**DiscovIR-LC** ™

Deposition and Detection System

Application Note 032
November 2009

LC-IR Characterization of Polyolefins

The DiscovIR-LC is a powerful new tool for materials analysis. When connected to the outlet of a LC column, the DiscovIR deposits LC eluants as a continuous solvent-free track on an infrared transparent substrate. The built-in interferometer simultaneously captures a set of time-ordered infrared spectra from the deposited track. Sample data collection and data processing are executed by GRAMS AI™ software resident on the DiscovIR system.

When analyzing polymers the chromatographic eluant deposits as a continuous track of sample, ranging from high molecular weight to low. This resultant map of molecular structure of all regions of a polymer GPC separation enables characterization of the distribution of the sample comonomers.
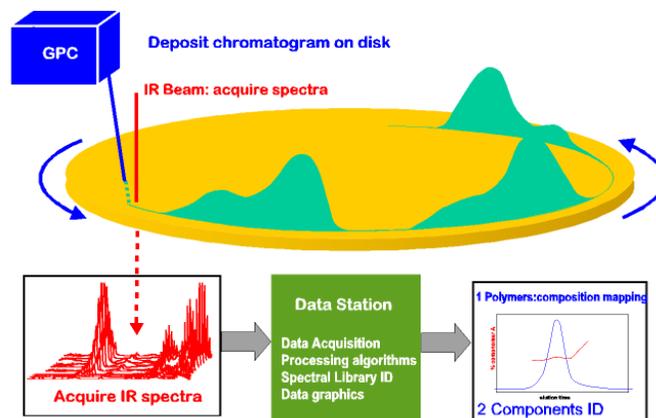
SUMMARY

A set of Dow Engage polyolefin elastomer samples (ethylene/octene copolymers) were analyzed by combined Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). The sample set included Engage™ 8100, 8200, 8401, 8540 and ENR6386 (ethylene/propylene). The object of the analysis was to evaluate the relative copolymer content across the MWD.

GPC eluant was directed to a Spectra Analysis DiscovIR instrument, and the polymer eluant deposited as a track on an IR transparent disk. Spectra were captured and processed as a time-ordered set of spectra, from which functional group chromatograms were extracted. Backbone (methylene) and branch (methyl) chromatograms were obtained and used to generate peak area absorbance ratio plots for the absorbance bands at approximately 1375 and 1465 cm^{-1} wavenumbers. The ratio of these IR absorbance bands reflects the ratio of methyl groups to methylene groups. An increase in the relative area for the 1375 cm^{-1} wavenumber absorbance band indicates an increase in the octene content of the copolymer.

Differences in the copolymer content are evident between the samples with the order of increasing octene content being 8540<8401<8200, 8100. The ratio plots show the Engage 8100 and 8200 samples to have essentially the same octene content. A sample of a polyethylene homopolymer was included in the analysis for comparison. The Engage 8200 and Engage 8401 exhibited compositional drift, the branch methyl contents trending downward with increased elution time (i.e. decreasing molecular weight).

The ability of the DiscovIR to obtain good quality IR spectra without the interference of mobile phase solvent absorbance bands and to detect compositional differences in the Engage polyolefin elastomers has been clearly demonstrated.

INTRODUCTION

Infrared Polyolefins Applications

Described here are some of the useful measurements of polyolefins that can be obtained by the use of LC-IR analysis.

 "Infrared (IR) spectroscopy is one of the most often used spectroscopic tools for the study of polymers."[1] Polyolefin spectra (Figure 1) are dominated by methylene bands (PE) and methyl + methylene bands (PP). At first glance, the spectra of polyolefins appear to provide sparse information. Lower intensity bands however can provide a wealth of information related to structure, composition, configuration and stereo regularity. Useful bands are found over the full range (4000 – 600 cm^{-1}) of the mid-infrared spectrum. By combining various chromatographic modes with IR spectral acquisition a wealth of information can be extracted from polymer samples.
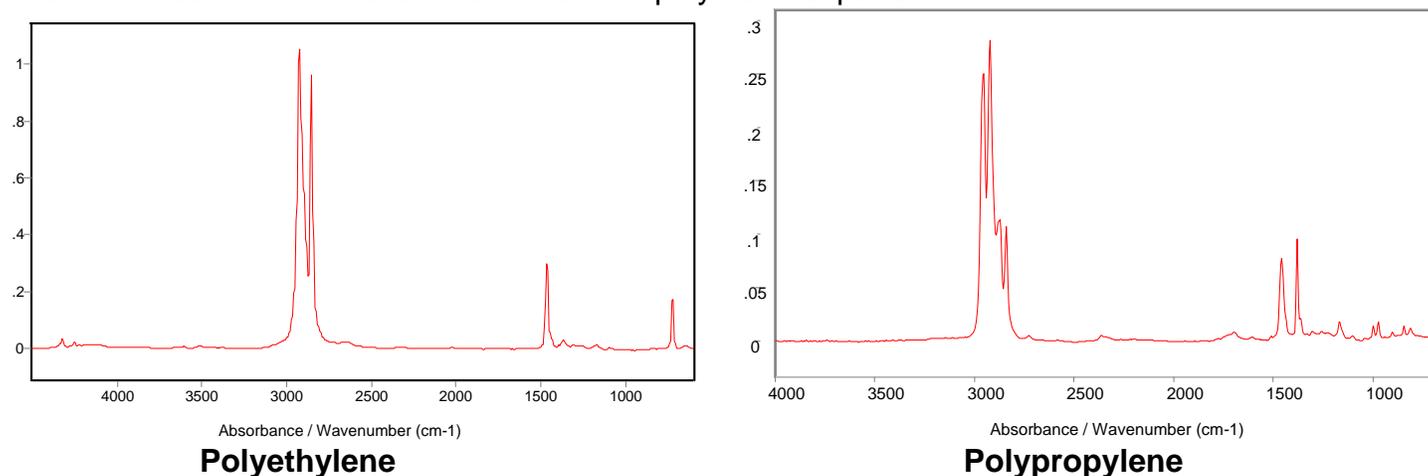

Polyethylene   **Polypropylene**

Figure 1 FTIR spectra of polyethylene and polypropylene

Identification of polyolefin types

A concise but comprehensive description of the infrared analysis of polyethylene is provided by Nishikida and Coates[2]. They describe the spectral characteristics that can be used to differentiate between low density (LDPE), linear low density (LLDPE), and high density (HDPE) polyethylenes. They also describe the IR identification of the α-olefins employed in production of low density polyethylenes, and the determination of crystallinity and density,

Short Chain Branching

Polyolefins are produced in many forms of copolymers and blends. LLDPE is a copolymer of ethylene with a comonomer that provides short chain branches that disrupt crystallinity of the methylene backbone. This results in modified physical properties, such as lower melting point, lower modulus, and increased pliability.

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[1] Spectroscopy of Polymers, Koenig, Jack L, 1999 Elsevier
[2] Nishikeda and Coates, Chapter 4, **Handbook of Plastic Analysis**, Hubert Lobo and Jose Bonilla,

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Identification and distribution of various polyolefin short chain branches is a frequent application, as reported by Harvey and Ketly[3].

Blitz and McFaddin similarly described useful absorption bands for short chain branching (SCB)[4].
"Traditional methodologies, using the methyl deformation band for qualitative and quantitative analyses, have recognized shortcomings. The methyl and methylene rocking bands, which are more characteristic of short chain branch type, were found to be more useful. Methyl, ethyl, butyl, isobutyl, and hexyl branches are qualitatively and quantitatively characterized in LLDPE copolymers by FTIR spectroscopy. . . .Fourier self-deconvolution was used to resolve overlapping bands for ethyl, butyl, and isobutyl branches. Using calibrations derived for LLDPE copolymers from 13C NMR data, FTIR spectroscopy was also used to characterize LLDPE terpolymers and LDPE resins. The FTIR and NMR data are in qualitative and quantitative agreement. In some cases correction were made to the FTIR results using data obtained from the methyl deformation band. The FTIR technique is less costly and faster than NMR spectroscopy."

Branch type	Wavenumber, cm^{-1} (Harvey and Ketly)	Wavenumber, cm^{-1} (Blitz and McFaddin)
methyl (branch)		935
ethyl (branch)		770
propyl (terminal)	740	
propyl (branch)	735	
n-butyl (branch)	724	893
Isobutyl (branch)		920
n-pentyl (branch)	723	
n-hexyl (branch)	722	888

Table 1 Absorbance bands of different branch types

Additives Analysis

Commercial polyolefin resins contain various additives (antioxidants, UV stabilizers, colorants, fillers). The soluble additives will elute as a non-resolved peak at the end of a GPC separation. Collection of this fraction and subsequent analysis by Absorption Chromatography – FTIR provides a rapid identification of multiple components. Alternatively a polymer sample may be extracted, and the extract then analyzed by (reverse phase) HPLC-FTIR via the DiscovIR LC.

Tacticity and Crystallinity

The regularity of the macromolecular structure influences the degree to which it has rigid, crystalline long range order or flexible, amorphous long range disorder. Polymers with a high degree of tacticity manifest crystallinity, while low tacticity (atactic) polymers, at low temperatures solidify into a vitreous glassy state. Infrared spectroscopy is frequently used as a simple and fast method for determining the level of tacticity in stereoregular polymers.[5]

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[3] **The Infrared Identification Of Short-Chain Branches In Polyolefins,** Harvey M.C., KetleyA.D., **J App Pol Sci,** V5 Issue 15, pp 247-250

[4] **The Characterization Of Short Chain Branching In Polyethylene Using Fourier Transform Infrared Spectroscopy,** Blitz J P, Mcfaddin D, **J.Appl. Pol. Sci.** Vol 51 Issue 1 pp 13-20

[5] **Polyolefins: processing, structure and properties**, James L White, David Choi, p26
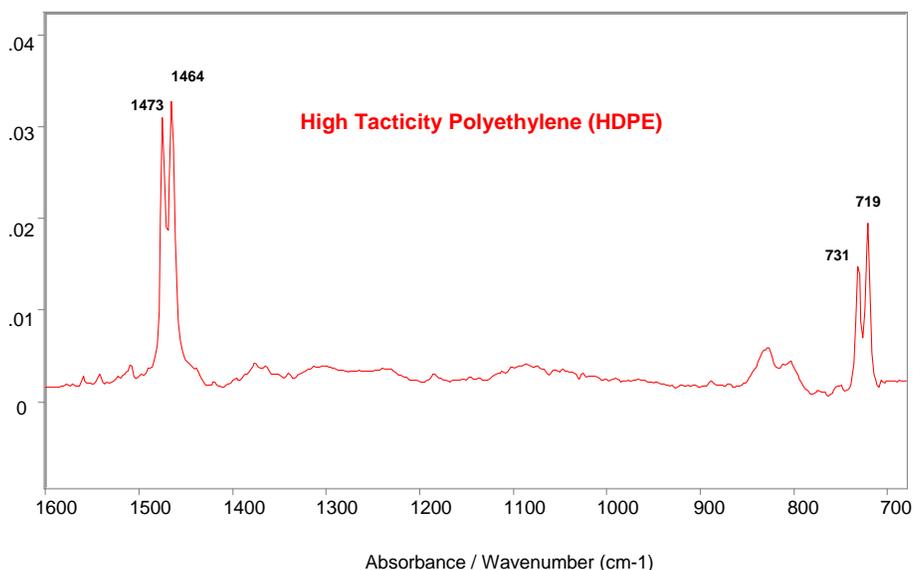
Figure 2 Peak splitting of crystalline polyethylene

Crystallinity of polyethylene manifests itself as peak splitting (Figure 2) of the 1,464 and 719 cm^{-1} peaks, with additional peaks found at 1,473 and 731 cm^{-1}. The crystallinity of a polyethylene sample can be determined from the ratio of the 731 to 719 cm^{-1} peaks[6].

Ethylene Propylene Copolymers and Blends

This commercially important group of polymers can readily be characterized by the hyphenated technique of GPC-FTIR. The methyl content of the polymer is readily determined by FTIR and can provide a measure of the propyl content of the polymer, provided one accounts for methyl-containing terminal groups.

Copolymerization of ethylene and propylene results in long sequences such as P-E-E-P, P-E-P. The random copolymerization of ethylene and propylene result in a triad of absorbance bands in the 700 - 800 cm^{-1} region. Deconvolution of this region will yield a triad of peaks. In a random EP copolymer, the ethylene-propylene ratio can be determined from the intensity ratio of the (deconvolved) peaks at 722, 736, and 751 cm^{-1}. [3]

Crosslinking of EP rubbers is achieved by adding a diene as a comonomer. The diene content in EPDM is customarily less than 10%. Infrared diene bands are weak, but usable in predicting crosslinking results.

TPO (Thermo Plastic Olefin) properties are sensitive to changes in molecular weight distribution and composition variation. "These polymers have been shown to have superior processing and/or better curing than comparable polymers of the same average composition but without the bimodal molecular weight/composition distribution"[7].

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[6] American Society for Testing and Materials D5576.

7 Datta,S. and Kresge, E.N., US Patent No. 4,722,971, Feb 2, (1988)

Polymer Degradation Analysis

Methods exist for infrared analysis of the degradation products of polyolefins. The various oxidation groups (ROOH, ROH, primary, secondary, tertiary), when derivitized, yield sets of unique, discrete infrared bands that characterize the oxidation entities and degradation mechanism.[8] The kinetics of photodegradation is coupled with the consumption of protectant additives (also identifiable via LC-IR methodology)[9].

Compositional drift

The bulk of the polyolefin products are produced as copolymers. The molecular weight distribution of a comonomer serves to modify the physical properties of a product. The characterization of comonomer drift is therefore a necessity for consistently producing product of specified properties.

EXPERIMENTAL

A set of Dow Engage polyolefin elastomer samples (ethylene/octene copolymers plus an ethylene/propylene polymer) were analyzed by combined Chromatography-Infrared Spectroscopy. The samples were injected onto a size exclusion chromatographic column, and the eluant was directed to the DiscovIR LC instrument. This instrument produced a time-ordered series of infrared spectra across the molecular weight distribution (MWD), as well as an infrared chromatogram of the eluate. The IR spectral data was then used to evaluate the relative copolymer content across the MWD.

Analysis conditions

Sample Conc.:	0.3% in TCB (with .02% Antioxidant)
Injection Volume:	80µl
Column:	Jordi DVB Mixed Bed, 10 x 500mm
Mobile Phase:	TCB, 1.0 ml/min.
IR Detector Res.:	8 cm-1
LC System:	Waters 150C, operating at 145 ºC

RESULTS

The following figure shows an overlay of the chromatograms obtained from the IR data for the deposited sample in the DiscovIR system and the RI detector in the Waters 150C high temperature chromatograph. The chromatograms obtained from the two different detection methods are essentially the same.

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[8] **Polymer photodegradation: mechanisms and experimental metho**ds, Jan F. Rabek,

[9] **Photodegradation of polyolefins,** Austin, M.E.   Hill, D.J.T.   O'Donnell, J.H.   Pomery, P.J. , Properties and Applications of Dielectric Materials, 1991., Proceedings of the 3rd International Conference, Publication Date: 8-12 Jul 1991On page(s): 55-58 vol.1
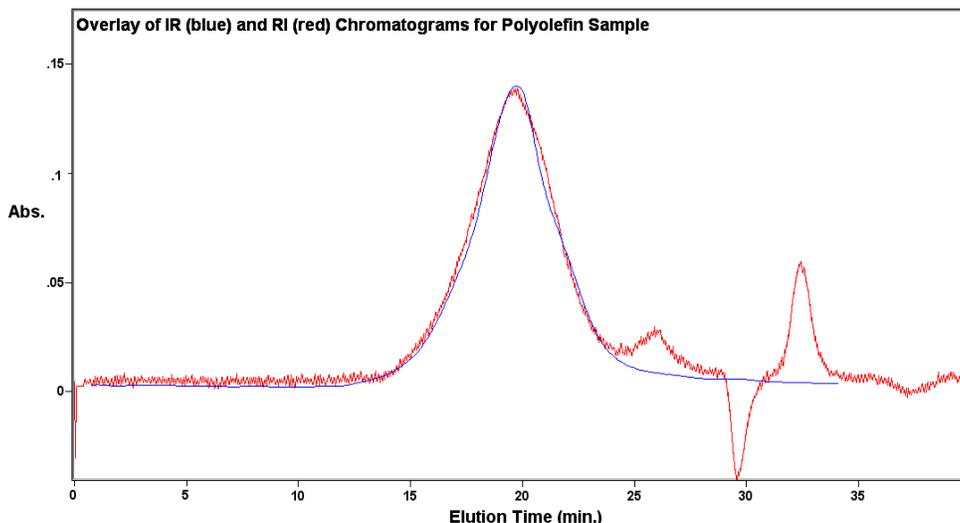
Figure 3 Overlay of polyethylene sample Refractive Index trace and IR chromatogram
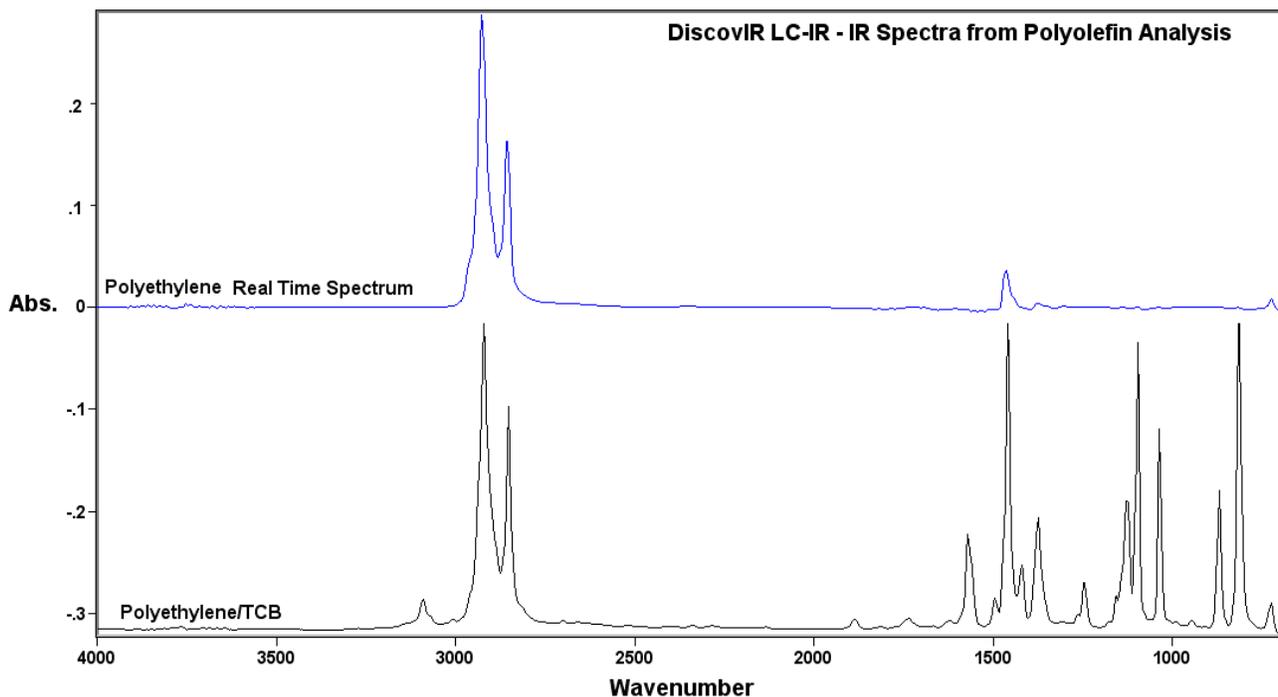

Figure 4 (Top): DiscovIR deposit from TCB-PE chromatogram (Bottom) Deposit plus trace of TCB

The DiscovIR deposits a polymer chromatogram free of any mobile phase. This permits the user to extract information from the whole range of the mid-IR spectrum. One of the analytical techniques used for the determination of short chain branching (SCB) processes a GPC column eluant through a heated flow cell to obtain direct transmission spectra in the 3000 cm^{-1} – 2800 cm^{-1} region. Mobile phase solvents such as TCB and ODCB present a "spectral window" in this mid-IR region. Determination of SCB is made by virtue of the presence of methyl bands in the 3000 cm^{-1} – 2800 cm^{-1} region. The methyl groups provide slight changes in the methylene asymmetric C-H stretch band, and

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chemometric analysis of such spectra is necessary for quantitation of methyl groups of branch units. Information about the branch types (see Table 1) requires data from other spectral regions.

A pair of spectra are shown in Figure 4. The upper spectrum was collected from the deposited sample track of the Engage 8200 sample. The bottom spectrum is a sample of Engage 8200 pipetted onto the Zn-Se sample collection disk. This sample contained a trace amount of the mobile phase, 1,2,3 trichlorobenzene (TCB) when scanned. There are three points of note in the above figure.

1. Chromatograph deposition using the DiscovIR is completely free of mobile phase, presenting only the spectral peaks of the olefin polymer.
2. The only spectral information accessible in the flow cell technique is the bands present in the 3000 cm^{-1} – 2800 cm^{-1} region. The wealth of information available in the fingerprint region is unavailable in the flow cell technique. Chemometric methods have to be developed for each branch type expected to be present in samples.
3. The flow cell technique only provides information about methyl groups, and not about branch types in a sample.

The IR spectra obtained for the deposited chromatograms of the samples were used to generate peak area absorbance ratio plots for the absorbance bands at approximately 1375 cm^{-1} and 1465 cm^{-1} wavenumber peaks. The ratio of these IR absorbance bands reflects the ratio of methyl groups to methylene groups.

$$\frac{a1}{a2} = \frac{\varepsilon1}{\varepsilon2} \bullet \frac{C1}{C2}$$

$a =$ absorbance (peak area)

$\varepsilon =$ extinction coefficient

$C =$ concentration

The IR spectrum in Figure 5 was obtained for the Engage 8100 sample and shows the absorbance bands used for the ratio plots. An increase in the relative area for the 1375 cm^{-1} wavenumber absorbance band indicates an increase in the side-branch methyl content of the copolymer[10].

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[10] **ASTM D2238 -92(2004), Standard Test Methods for Absorbance of Polyethylene Due to Methyl Groups at 1378 cm**
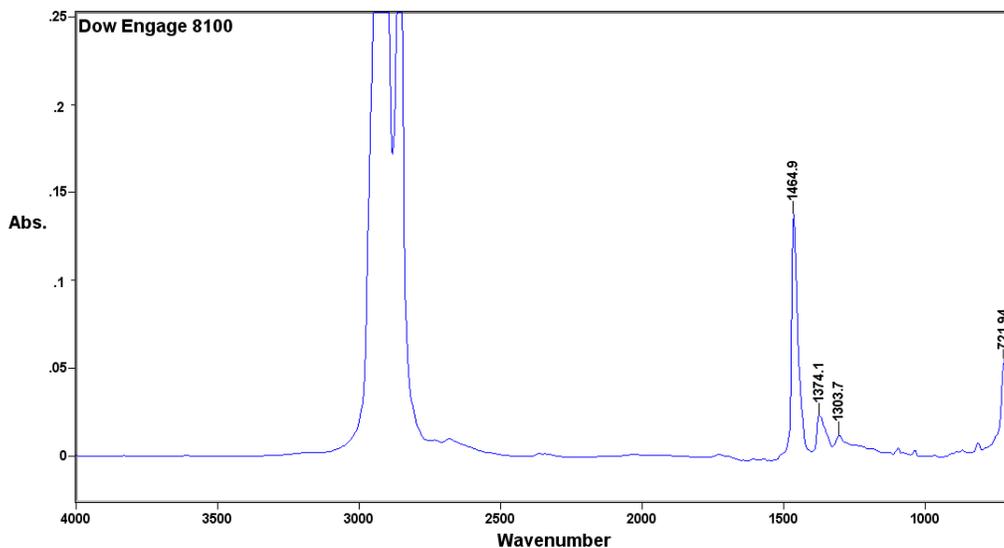
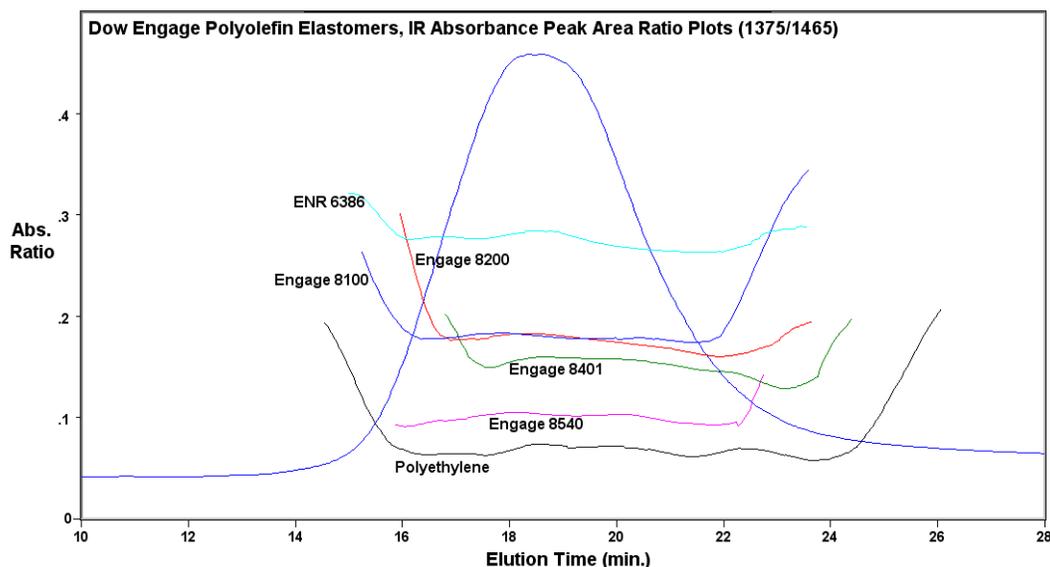**Figure 5 Infrared bands used for ratio chromatograms**

Figure 6 Absorbance area ratio chromatograms overlaid on a representative total IR chromatogram

As can be seen in Figure 6, the various products of this family of elastomers exhibit different overall levels of the methyl/methylene content, as evidenced by the differing values of their methyl/methylene ratio chromatograms. Differences in the copolymer content are evident between the samples with the order of increasing branch methyl content being 8540<8401<8200≅8100<ENR6386. The ratio plots show the Engage 8100 and 8200 samples to have essentially the same bulk octene content. A sample of a polyethylene homopolymer was included in the analysis for comparison.
 The methyl/methylene levels exhibit very little variation over the molecular weight distribution for Engage 8100, Engage 8540, and the polyethylene homopolymer. The Engage 8200 and Engage 8401 however exhibit measurable compositional drift, the branch methyl contents trending downward with increased elution time (i.e. decreasing molecular weight).

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Figure 6 plots the absorbance ratio of the comonomers vs. elution time. If it is desired to display the data as a %-branch comonomer vs. elution time, algebraic substitution will provide an expression of concentration of methyl-containing comonomer vs. elution time[11].

$$C_{branch\%,t} = \frac{q_t}{(1 + q_t)} \bullet 100$$

Where the variable q_t is defined as

$$q_t = \frac{1}{k} \bullet \frac{A_{methyl,t}}{A_{methylene,t}}$$

If the bulk value of the branch comonomer is known, the constant k can be determined by integration of the individual comonomer absorbance chromatograms. The elution time axis of the plot of the chromatograms can similarly be transformed to molecular weight by using column calibration plots. These operations are readily executed with the DiscovIR Data Processing software. Note: the data sets shown in Figure 6 were not corrected for chain terminal methyls.

These ratio chromatograms clearly differentiate the degree of short chain branching in these polymer products, and characterize the compositional drift characteristics of the branching groups. Inasmuch as composition drift modulates the physical properties of thermoplastic polyolefin (TPO) products as well as affecting their processing properties, the characterization of such drift is an important tool for manufacturing control.

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[11] Application note 18, **Copolymer Composition Drift Measurement**, Spectra Analysis, Inc. Jan 2008