CASE STUDY – Polymer Ratio Determination using ^{13}C Nuclear Magnetic Resonance (NMR).

OBJECTIVE

The purpose of this work was to determine the monomer type and the monomer ratio in a polypropylene-polyethylene blend.

ANALYTICAL STRATEGY

^{13}C Nuclear Magnetic Resonance (NMR) was used to identify chemical structures and to calculate the monomer ratio in the sample.

CONCLUSIONS

Carbon NMR was successfully applied to determine the monomer type in a suspected polypropylene-polyethylene blend. The sample was found to contain signals for propylene, ethyelene and hexene (butyl branches). The monomer ratio in the sample was found to be ~ 74.2 ethylene, ~ 24.4% of polypropylene and ~ 1.4% of hexyl monomer. The sample is most consistent with a polypropylene homopolymer and a linear low density polyethyelene containing hexyl comonomer.

Final Report

Jordi Labs LLC
Case Study

Polymer Ratio Determination using 13C Nuclear Magnetic Resonance (NMR)

Date: xx/xx/xx

Released by:
Dr. Mark Jordi
President
Jordi Labs LLC

Company Name Confidential

Date

Client Name
Company Name

P: xxx-xxx-xxx
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Dear Client,

Please find enclosed the test results for your samples described as:

1. Polypropylene
2. High Density Polyethylene
3. Polypropylene/ Polyethylene Blend

The following test were performed:

1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Objective

NMR was used to determine the monomer ratio in a Polypropylene/Polyethylene Blend.

Summary of Results

Carbon NMR was successfully applied to determine the monomer ratio in an unknown polypropylene-polyethylene blend. Analysis of a polypropylene and a high density polyethylene reference sample were used to aid in identification of the unknown spectrum. The unknown blend was found to contain ~ 74% ethylene, ~ 24% of propylene and ~ 1.4% of hexyl monomer (butyl branches). The observed pattern was most consistent with a polypropylene homopolymer blended with a linear low density polyethylene (polyethylene-hexene copolymer).

Individual Test Results

A summary of the individual test results is provided below. All accompanying data, including spectra, has been included in the data section of this report.

^{13}C NMR

^{13}C-NMR spectra were acquired in 1,2,4-trichlorobenzene at 125°C with a 15-sec pulse delay to provide an integrated data set for the determination of the chemical composition of the materials.

Sample 1: Polypropylene. **Table 1** contains the identifications for each peak observed. Three resonances were observed at 46.53, 28.94, and 21.86 ppm, (for the –CH–, $–CH_2–$, and $–CH_3$, respectively) corresponding to the backbone structure of isotactic polypropylene. **Figure 1** shows the assignments for each peak. The methyl resonances are actually a group of related peaks, the smaller ones account for ~ 6% of the overall integrated area and correspond with the minor stereochemical isomers in the polymer. Three minor peaks at 37.9, 31.0 and 24.8 ppm suggest the presence of a small amount of ethylene (~1.5%).

Table 1
Polypropylene NMR Results

Identification	Chemical Shift (ppm)
P1	46.53
P2	28.94
P3	21.86

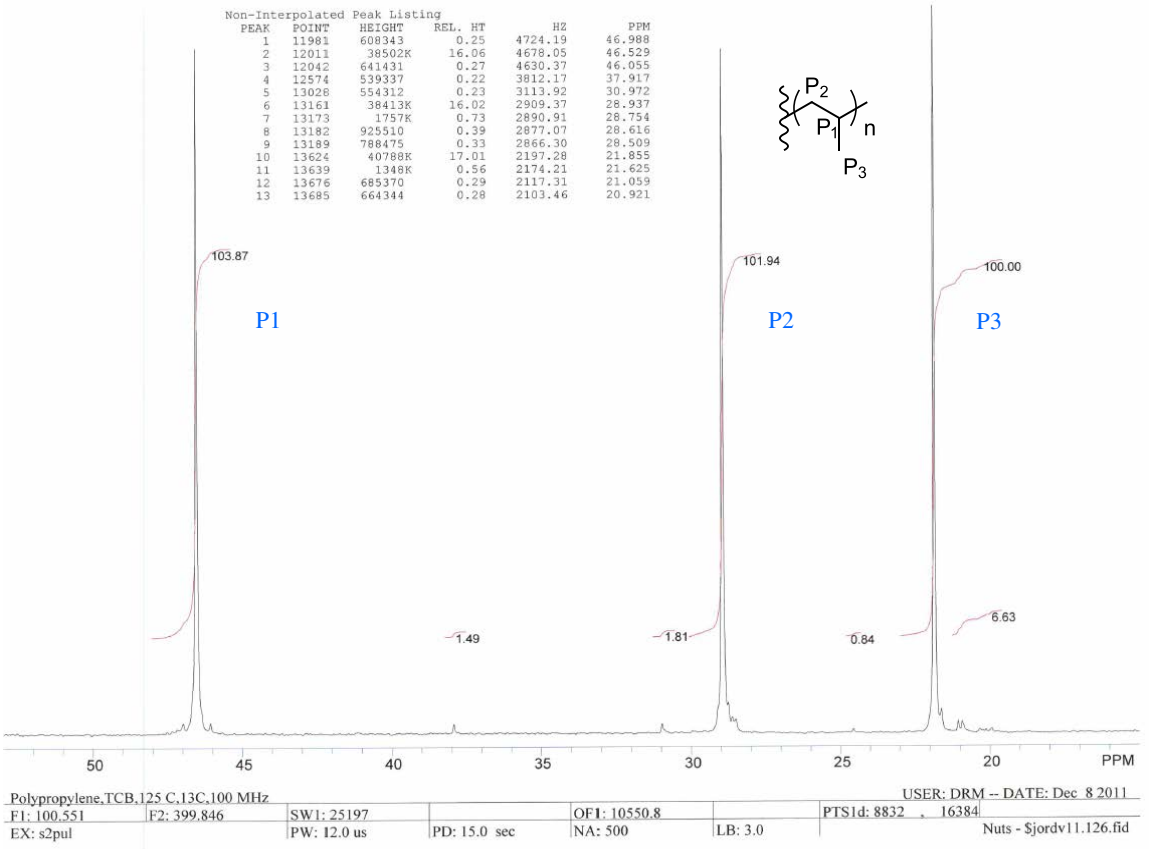

Figure 1. Expansion of the aliphatic region for Sample 1, Polypropylene.

Sample 2: High Density Polyethylene (HDPE). A single resonance was observed at 30.00 ppm **(Table 2** and **Figure 2)**, which is consistent with a structure that contains only $–CH_2–$ carbons, the expected structure for HDPE.

Table 2 High Density Polyethylene NMR Results	
Identification	Chemical Shift (ppm)
A1	30.00

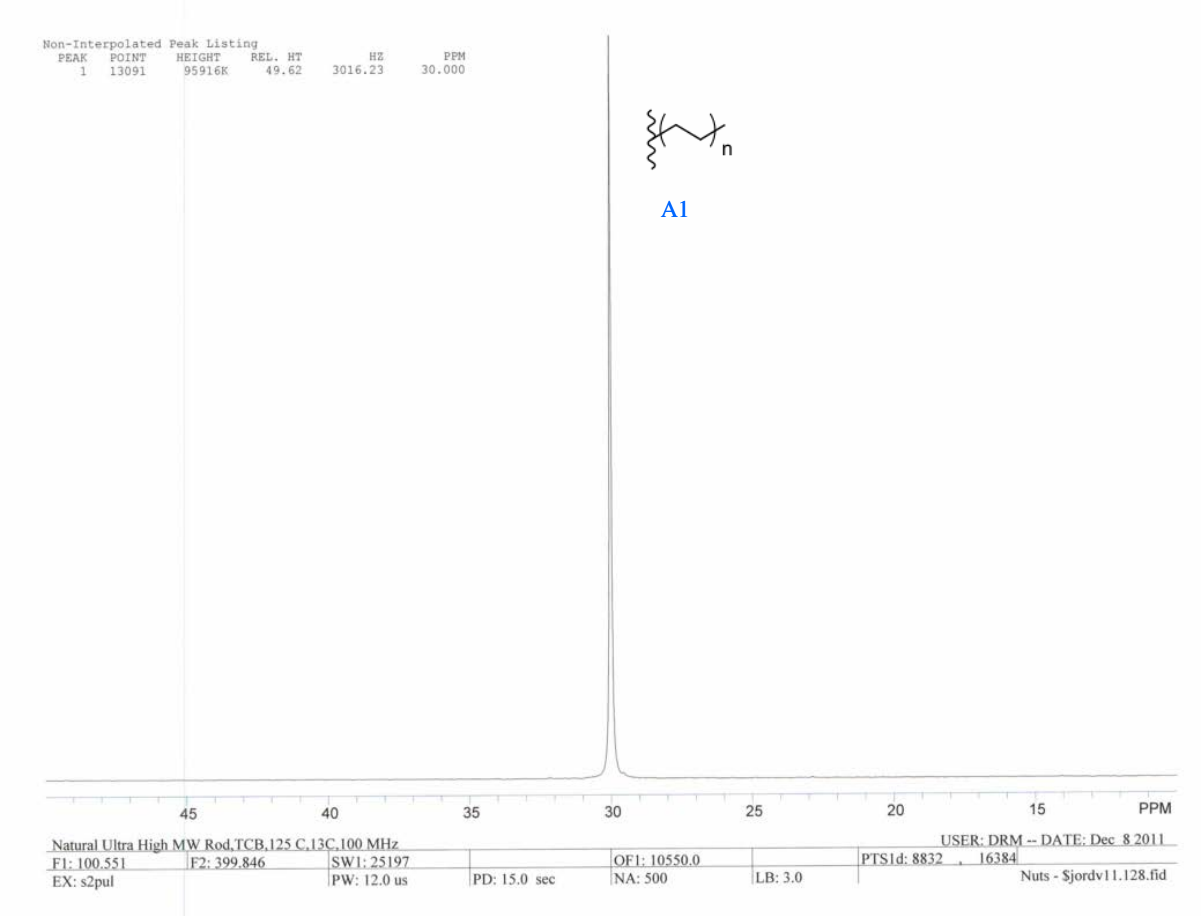

Figure 2. Expansion of the aliphatic region for Sample 2, High Density Polyethylene (HDPE).

Sample 3: Polypropylene/Polyethylene Blend. **Table 3** contains the peak identifications for this polymer mixture. **Figure 3** shows an expansion of the region where polymer short chain branching is expected. The largest resonance (A5) was observed at 30.00 ppm and is consistent with polyethylene. Resonances for polypropylene (P1, P2, P3) were found at 46.52, 28.93 and 21.86 respectively.

A modest amount of butyl branching was observed in the sample (hexene monomer). Resonances for polymer branching were observed at 38.15 ppm and 34.54 ppm (backbone tertiary carbon (A1) and adjacent carbon (A2)) and for the neighboring polyethylene repeat unit (A3) and (A4) at 27.29 and 30.47 respectively. The peaks for the butyl branches are labeled as B in **Figure 3**. The lack of a peak at 24.8 ppm suggests that the polypropylene is a homopolymer (see **Figure 1**). Thus it is concluded that the hexene is contained in the polyethylene segment. The data is most consistent with an identification of a linear low density polyethylene since only butyl branches were observed.

Table 3 Polypropylene/Polyethylene Blend NMR Results		
Identification	Chemical Shift (ppm)	Integration
P1	46.52	100.39
P2	28.93	~104.43
P3	21.86	100.00
A1	38.15	7.56
A2	34.54	~ 8.01 (13.72-B1)
A3	27.29	~ 8.01
A4	30.47	~ 8.01
A5	30.00	588.28
B1	34.16	~ 5.61
B2	29.53	~ 5.61
B3	23.38	5.39
B4	14.12	5.84

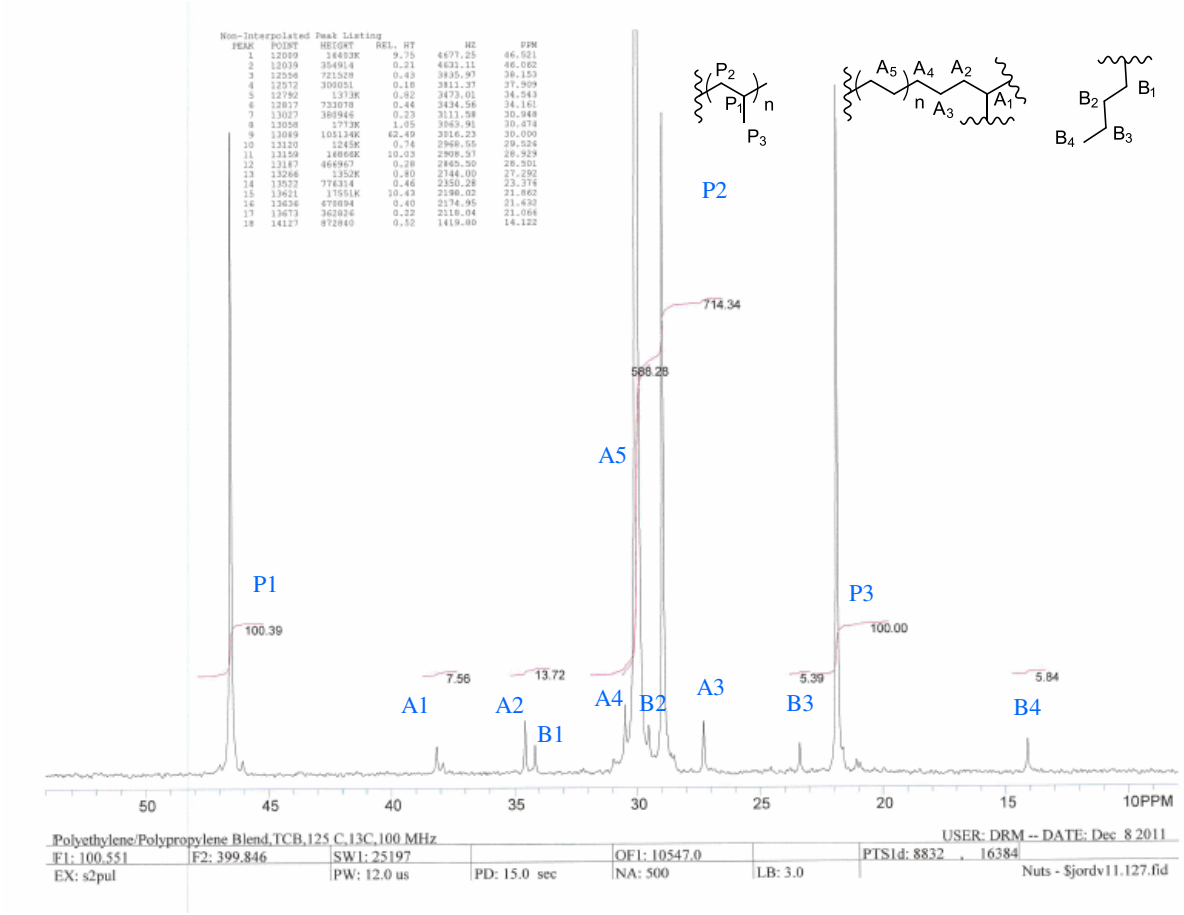

Figure 3. Expansion of the aliphatic region for unknown polypropylene/polyethylene blend

The integration values for each carbon type were used to estimate the percentage of each monomer.

Butyl = 1.37%
Propylene = 24.43%
Ethylene = 74.20%

Analysis Conditions

^{13}C NMR

This section of a Jordi report provides information on the methods used including instrument type, temperatures, solvents, sample preparation, etc. The specific conditions have been removed for this case study.

Closing Comments

Deformulation of an unknown material is intended to provide a best estimate of the chemical nature of the sample. All chemical structures are supported by the evidence presented but are subject to revision upon receipt of additional evidence. Additional factors such as material processing conditions may also affect final material properties.

Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

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