ( $1378\text{ cm}^{-1}$ ), methylene band position ( $1369\text{ cm}^{-1}$ ), and the  $\text{CH}_2$  band position in unsaturated groups of  $\text{RCH}=\text{CH}_2$  ( $908\text{ cm}^{-1}$ ) and  $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$  ( $888\text{ cm}^{-1}$ ), the type of PE can be determined. Ethyl, butyl, and hexyl types in polyolefine are readily distinguished by the branched chains absorption bands at  $700 \sim 900\text{ cm}^{-1}$  regime.

TABLE II  
The Content of  $\alpha$ -Olefin Measured by  
DSC and  $^{13}\text{C}$  NMR

	Sample	DSC (mol %)	$^{13}\text{C}$ NMR (mol %)
Figure 8	LLDPE-a	3.31	—
	LLDPE-b	2.69	—
	LLDPE-c	3.66	3.68
Figure 9	LDPE-a	8.43	6.87
	LLDPE-b	5.25	4.43
	HDPE-c	2.52	2.05

Improved thermal fractionation technique confirms that polyethylene copolymers are formed with various sizes of molecular, which contains the chains with different branching degree. It gives a satisfied result for characterizing the content of  $\alpha$ -olefin by multiple melting temperatures.

A combination of the two techniques, DSC and FTIR, can rapidly and reliably provide copolymer type and the content of  $\alpha$ -olefin in polyolefine copolymer. Therefore, this simple and efficient method can be put into practice.

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