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Project B.10 – Study of Flammability of Materials

**Determination of Mol-% Ethylene in Propylene/Ethylene Copolymer Samples
by Pyrolysis/Gas Chromatography/Mass Spectroscopy Analysis**

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ABSTRACT

This report describes experimental work conducted pursuant to an agreement between General Motors and the United States Department of Transportation. This report describes a laboratory method for the determination of the mol-% ethylene in propylene/ethylene copolymer samples. This method is based on pyrolysis/gas chromatography/mass spectroscopy analysis. Samples of propylene / ethylene copolymers with known ethylene content were analyzed to generate a calibration curve for this method.

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INTRODUCTION

The work described in this report was conducted by General Motors (GM) pursuant to an agreement between GM and the United States Department of Transportation as part of Project B.10 (Study of Flammability of Materials). Parts or components used in motor vehicles that contain the label <PP> may be poly(propylene) homopolymer¹ or may be a propylene/ethylene copolymer with an ethylene content in the range of a few mol-% to 20 – 30 mol-%. When analyzed by pyrolysis/gas chromatography/mass spectroscopy, poly(propylene) homopolymer and propylene/ethylene copolymer yield many of the same thermal decomposition products, and are often difficult to distinguish by cursory visual inspection of the chromatograms from these analyses. Closer inspection of the chromatograms reveals that samples of propylene/ethylene copolymers yield unique decomposition products not produced by thermal decomposition of either poly(ethylene) homopolymer or poly(propylene) homopolymer. Detection of these products in the pyrolysate from a sample indicates that the polymer is a propylene/ethylene copolymer and not poly(propylene) homopolymer. In addition, the ethylene content of the propylene/ethylene copolymer can be determined by quantification of these unique thermal decomposition products.

This report describes a method based on pyrolysis/gas chromatography/mass spectroscopy analysis for the determination of the mol-% ethylene in propylene/ethylene copolymer samples. A calibration curve for this method was generated by analysis of samples of propylene / ethylene copolymers with known ethylene content.

EXPERIMENTAL

The analytical instrumentation consisted of a Pyroprobe 2000 sample pyrolyzer (CDS Analytical, Inc, Oxford, PA), a Model 6000 Purge and Trap Sample Concentrator (CDS Analytical, Inc.), a Model 5890 Series II Gas Chromatograph (Hewlett Packard Co., Palo Alto, CA), and a Model 5989B Mass Spectrometer (Hewlett Packard Co.).

Pyrolysis. The sample (< 1 mg) was loaded into an open-ended quartz tube. The sample was held in place by two plugs of quartz wool. The quartz tube was inserted into the Platinum heating coil in the pyroprobe, and the pyroprobe installed in the pyrolysis interface chamber in the purge

¹ The term homopolymer indicates that the polymer contains only one type of monomeric subunit. For example, poly(propylene) homopolymer indicated that the polymer is pure poly(propylene) and does not contain other monomeric subunits such as ethylene or styrene.

and trap concentrator. The sample was purged with Helium at flow rate of 30 mL/min for 2 minutes before being heated.

A two-step temperature program was used for pyrolysis: from ambient temperature to a final temperature of 750°C at 20°C/ms; and hold at 750°C maintained for 40s. The sample was purged with Helium at flow rate of 30 mL/min during the pyrolysis. The effluent from the pyrolysis chamber passed through a trap packed with Tenax absorbent maintained at ambient temperature, which retained the thermal decomposition products from the sample. The desorber, valve oven, and transfer line were maintained at a temperature of 300 °C. The trap rest and trap initial temperature was 40°C. The trap final temperature was 300 °C.

After pyrolysis of the sample, the Tenax trap was heated to 300°C to desorb the trapped pyrolysate, which was cyro-focused onto the head of the GC column. The cyrogenic trap at the head of the GC column was cooled with liquid nitrogen. The rest temperature was 275 °C, the trapping temperature was -60 °C, and the desorption temperature was 300 °C. The desorber purge time was 6 minutes.

Gas Chromatography. The chromatography column was a crosslinked methyl silicone capillary column (HP-1, 50 length, 0.2 mm i.d. of 0.33 µm film thickness). After sample transfer from the Tenax trap to the GC column was complete (5 min), the cyro-focus trap was heated from -60 to 300°C at a rate of approximately 12°C/min. The temperature of the chromatographic column was held at 40°C for 2 min, then programmed from 40 to 315°C at a rate of 12°C/min, and held at 315°C for 10 min. The carrier gas was Helium, and the GC was operated in the constant flow mode at a flow rate of 0.8 mL/min. Both the injector temperature and mass spectrometer interface temperatures were 275°C.

Mass Spectrometry. The ionization source temperature was 200°C and the analyzer temperature was 100°C. The mass spectrometer was operated in positive ion mode. The mass spectrometer was scanned continuously from 40 to 600 amu at a rate of 1.2 scans/s. The peaks corresponding to 4-methyl-2-heptene, 2,5-dimethyl-1,5-hexadiene, 2,4-dimethyl-1-heptene and 1-octene were integrated manually.

Propylene/Ethylene Copolymer Standards. Propylene/ethylene copolymer standards were obtained from 200°C and the analyzer temperature was 100°C. The propylene/ethylene materials used as standards in this study were obtained from Huntsman Corp. (Marysville, MI).

RESULTS

Poly(ethylene), poly(propylene), and propylene/ethylene copolymers are part of a class of polymers called polyolefins. Pyrolysis or thermal decomposition of polyolefins involves scission of C-C bonds in the polymer chain to yield successively smaller fragment molecules that retain some of the original molecular structure of the parent polymer molecule. For example, Figure 1 shows a chromatogram of pyrolysis products from a sample poly(ethylene) homopolymer.

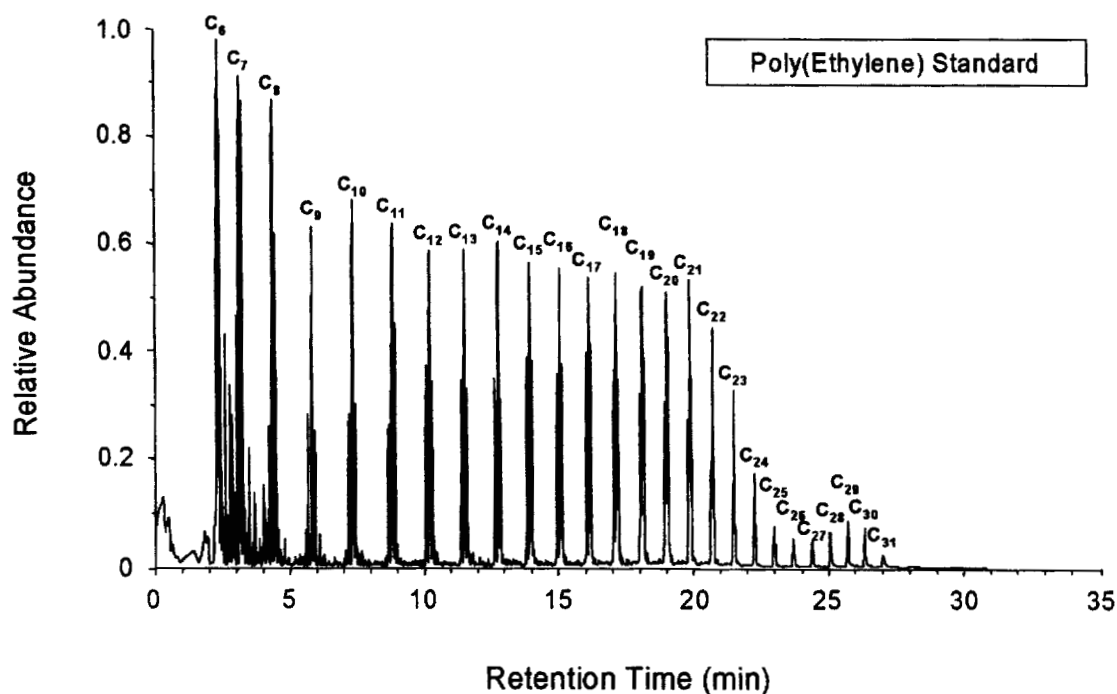


Figure 1. Chromatogram of the thermal decompositions of a sample of poly(ethylene) homopolymer.

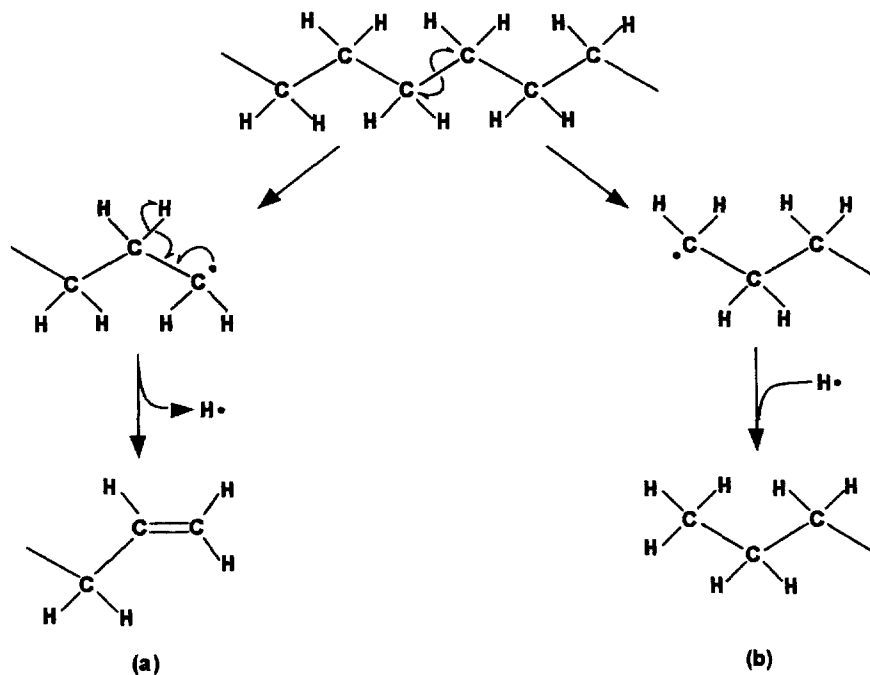
The peaks in this chromatogram were identified from their mass spectra, and were a homologous series of *n*-alkanes (C_nH_{2n+2}), a homologous series of terminal alkenes (C_nH_{2n}), and a homologous series of terminal alkadiene (C_nH_{2n-2}) with the following order of elution: $C_nH_{2n-2} < C_nH_{2n} < C_nH_{2n+2}$. The labels (C_n) indicate the number of carbon atoms (n) in each group of three peaks.

Poly(ethylene) is a linear aliphatic molecule composed of ethylene monomer subunits. Pyrolysis of materials containing poly(ethylene) yielded a mixture of *n*-alkanes, *n*-alkenes, and *n*-

alkadienes. The sequence of chemical reactions proposed to occur during pyrolysis (thermal decomposition) of poly(ethylene) is shown in Scheme I [1-4].

The first step in this reaction sequence is homolytic cleavage of a C-C bond, which yields a pair of carbon-centered radicals. Loss of H• yields a terminal ethylene group (a). Intermolecular H• transfer yields a terminal methyl group (b). Fragments of poly(ethylene) produced by this reaction mechanism can contain no carbon-carbon double bonds (alkane), one carbon-carbon double bond (an alkene), or two carbon-carbon double bonds (an alkadiene).

Scheme I



Scheme II shows a section of a poly(ethylene) molecule and the C_8 thermal decomposition products from poly(ethylene). The brackets indicate an eight carbon segment of the poly(ethylene). Thermolytic cleavage of the carbon-carbon bonds intersected by the brackets can yield 1,7-octadiene (1), 1-octene (2), or n-octane (3), which are the products identified as C_{10} pyrolysis products in the chromatogram shown in Figure 1. The ratio of the peak areas [alkadiene]:[alkene]:[alkane] in the chromatogram in Figure 1 is approximately 1:2:1, indicating that $\text{H}\cdot$ transfer was not directed and carbon-carbon double bond formation in the thermal decomposition products is random.

Scheme II

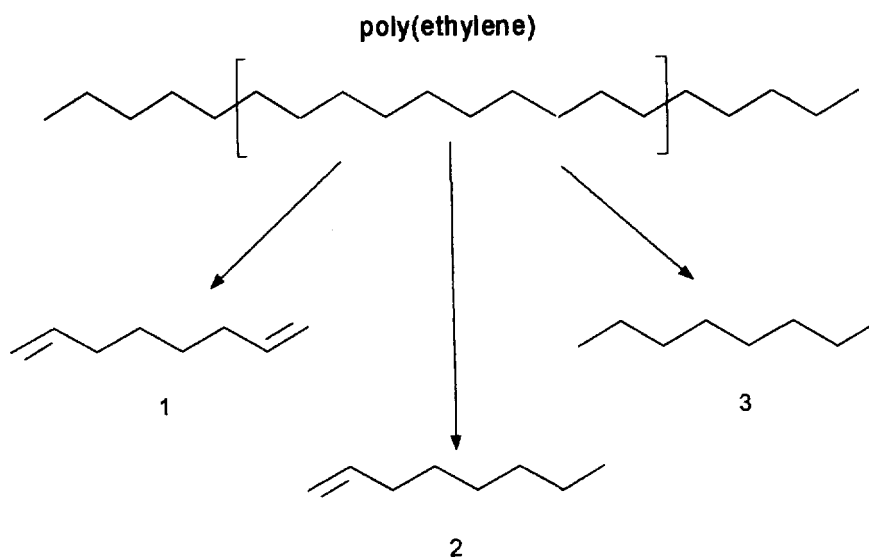


Figure 2 shows chromatograms of pyrolysis products from a sample of poly(propylene) homopolymer.

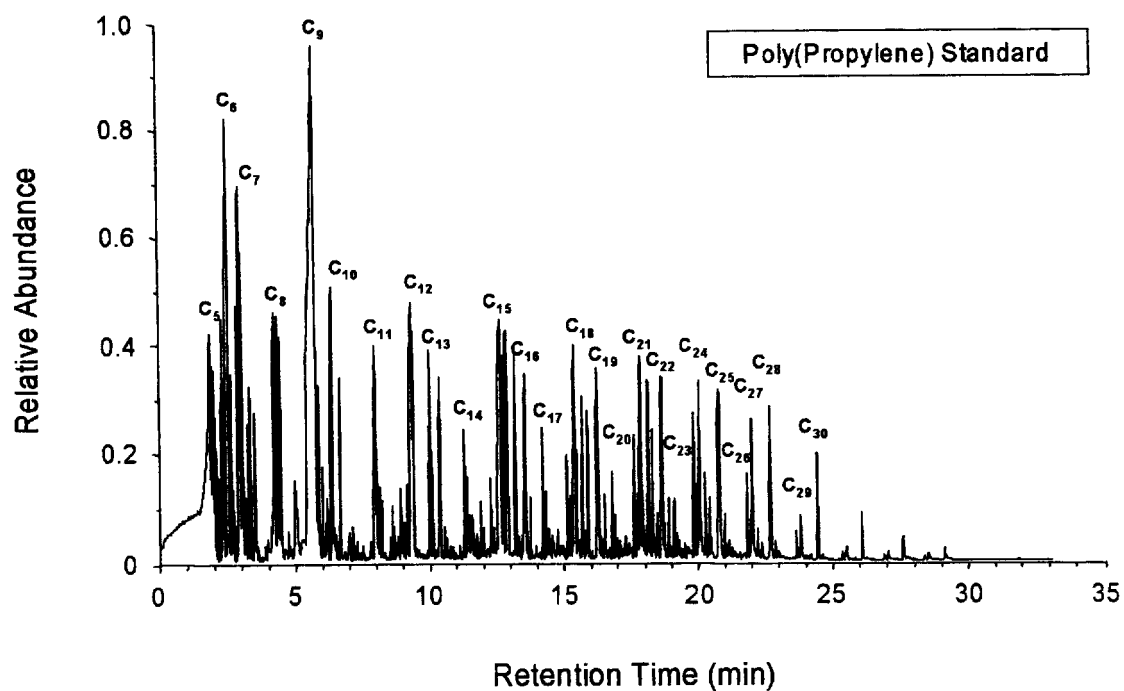
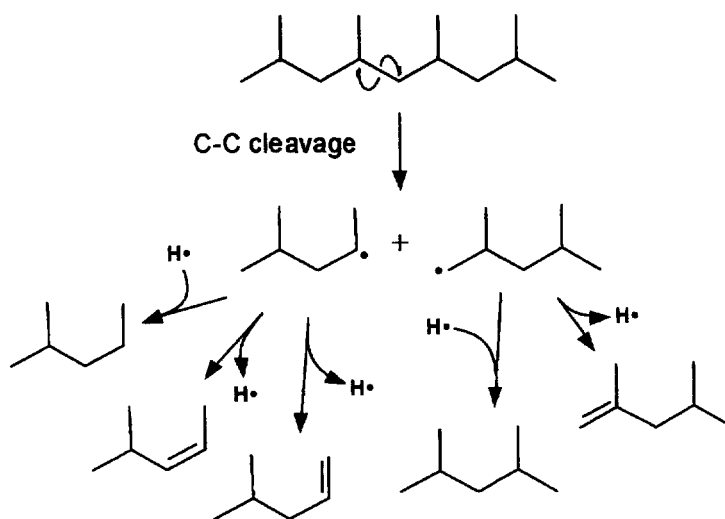


Figure 2. Chromatogram of the thermal decompositions of a sample of poly(propylene) homopolymer.

The peaks were identified from their mass spectra. The labels (C_n) indicate the number of carbon atoms (n) in the products. Each group of labeled peaks consisted of methyl-branched alkanes, alkenes, and alkadienes.

Poly(propylene) is a methyl-branched aliphatic molecule composed of propylene monomer subunits. Pyrolysis of materials containing poly(propylene) yielded a mixture of methyl-branched alkanes, alkenes, and alkadienes. One sequence of chemical reactions proposed to occur during thermal decomposition of poly(propylene) is shown in Scheme III [1-4].

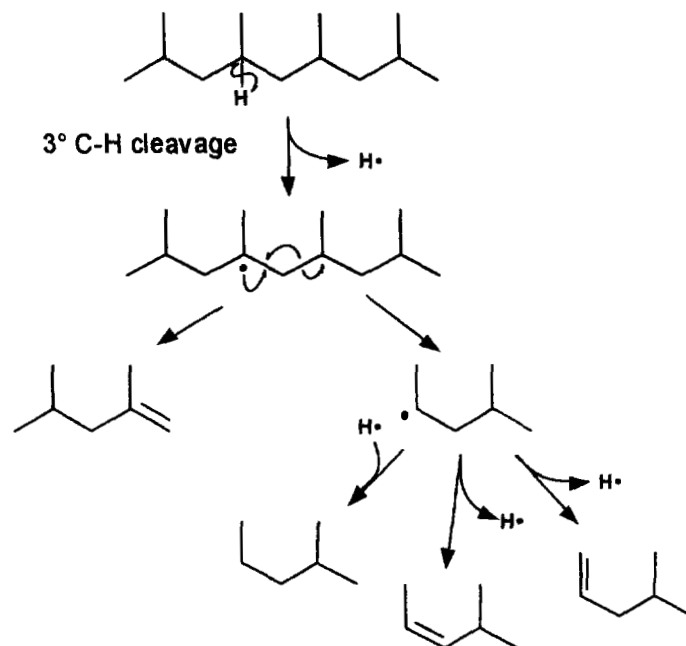
Scheme III



As with thermal decomposition of poly(ethylene), the first step in this reaction sequence is homolytic cleavage of a C-C bond, which yields a pair of carbon-centered radicals. Inter- and intramolecular H^\bullet transfer yields products that contain no carbon-carbon double bonds (alkanes) or products that contain one carbon-carbon double bond (alkenes). The methyl-branched structure of the parent poly(propylene) molecule is retained in its thermal decomposition products.

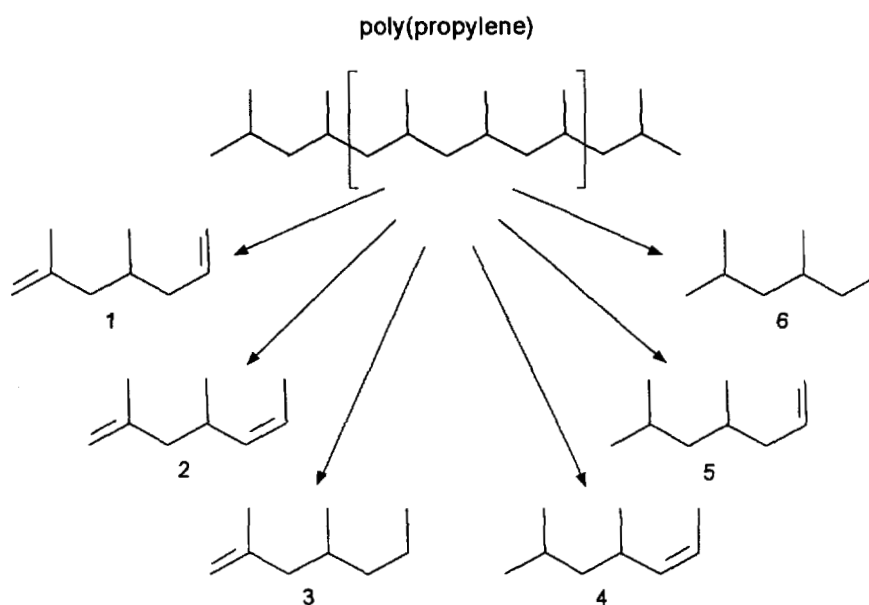
A second reaction pathway has been proposed to occur during thermal decomposition of poly(propylene) [1-4]. This reaction pathway is shown in Scheme IV. The first step in this pathway involves homolytic cleavage of a 3° C-H bond, yielding a radical at the 3° carbon. Scission of an C-C bond adjacent to the radical, followed by intra- and inter-molecular H^\bullet transfer yields a mixture of alkanes and alkenes. These products are identical to the thermal decomposition products in the reactions shown in Scheme III.

Scheme IV



Scheme V show a section of a poly(propylene) molecule and C₉ thermal decomposition products from poly(propylene).

Scheme V



The brackets indicate a segment in the poly(propylene) molecule containing 9 carbons. The products resulting from thermolytic cleavage of the C-C bonds intersected by the brackets during thermal decomposition are 2,4-dimethyl-1,6-heptadiene (1), 2,4-dimethyl-1,5-heptadiene (2), 2,4-

dimethyl-1-heptene (3), 4,6-dimethyl-2-heptene (4), 4,6-dimethyl-1-heptene (5), and 2,4-dimethylheptane (6).

Figure 3 shows chromatograms of pyrolysis products from a sample of an (ethylene/propylene) copolymer.

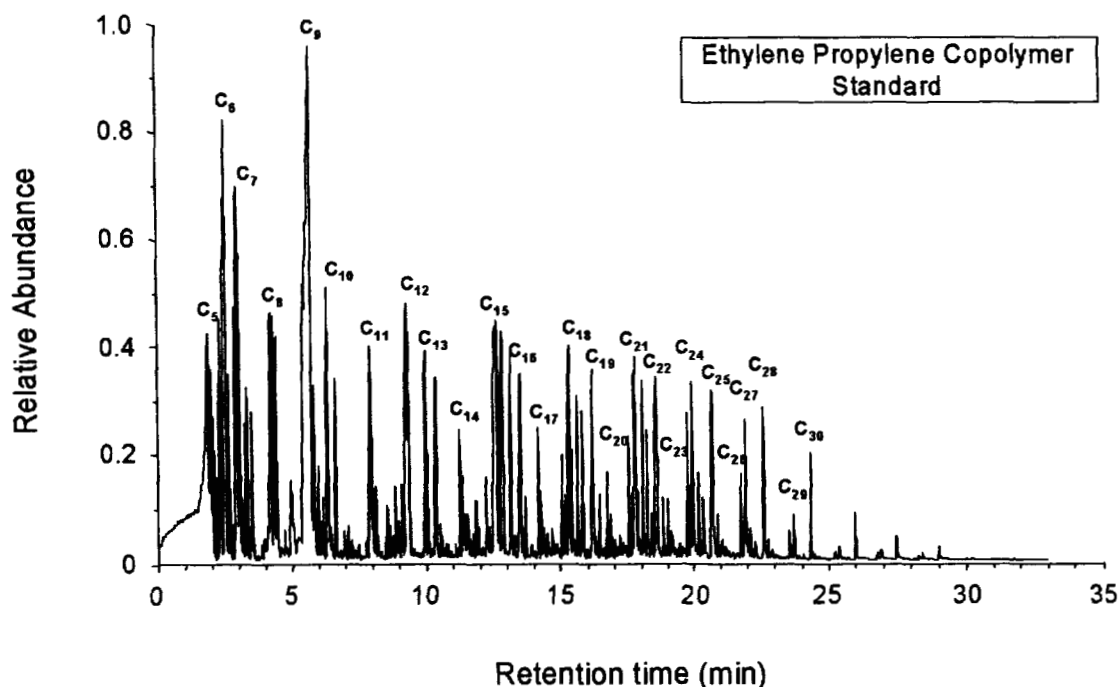


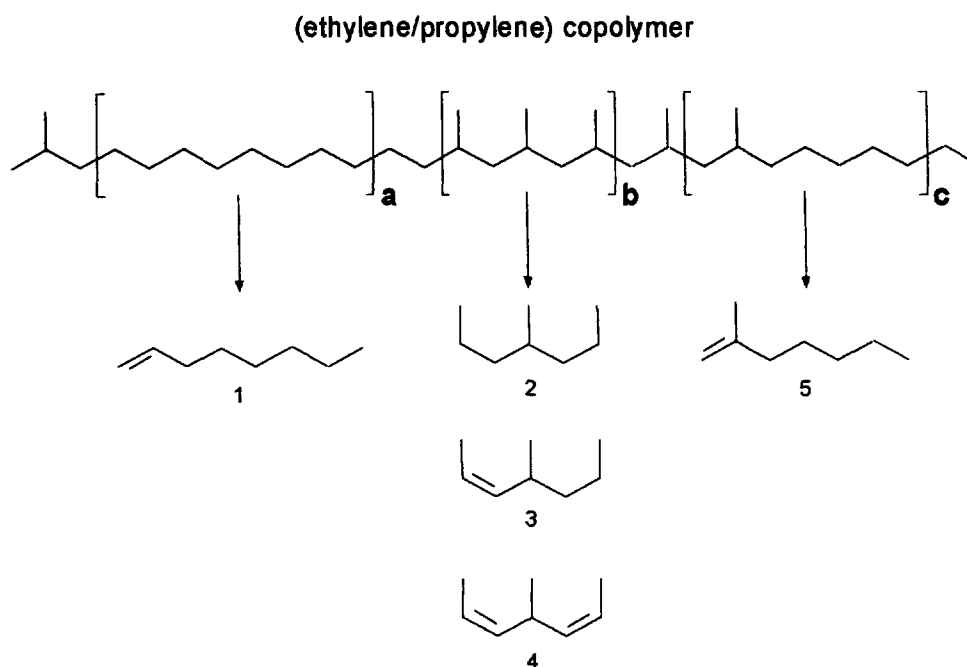
Figure 3. Chromatogram of the thermal decomposition products from a sample of propylene/ethylene copolymer.

The peaks were identified from their mass spectra. The labels (C_n) indicate the number of carbon atoms (n) in the products. Each group of labeled peaks consists of normal and methyl-branched alkanes, alkenes, and alkadienes.

(Ethylene/propylene) copolymer is a methyl-branched aliphatic molecule composed of ethylene and propylene monomer sub-units distributed randomly in the polymer. Pyrolysis of materials containing (ethylene/propylene) copolymer yielded a mixture of normal and methyl-branched alkanes, alkenes, and alkadienes. The chemical mechanism(s) of thermal decomposition of (ethylene/propylene) copolymer are similar to the chemical reactions involved in thermal decomposition of poly(ethylene) (Scheme I) and poly(propylene) (Schemes III and IV). Thermolysis results in cleavage of the C-C bonds in the polymer backbone, yielding both saturated and unsaturated aliphatic compounds. Scheme VI shows a section of an (ethylene/propylene) copolymer molecule and the C₈ thermal decomposition products from

(ethylene/propylene) copolymer. The brackets labeled **a** indicate a C_8 segment containing only ethylene monomer. The brackets labeled **b** indicate a C_8 containing only propylene monomer. The brackets labeled **c** indicate a C_8 segment containing ethylene and propylene monomer.

Scheme VI



Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **a** yields 1-octene (1). Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **b** yields 4-methylheptane (2), 4-methyl-2-heptene (3), or 4-methyl-2,5-heptadiene (4). Thermolytic cleavage of the C-C bonds intersected by the brackets designating segment **c** yields 2-methyl-1-heptene (5). Note that small amounts of other products may be formed by thermal decomposition of propylene/ethylene copolymer. For example, 4-methyl-1-heptene, 4-methyl-2,6-heptadiene, and 4-methyl-1,6-heptadiene can be produced from segment **b**. Formation of these products requires cleavage of the C-C bonds intersected by the brackets, followed by carbon-carbon double bond formation involving a branching methyl group, which is less probable than double bond formation involving carbons on the polymer backbone as shown in scheme VI. 4-Methyl-1-heptene would have coeluted with 4-methyl-2-heptene, and 4-methyl-2,6-heptadiene, and 4-methyl-1,6-heptadiene would have coeluted with 4-methyl-2,5-heptadiene in the chromatographic analysis used here.