



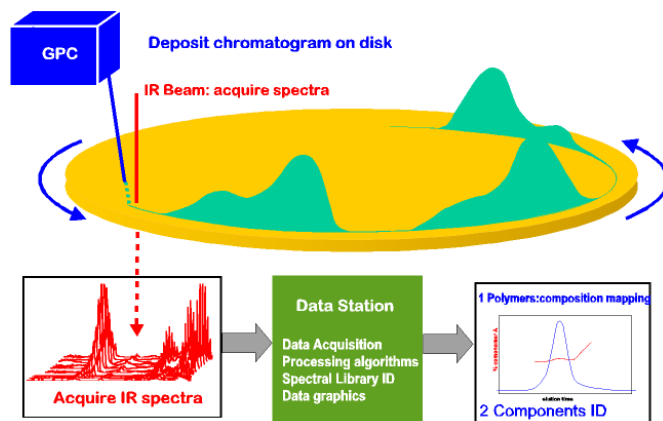
DiscovIR-LC™ Deposition and Detection System

Application Note 34

Full Scan GPC-IR Characterization of Polyolefin Copolymers & Blends

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.



INTRODUCTION

Infrared spectroscopy is the premier analytical tool for determining the composition and structure of polyolefin products. The coupling of IR spectroscopy with GPC/SEC chromatography provides a map of changing composition across the molecular weight distribution.

The characterization of polyolefin products by FTIR has many aspects, and calls for examination and measurement of adsorption bands across the full range of infrared spectrometers. Currently infrared flow cells are used in conjunction with GPC to obtain information about the distribution of short chain branching (SCB) of polyolefins by virtue of bands in the C-H stretch region (2800-3000 cm^{-1}).

Chemometric methods are used to quantify the branch distribution. This document describes a number of other composition and configuration aspects of polyolefins that can be characterized by utilizing the whole of the mid-infrared spectral region. The DiscovIR, coupled with GPC, is a powerful tool for revealing composition and structural characteristics of the many polyolefin products in use.

Present documented analytical procedures include:

- Short chain branching (branch identification, amount of branching)
- Identification of polyethylene type
- Resolution of blended polyolefin products
- Assessment / quantification of crystallinity
- Polyolefin copolymers – compositional drift
- Different forms of HDPE, LLDPE
- Polymer degradation
- tacticity of polymers
- Additives analysis

TECHNOLOGY DESCRIPTION

The DiscovIR system deposits the sample on a rotating ZnSe disk for continuous full scan FTIR analysis across the MWD. Decreasing the disk rotation speed increases the thickness of the polyolefin layer in the IR beam. The disk speed feature can be utilized to obtain quality fingerprint region spectral information across the entire MWD with no changes to the chromatographic conditions.

The technique consists of two consecutive injections. The first injection is made with standard conditions using TCB solvent with antioxidant at 145°C at 1ml/min elution rate. A 100 µl injection and a disk speed of 3mm/min captures FTIR spectra suitable for traditional SCB calculations using the major absorbance bands from 2800-3000 cm⁻¹.

The second injection uses the same chromatographic conditions, but the ZnSe disk rotation is slowed by a factor of 10, resulting in a layer 10 times thicker in the IR beam. The resultant high intensity IR spectra provide a wealth of information within the fingerprint region throughout the MWD deposit track.

First Injection: Full Scan FTIR spectra 4000-650 cm⁻¹

Second Injection: High intensity Full Scan FTIR spectra 4000-650 cm⁻¹ for in depth structural and compositional information. The following sections detail the extra information derived from the fingerprint region.

Short Chain Branching (Branch Identification, Branching Amount)

Short chain branching is a shared characteristic of all of the low density polyethylenes. Spectral bands associated with short chain branching can be found across the full range of mid-IR spectra. Branching is measured by virtue of the methyl groups present on the branch moiety. GPC-FTIR flow cell techniques are limited to the C-H stretch region (2800-3000 cm⁻¹, the only spectral window for the high boiling point solvents used for high temperature GPC). By contrast the solvent removal inherent to the DiscovIR-LC process makes the whole mid-IR spectral range accessible to the analyst. This opens up a wide selection of characterization measurements, which are unavailable to users of flow cell methods of GPC-FTIR.

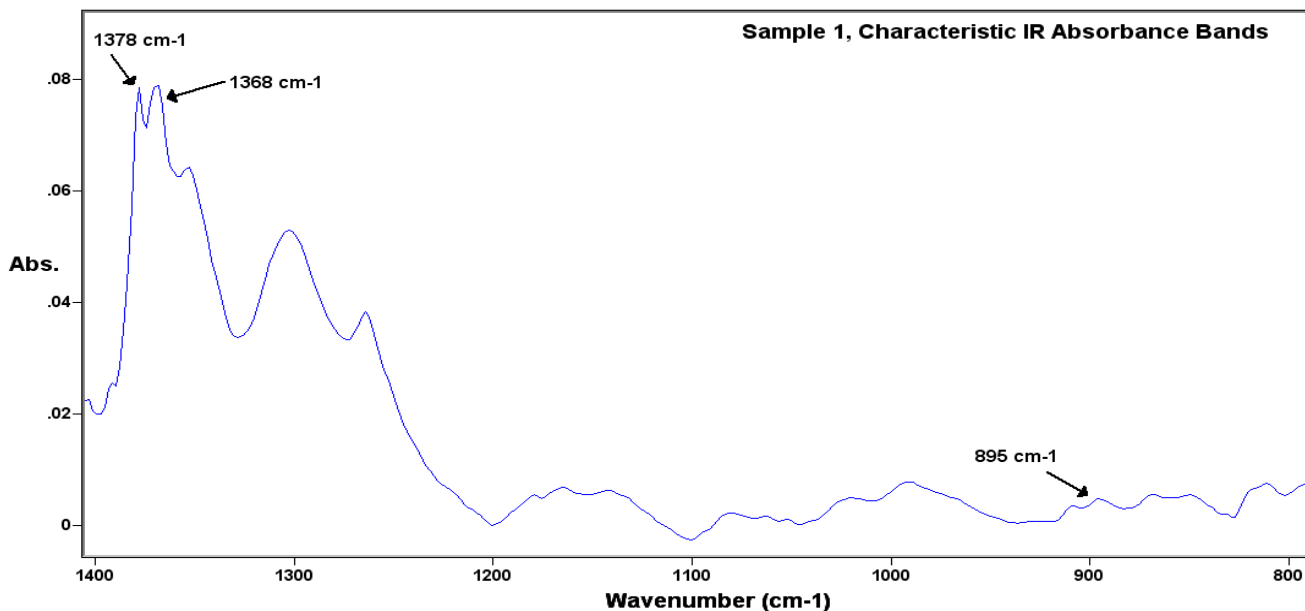


Figure 1. Single spectrum taken from a GPC-FTIR analysis of a butyl branched polyethylene

Identification of the Branch Comonomer

If the comonomer is unknown, “identifier bands” shown in the third column of Table 1 can be used to identify the branch type. If the comonomer is not known a priori, the presence of bands at 772 cm^{-1} , 895 cm^{-1} , and 890 cm^{-1} can be used to identify ethyl (minimum of 1 branch per 1000 carbons), butyl (minimum of about 5 branches per 1000 carbons), and hexyl (minimum of about 5 branches per 1000 carbons) branches, respectively.

Table 1. Frequencies used to identify and quantify short chain branches

Branch type	Bending frequency (cm^{-1})	Identifier (cm^{-1})
Methyl	1377	1151
Ethyl	1379	772
n-butyl	1378	894
i-butyl	1383, 1385 (gem dimethyl)	1169
n-hexyl	1380	890

Polyolefin Copolymers – Compositional Drift

The sample used in Figure 1 has butyl side chain branching. It is essentially a copolymer of ethylene and hexene. Most copolymers exhibit compositional drift across the molecular weight range of the polymer. Compositional drift will affect the physical/mechanical properties of polymers, and the synthesis process is designed to achieve a composition drift (or lack thereof) that maximizes product performance. The degree of short chain branching of polyethylenes is commonly determined by measuring the intensity of methyl bending in the $1377 - 1380\text{ cm}^{-1}$ region. Generating a ratio

chromatogram of A_{1378}/A_{1368} serves to cancel out the varying film thickness of the deposited chromatogram. Butyl branch content was calculated from a GPC–FTIR ratio chromatogram of A_{1378}/A_{1368} and is shown in Figure 2 below. It is apparent this particular material exhibits a significant increase in butyls/1000 C as a function of elution time.

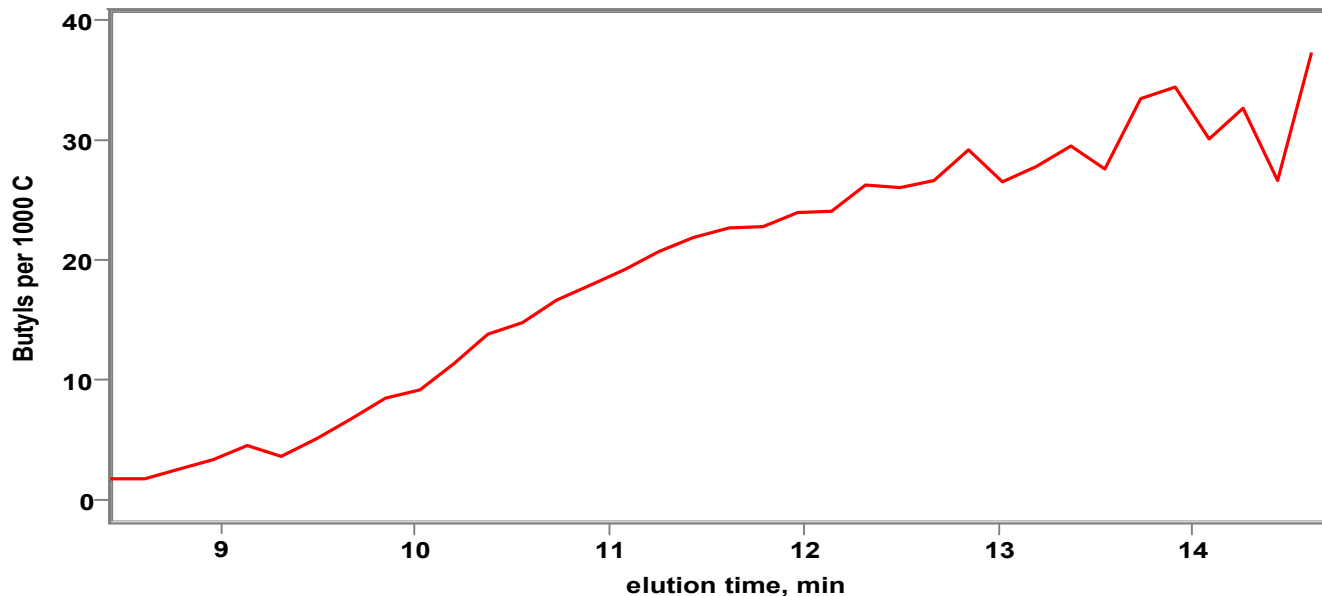


Figure 2. Butyl branch content as a function of elution time

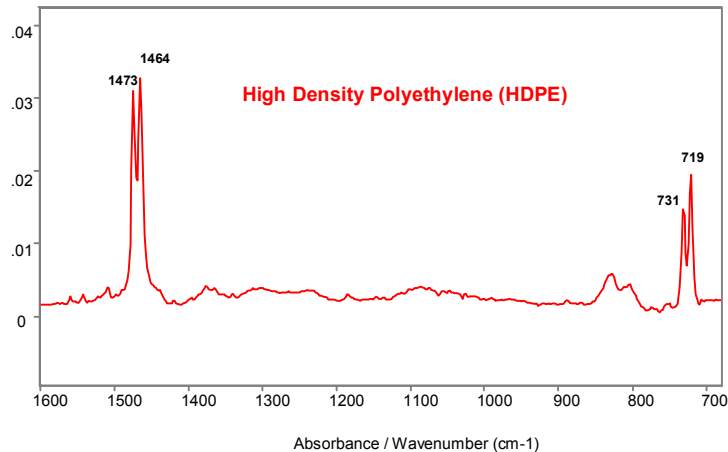
Identification of Polyethylene Type

The analyst may have a need to determine whether an unknown sample is a high density (HDPE) or low density (LDPE, LLDPE) material. HDPE is essentially polymethylene, and will not present a band in the 1370 cm^{-1} - 1380 cm^{-1} region. Both LDPE and LLDPE will show a band in this region. Examine bands in the $990 - 890\text{ cm}^{-1}$ region to determine the type of LDPE. A pair of bands at 990 cm^{-1} and 910 cm^{-1} is indicative of a terminal vinyl group. A band at 890 cm^{-1} is assigned to vinylidene. LLDPE presents a pair of weak bands at 890 cm^{-1} and 910 cm^{-1} , of approximately equal intensity. LDPE presents just the 890 cm^{-1} band, and it is relatively stronger than that produced by LLDPE. In this way it is possible to differentiate between HDPE, LDPE and LLDPE using the infrared fingerprint region.

Assessment and Quantification of Crystallinity

Polyethylene, absent branching, consists of chains of polymethylene, having identical conformation. As such they will intrinsically manifest a high degree of crystallinity in the solid phase. Crystallinity bands arising from inter-chain interactions of polyethylene can be observed in the splitting of the CH_2 rocking band into a pair of bands at 730 cm^{-1} and 720 cm^{-1} . The 1470 cm^{-1} band similarly exhibits crystal splitting. Qualitatively, the degree of crystallinity may be estimated from the degree of splitting of these bands. The degree of crystallinity can be determined from the ratio of 731 cm^{-1} to 719 cm^{-1} peaks.¹

¹ ASTM D5576; ² John Coates, Book "Infrared and Raman Analysis of Polymers", Page 15.



Polypropylene produced by a stereoregular head-to-tail polymerization is isotactic and is also crystalline. Bands reflecting this crystallinity are found at 1167 cm^{-1} , 998 cm^{-1} , 899 cm^{-1} , and 842 cm^{-1} . Copolymers of ethylene and propylene may exhibit crystallinity of either comonomer, and may also exhibit changes in the degree of crystallinity in different regions of a chromatogram.

The degree of polyethylene crystallinity may be estimated from a peak ratio algorithm, which eliminates the necessity of film thickness measurement.² The absorbances at 1303 cm^{-1} and 1901 cm^{-1} represent respectively the crystalline and amorphous regions.

$$X = 337/[A_{1303}/A_{1901} + 3.37]$$

$$X (\%) = \text{degree of crystallinity}$$

Tacticity of Branched Polymers

Tacticity is a measurement of the stereoregularity of polymer chains possessing chiral centers. High tacticity levels are associated with high melting points, higher solvent resistance, and increased mechanical moduli. Polypropylene produced with Ziegler-Natta catalysts is isotactic and crystalline. The isotactic polypropylene presents sharp infrared bands at 1167 cm^{-1} , 998 cm^{-1} , 899 cm^{-1} , and 842 cm^{-1} , whereas atactic polypropylene does not exhibit these bands.

Figure 6 on page 8 shows a peak ratio chromatogram of a polymer blend, in which one of the blend components was isotactic polypropylene homopolymer, and one was ethylene propylene copolymer. An infrared chromatogram of the ratio of spectral bands 1155 cm^{-1} and 1169 cm^{-1} is a plot of the concentration ratio chromatogram across the elution profile of the sample. The molecular weight average of the two components was quite similar, but the tacticity difference of the two components is quite evident here. It is also possible to see such tacticity profiles in single component copolymer samples containing blocks of different stereo-regularities.

The four isotactic polypropylene bands cited above are sensitive to crystallinity, and an empirical equation has been developed to measure polypropylene crystallinity (reference)

$$X(\%) = 109 \cdot \frac{A_{998} - A_{920}}{A_{974} - A_{920}} - 31.4$$

Additives Analysis

Polyolefin products contain numerous additives, including polymers as well as small molecules. The small molecule substances often will be seen as a separate peak following the polymer elution. Extraction of the additives, and a reverse-phase or normal-phase chromatography run serves to provide adequate separation for identification of these components by HPLC – FTIR, using the DiscovIR instrument.

Polymer Blends

Polymer blends are ubiquitous in the polyolefins industry. Deformulation of such blends is a challenging task, particularly given similar solubilities and molecular weight distributions of the product. The combination of GPC chromatography and infrared spectroscopy of the eluant often provides insights into the individual components of the blend. The following sample illustrates the ability to characterize the individual components of a blend, even when those components are not chromatographically resolved. A three component blend material was directly injected onto the sample disk of the DiscovIR instrument. No chromatographic separation was utilized. The figure below shows the bulk IR spectrum of the blend (Sample 3). A high loading was chosen to bring up the intensity of the bands in the fingerprint (1400 cm^{-1} - 680 cm^{-1}) region.

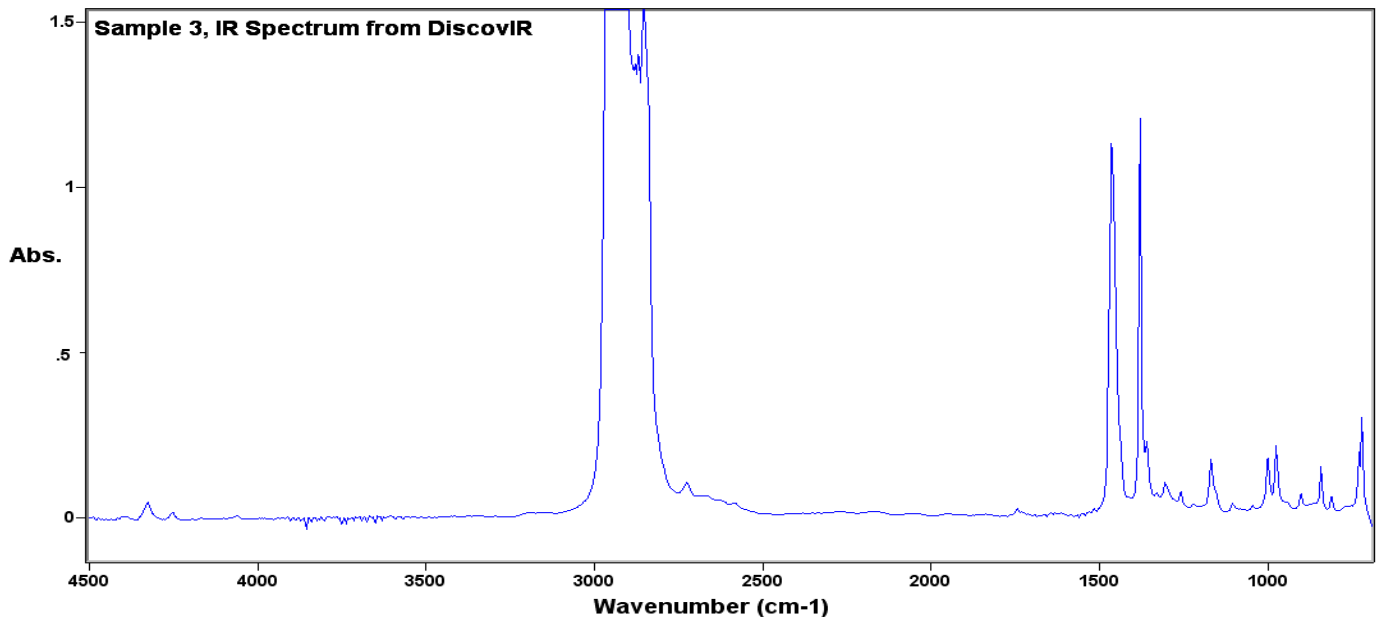


Figure 3. Bulk sample of a 3-component polyolefin blend

Close examination of the fingerprint region of Figure 3 revealed a number of characteristic bands, a few of which are summarized in Table 2.

Table 2. Tentative band assignments.

Wavenumber, cm^{-1}	Possible assignment
1168	Polypropylene (isotactic)
1155	Methyl Branch
974	Polypropylene (isotactic)
772	Ethyl branch (ethylene-butene)
720	Polyethylene (non-crystalline)

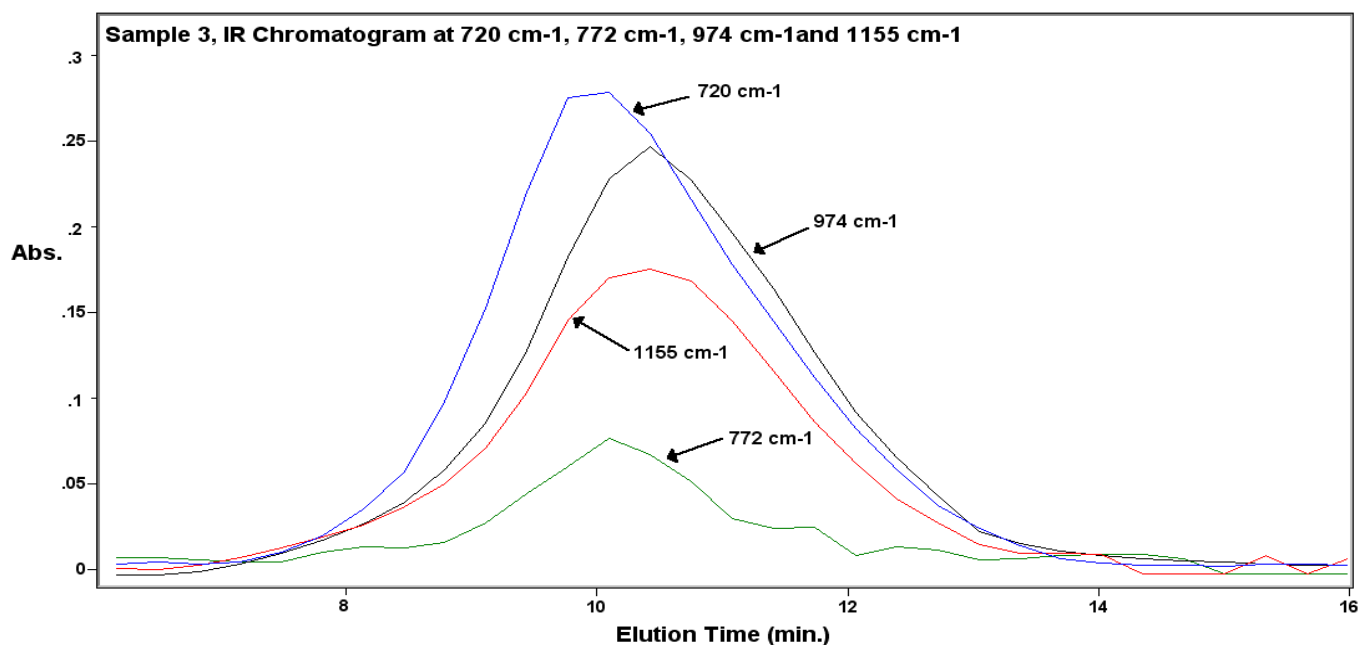


Figure 4. Functional group chromatograms of infrared bands

Figure 4 shows some Infrared band chromatograms extracted from a GPC-FTIR run of the sample. All of the chromatograms are overlapped, but not completely. The 974 cm^{-1} and 1155 cm^{-1} chromatograms have the same retention time maxima. The 772 cm^{-1} chromatogram is a bit noisy (due to the very small absorbance of this band), but appears to be generated by a component eluting somewhat earlier. The 720 cm^{-1} chromatogram peaks earlier still, and arises from a higher MW component.

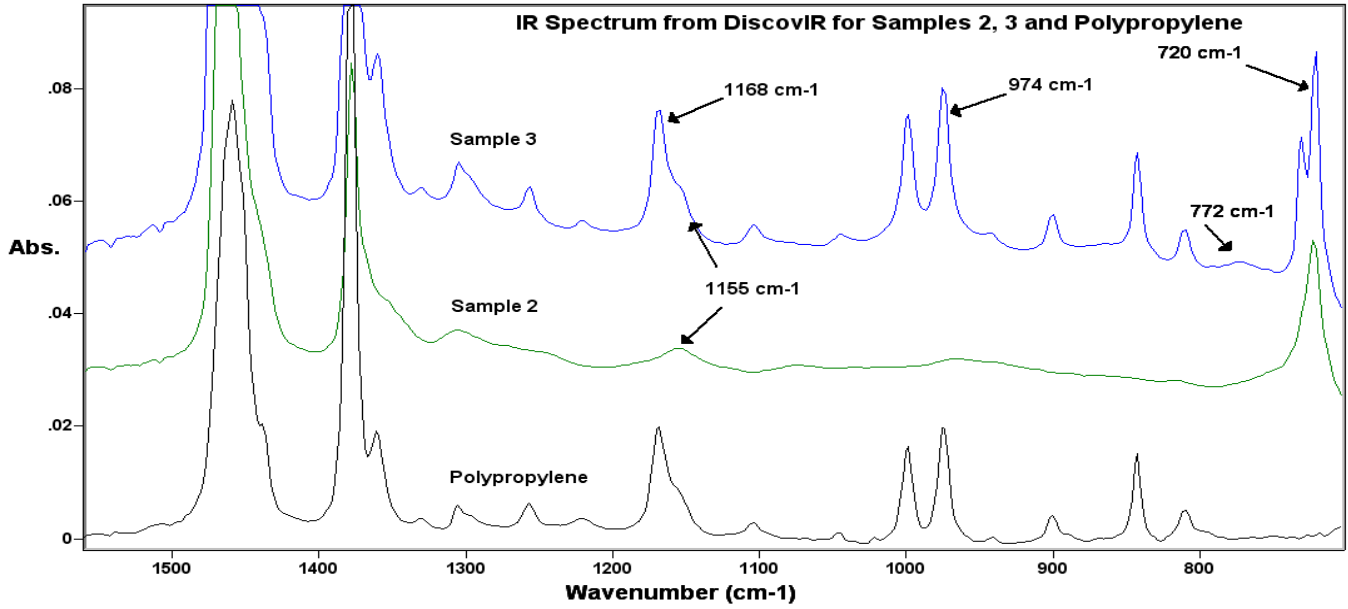


Figure 5. Mid-IR spectra of 3-component polyolefin blend (Sample 3), polypropylene homopolymer and ethylene-propylene copolymer (Sample 2).

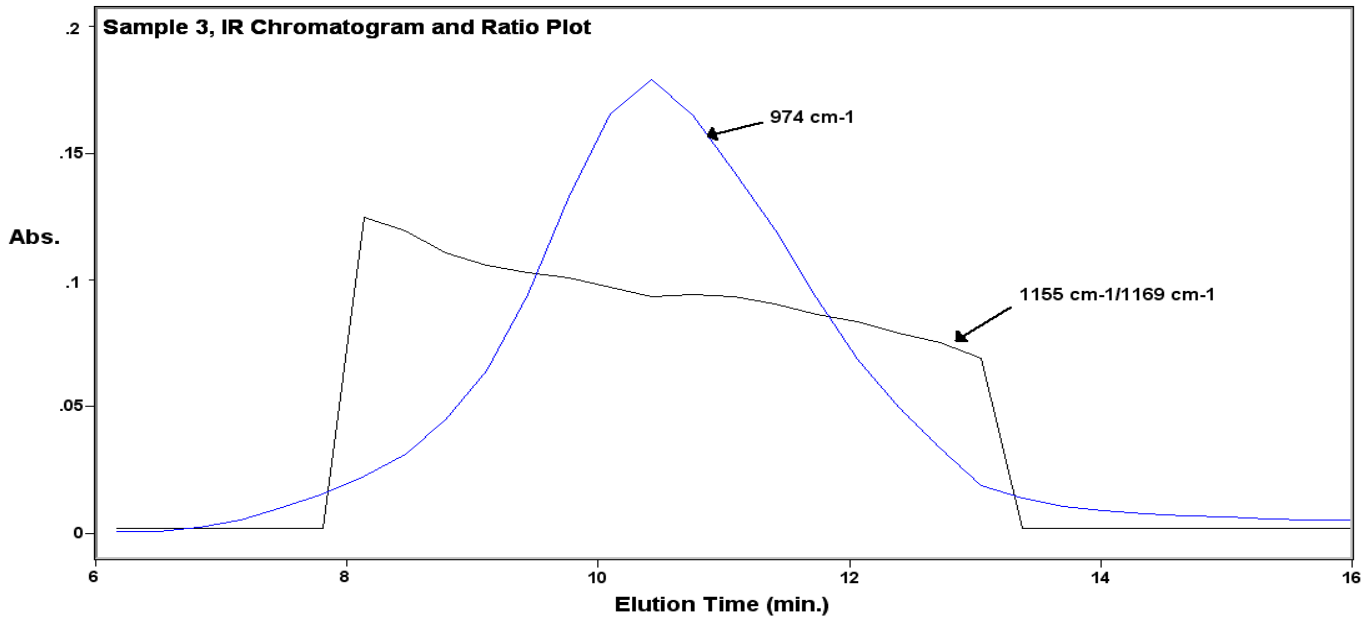


Figure 6. Chromatograms of a single band 974 cm⁻¹ and band ratio 1155 cm⁻¹/1169 cm⁻¹

Referring again to Figure 3, the 720 cm⁻¹ is characteristic of a polyethylene, and the splitting of this band suggests that the ethylene content has some degree of crystallinity. These features indicate that one component of the blend is ethylene (crystalline)/propylene (atactic). Crystal splitting of the ethylene is attributed to this copolymer.

Polypropylene generates characteristic bands at 974 cm^{-1} and 1155 cm^{-1} , and isotactic polypropylene produces a stronger band at 1168 cm^{-1} . Figure 6 displays the 974 cm^{-1} chromatogram (blue) showing the molecular weight distribution of component(s) with this characteristic. Overlaid is a ratio chromatogram that shows the relative concentrations of these components. Atactic polypropylene will not exhibit the 1168 cm^{-1} band.

1. Comparison of the 1155 cm^{-1} and 974 cm^{-1} band chromatograms in Figure 6 shows there are two distributions of propylene containing polymers. The 974 cm^{-1} band is unique to isotactic polypropylene.
2. The 1155 cm^{-1} band is common to both ethylene/propylene copolymers and polypropylene. The 1155 cm^{-1} band chromatogram shows a higher molecular weight distribution relative to the 974 cm^{-1} band chromatogram, indicating the presence of Ethylene/propylene co-polymer. Ethylene-Propylene copolymers such as Sample 2 in Figure 5 can be synthesized with varying degrees of propylene tacticity.
3. The 772 cm^{-1} band chromatogram, although is indicative of ethylene-butene copolymer.
4. Comparison of the 720 cm^{-1} band chromatogram and the 772 cm^{-1} band chromatogram indicates there are two ethylene containing polymers in the mixture. One is obviously ethylene/butene and its molecular weight distribution is represented by the 772 cm^{-1} band chromatogram. The data is also consistent with a second co-polymer of ethylene/propylene (Sample 2) with a higher molecular weight distribution.

These indications represent a first effort at deformation of the blend of polymers, which includes both homopolymer and copolymers. The characteristic bands serve to indicate the chemical structure of the comonomers, and configuration characteristics such as crystallinity and tacticity are also made evident in the spectral data set. By being able to obtain individual band chromatograms of identifying characteristics, one can discern the composition of the blend components. The use of column sets which would maximize the chromatographic resolution would provide more conclusive results, as would other corroborative methods.

This analysis is made possible because of the ability to capture spectral information across the whole of the mid-IR range; something not possible with the IR flow-cell equipment. The information utilized comprised both primary composition IR bands, and bands arising from configuration/conformation aspects of the materials.

In sum it appears that this blend Sample 3 consists of an ethylene-butene copolymer, an ethylene-propylene (atactic) copolymer, and a polypropylene (isotactic) homopolymer.

