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**DREA TECHNICAL MEMORANDUM 95/216**

June 1995

**PYROLYSIS GAS CHROMATOGRAPHY/MASS  
SPECTROMETRY IDENTIFICATION OF  
ELASTOMERIC MATERIALS**

John A. Hiltz — John J. Power

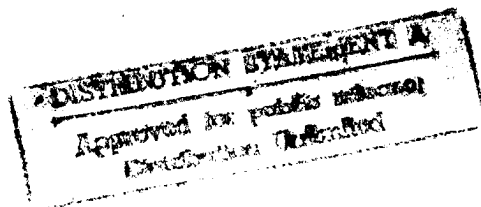
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John A. Hiltz — John J. Power

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Approved by H.M. Merklinger  
Research Manager / Naval Platforms

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Research Manager / Naval Platforms

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## Abstract

Elastomers and thermoset polymers can be difficult to identify as a result of their cross-linked structure. Techniques such as transmission infrared spectroscopy have limited application to these materials because of difficulty in preparing thin films. Surface infrared techniques including multiple internal reflectance and total attenuated reflectance are more useful but their application can be hampered by the presence of additives such as carbon and plasticizers. Pyrolysis coupled with gas chromatographic separation and mass spectrometric identification of degradation products provides a rapid reproducible method of degrading cross-linked materials and identifying their degradation products. As the degradation products are related to the structure of the polymer, these can be used to identify the polymer. In this paper, the pyrolysis products of samples natural rubber, butyl rubber, polychloroprene rubber, and three samples of polyacrylonitrile-butadiene rubber are studied to identify degradation products that are characteristic of each type of elastomer. Knowledge of characteristic degradation products allows the rapid, unambiguous identification of elastomer types. This information is critical in the selection of elastomers for use in a particular application or in determining why an elastomer failed in a particular environment.

## Résumé

Il peut être difficile de caractériser les élastomères et les polymères thermodurcissables, en raison de leur structure réticulée. L'application de techniques comme la spectroscopie de transmission infrarouge est limitée, car il est difficile de préparer des pellicules minces. Les techniques infrarouges applicables à des surfaces, dont la réflectance interne multiple et la réflectance atténuée totale, sont plus utiles, mais la présence d'additifs comme du carbone et des plastifiants peut diminuer leur efficacité. La pyrolyse couplée à la séparation par chromatographie en phase gazeuse et à la caractérisation par spectrométrie de masse des produits de dégradation constitue une méthode rapide et reproductible pour décomposer les matières réticulées et pour caractériser leurs produits de dégradation. Comme les produits de dégradation dépendent de la structure polymérique, ils peuvent servir à caractériser le polymère. Dans cette communication, on étudie les produits de pyrolyse d'échantillons de caoutchouc naturel, de butyle et de polychloroprene et de trois échantillons de polyacrylonitrile-butadiène, afin de caractériser les produits de dégradation caractéristiques de chaque type d'élastomère. On peut caractériser rapidement et sans ambiguïté les types d'élastomères si l'on connaît les produits de dégradation caractéristiques. Cette information est très importante lorsqu'il s'agit de choisir quels élastomères à utiliser dans une application particulière ou de déterminer pourquoi un élastomère a cédé dans un milieu particulier.

## EXECUTIVE SUMMARY

DREA Technical Memorandum "PYROLYSIS GAS CHROMATOGRAPHY/MASS SPECTROMETRY IDENTIFICATION OF ELASTOMERIC MATERIALS", John A. Hiltz and John J. Power.

Elastomeric materials are used in a number of applications on board CF ships. These include materials for o-rings, gaskets, and engine mounts. Although these materials can be inexpensive, their failure in service can result in downtime and costly maintenance. When they are used in fuel or high pressure liquid oxygen systems, failure can result in fire, explosion and loss of life. The type of elastomer selected for a particular application depends on the in-service environment. For instance, some elastomers have superior fuel and oil resistance while others have superior resistance to ester-based synthetic lubricants.

There is a vast amount of information on the types of elastomers recommended for particular applications/service environments. However, often persons installing elastomeric materials on board ship are not certain if the material they have received from the stores system is the specified material. To make certain they have the specified material, analytical methods that can be used to positively identify various elastomers are required. These methods can also be used in failure investigations to identify the material and ascertain whether or not the failure was material related.

Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) is well suited to the identification of cross-linked materials such as elastomers. The method uses rapid, reproducible heating to thermally degrade materials and produce molecular fragments that can be separated and identified. The nature of the fragments is related to the structure of the polymer and can therefore be used to positively identify it. This paper describes a study of the pyrolytic degradation of four common elastomers. Degradation products are identified that are characteristic of each of the elastomers and can therefore be used to identify these materials. This technique is also very useful in identifying additives, such as plasticizers and extenders, in the elastomers. This not only gives a more thorough knowledge of the formulated elastomer but may allow differentiation of samples of the same type, but from different suppliers.

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## 1.0 INTRODUCTION

Elastomeric materials are used in a wide range of applications including gaskets, o-rings, seals, and as sound and vibration damping materials. The mechanical properties of an elastomer depend on a number of factors including the nature of the polymer(s), the degree of cross-linking, and the type of fillers and additives used in the preparation of the elastomer. Mechanical properties can also be influenced by the interaction of the elastomer with the environment. This interaction is particularly important when it has an adverse effect on the properties and therefore the performance of the elastomer. Degradation of the properties of the elastomer can lead to failure of the elastomer to perform as designed, result in increased maintenance costs and downtime, and lead to fire and explosion hazards in systems where flammable fluids are used.

The susceptibility of elastomers to chemical attack requires a knowledge of the chemical environment in which the elastomer is to be used and the resistance of the elastomer to that particular environment. Experience and experimentation have resulted in a large body of knowledge concerning elastomer type and chemical resistance. For instance, poly(acrylonitrile-butadiene) - based elastomers are known to have better resistance to fuels than poly(chloroprene) - based elastomers. However, in practise, elastomeric materials used to fabricate gaskets and o-rings are often supplied to the user without identification or are labelled as conforming to a particular specification that does not indicate their type.

To ensure that materials with the properties and chemical resistance for a particular application are used, analytical techniques that allow the rapid, accurate identification of these materials are required. For intractable polymers, such as cross-linked elastomers and thermoset plastics, analysis by techniques such as transmission infrared (IR) spectroscopy is hampered by difficulty in preparing thin films. Although non-transmission IR techniques, such as total attenuated reflectance and multiple internal reflectance, have been applied successfully to analysis of these intractable materials, carbon black used in a large number of elastomer formulations reduces IR response and therefore the ability of these techniques to identify elastomers.

Pyrolysis gas chromatography (py-GC) and pyrolysis gas chromatography/mass spectrometry (py-GC/MS) analysis have been successfully employed in the study of a wide range of polymeric materials<sup>1-20</sup>. Pyrolysis provides a reproducible means of thermally

degrading polymeric materials, while capillary gas chromatography coupled with mass spectrometric detection can separate and identify the complex mixture of degradation products. As the degradation products of a polymer are related to its structure, knowledge of these products and the degradation mechanisms of polymeric materials can be used to identify polymeric materials. Further, degradation products that are unique to a particular polymeric material can be used to positively identify the polymer and/or differentiate it from other polymers.

The presence of additives such as plasticizers and extenders complicate the analysis of a polymer using py-GC/MS<sup>21</sup>. However, if these can be identified in the pyrolysis products, they give additional information about the formulation of the polymer. Knowledge of the nature of plasticizers and extenders is also important if the polymer is to be exposed to a particular chemical environment. For instance, additives may be leached from the elastomer when it is exposed to certain chemicals and this may lead to a change in the properties of the polymer<sup>22</sup>.

This paper describes a study of the pyrolytic degradation of four types of elastomers. The aim of the study is to identify degradation products of each elastomer that are characteristic of that particular elastomer type and correlate their formation to the structure of the elastomer. The characteristic degradation products can then be used to positively identify elastomer types. This method can also be used to identify additives and their degradation products which provides further information on the elastomer formulation.

## **2.0 EXPERIMENTAL PROCEDURE**

### **2.1 Materials**

The six elastomers used in this study, namely poly(butadiene-acrylonitrile) or Buna N rubber, black poly(acrylonitrile-diene) or nitrile rubber, white nitrile rubber, poly(2-methylpropene-diene) or butyl rubber, poly(chloroprene) rubber, and poly(cis-isoprene) or natural rubber, were obtained commercially.

## 2.2 Instrumentation

A CDS model 177 pyroprobe (Chemical Data Systems, Oxford, PA.) was used for all pyrolyses. Pyrolyses were carried out in a platinum coil pyroprobe (25 mm quartz tube) at 700°C using a heating ramp of approximately 600°C/s and a hold time of 10 seconds. Typically 0.5 mg of sample was pyrolysed. The pyrolysis products were separated on a 30 m long X 0.25 mm inside diameter 100% methyl silicone (5 µm thick stationary phase) capillary column. The linear flow rate of the carrier gas (He) was 0.3 m/s at 40°C. The temperature program used to control the heating of the GC oven consisted of holding the temperature at 40°C for 4 minutes, then ramping the temperature to 300°C at a rate of 10°C/min, and finally holding the temperature at 300°C for 10 minutes. Each GC run took 40 minutes to complete.

A quadrupole MS was used to detect and identify the pyrolysis products. The MS was used in the full scan mode, scanning from 30 atomic mass units (amu) to 300 amu during each 2.0 second scan. The MS data system was equipped with the NIST Library of approximately 38,000 mass spectra.

## 3.0 RESULTS AND DISCUSSION

In the following sections the pyrograms of the elastomers, that is, the chromatograms resulting from the pyrolytic degradation products of the elastomers, are presented and discussed. Emphasis is placed on the identification of degradation products that are characteristic of the elastomers. It should be noted that the pyrolytic degradation products resulting from a particular type of elastomer are also dependent on the additives used in the elastomer formulation. If extenders and processing aids are used in the preparation of the elastomers, then these additives or their degradation products will be present in the pyrograms. Although these pyrolysis products can complicate the pyrogram, they can also be used to derive a more thorough understanding of the formulated elastomer and therefore how it might perform in service.

### 3.1 Natural Rubber

Natural rubber is a naturally occurring polymer comprised of cis-isoprene (cis-2-methyl-1,3-butadiene) units that has been compounded and cross-linked. It differs from synthetic poly(cis-isoprene) in that it contains other natural products as impurities.

The reconstructed ion chromatogram (RIC) of a sample of natural rubber following pyrolysis at 700°C is shown in Figure 1. Mass spectral analysis indicated that the major peak in the pyrogram of natural rubber was 1-methyl-4-(1-methylethenyl)cyclohexene ( $C_{10}H_{16}$ ) (scan 294). 1-methyl-4-(1-methylethenyl)cyclohexene is the dimer of the monomeric unit of natural rubber (2-methyl-1,3-butadiene or *cis*-isoprene,  $C_5H_8$ ). A small amount of monomer, 2-methyl-1,3-butadiene (scan 48), was also released from the pyrolytic degradation of natural rubber. Compounds with molecular weights corresponding to the trimer ( $C_{15}H_{24}$ ), tetramer ( $C_{20}H_{32}$ ), pentamer ( $C_{25}H_{40}$ ) and hexamer ( $C_{30}H_{48}$ ) of 2-methyl-1,3-butadiene were found in the groupings of peaks centered at scan 500, scan 675, scan 780, and scan 880 respectively. Other degradation products included structural isomers of the dimer, trimer, tetramer, pentamer and hexamer, that is, compounds containing 10, 15, 20, 25 and 30 carbon atoms, and aromatics, such as 1-methyl-4-(1-methylethenyl)benzene (scan 330), that are formed by dehydrogenation of the the major degradation products.

The thermal degradation pathways leading to the formation of the monomer, dimer, trimer and tetramer of 2-methyl-1,3-butadiene are shown in Scheme 1. The presence of the dimer and the the groupings of peaks corresponding to compounds containing 15, 20, and 25 carbons are characteristic of the thermal degradation of natural rubber. The presence of these degradation products in a pyrogram can be used to positively identify natural rubber.

### 3.2 Butyl Rubber

Butyl rubber is prepared from 2-methylpropene and a diene, such as 2-methyl-1,3-butadiene. The diene is generally present in much lower concentration (1.5% - 4.5%) than 2-methylpropene and is added to introduce unsaturation into the polymer chain and enable subsequent cross-linking. As a result of the high percentage of 2-methylpropene in butyl rubber, the major degradation products are related to the poly(2-methylpropene) portion of the elastomer.

The RIC of a sample of butyl rubber pyrolysed at 700°C is shown in Figure 2. Mass spectral analysis of the most intense peak (scan 48) indicated that it was 2-methylpropene, the monomeric unit of poly(2-methylpropene). The mass spectra of the other major peaks at scans 321, 478, 607, 716, and 813 indicated that these peaks were due to compounds with molecular formulas  $C_{12}H_{24}$ ,  $C_{16}H_{32}$ ,  $C_{20}H_{40}$ ,  $C_{24}H_{48}$ , and

$C_{28}H_{56}$ . These correspond to the trimer, tetramer, pentamer, hexamer and heptamer of 2-methylpropene. The dimer ( $C_8H_{16}$ ) is also present in the pyrolysis degradation products at scan 104.

The formation of several of the pyrolytic degradation products of butyl rubber are shown in Scheme 2. The first step in the degradation of butyl rubber involves the homolytic cleavage of the bonds in the polymer backbone. The next step leads to the release of fragments of the general formula  $C_nH_{2n}$ , where  $n = 1, 2, 3$  etc.

Two degradation products with molecular formula  $C_8H_{16}$ , 2,4,4-trimethyl-1-pentene (scan 104) and 2,4,4-trimethyl-2-pentene (scan 114), were formed during the pyrolysis of the butyl rubber sample. The compounds were differentiated on the basis of their mass spectra. That is, differences in the ions in the mass spectra of the two structural isomers could be related to differences in the structures of the two compounds. The major ion in the mass spectra of 2,4,4-trimethyl-1-pentene was at mass to charge ratio ( $m/e$ ) 57, while the major ion for 2,4,4-trimethyl-2-pentene was at  $m/e$  97. The higher relative amount of the ion at  $m/e$  97 for 2,4,4-trimethyl-2-pentene results from resonance stabilization of the ion, while the structure of 2,4,4-trimethyl-1-pentene favors the formation of the ion at  $m/e$  57. Formation of the ions at  $m/e$  97 and  $m/e$  57 by trimethyl-2-pentene and trimethyl-1-pentene respectively are shown in Scheme 3.

A similar analysis of the mass spectra of the compounds at scan 321 and scan 333 indicated that they were 2,4,4,6,6-pentamethyl-2-heptene and 2,4,4,6,6-pentamethyl-1-heptene respectively. As was found for the trimethyl substituted pentenes, these two degradation products could be differentiated on the basis of their mass spectra. The major ion in the mass spectrum of pentamethyl-2-heptene was at  $m/e$  97, while the major ion in the mass spectrum of pentamethyl-1-pentene was at  $m/e$  57. Further, the mass spectrum of pentamethyl-2-heptene had an ion at  $m/e$  112 while the mass spectrum of pentamethyl-1-pentene had an ion at  $m/e$  113. Formation of the major ions by the structural isomers is shown in Scheme 3.

2-Methylpropene and the compounds corresponding to the dimer, trimer, tetramer and pentamer of 2-methylpropene are characteristic of the thermal degradation of butyl rubber. The presence of these degradation products in a pyrogram can be used to positively identify butyl rubber.

### 3.3 Poly(chloroprene) Rubber

Poly(chloroprene) rubber is prepared by the polymerization of 2-chloro-1,3-butadiene (chloroprene). The RIC of a sample of polychloroprene rubber pyrolysed at 700°C is shown in Figure 3. The pyrolytic degradation of polychloroprene rubber results in the formation of a large number of degradation products. However, 1-chloro-4-(1-chloroethenyl)cyclohexene (scan 412), is a major degradation product that is characteristic of polychloroprene rubber. 1-chloro-4-(1-chloroethenyl)cyclohexene can be formed by two mechanisms; the cycloaddition of two 2-chloro-1,3-butadiene molecules, or directly from the radical formed by the thermal cleavage of the polychloroprene backbone. The two mechanisms are shown in Scheme 4.

The dehydrohalogenation of polychloroprene rubber and subsequent secondary reactions lead to the formation of a number of aromatic compounds such as ethyl benzene (scan 199) and styrene (scan 219). Some of the compounds located in the pyrogram between scans 600 and 900 are due to additives in the polychloroprene rubber. For instance, hexadecanoic acid (scan 678) and octadecanoic acid (scan 736) are both additives used in the preparation of rubber and are released during the heating of the sample.

Some 1-methyl-4-(1-methylethenyl)cyclohexene, which is characteristic of the thermal degradation of natural rubber, was also found in the degradation products of this sample of chloroprene rubber. This may indicate that some isoprene (2-methyl-1,3-butadiene) was used in the preparation of the rubber or that some natural rubber was blended with the polychloroprene rubber in this particular formulation. Alternatively, 1-methyl-4-(1-methylethenyl)cyclohexene might result from the dehydrochlorination of the polychloroprene rubber backbone and subsequent thermal rearrangement.

### 3.4 Nitrile Rubbers

Poly(acrylonitrile-butadiene) rubber, or Buna N rubber, is the best known of the nitrile rubbers. The excellent resistance of this class of elastomer to fuels and oils is related to the acrylonitrile portion of the elastomer. The acrylonitrile content of these rubbers can vary significantly, and therefore so do properties such as fuel and oil resistance. In the following section the results of the pyrolytic degradation of three nitrile rubbers, one white in color, one black in color, and a sample of Buna N rubber, will be discussed.

The RICs of samples of white nitrile rubber, black nitrile rubber, and Buna N are shown in Figures 4 through 6 respectively. Unlike natural rubber and poly(chloroprene) rubber, the nitrile rubbers do not produce a characteristic dimer following pyrolytic degradation. However, there are degradation products that are characteristic of the acrylonitrile and diene portions of this rubber. All three rubbers release degradation products at approximately scan 690 and scan 755. That is, at scan 693 and scan 756 for the white nitrile rubber, at scan 689 and scan 755 for the black nitrile rubber, and at scan 691 and scan 755 for the buna N rubber. Analysis of the mass spectra of the compounds giving rise to these peaks indicates that they are both alkyl nitriles.

Other degradation products of these rubbers are 1,3-butadiene (scan 54 in Figure 4, scan 52 in Figure 5 and scan 58 in Figure 6), which is the monomeric unit of the butadiene portion of the rubber and compounds containing eight carbon atoms, such as ethenylcyclohexene (scan 210 in Figure 6) which is the dimer of 1,3-butadiene, ethylbenzene, and 1,3,5,7-cyclooctatetrene (scan 250 in Figure 4, scan 240 in Figure 5 and scan 247 in Figure 6) which arise from the dimeric unit of 1,3-butadiene, and compounds containing twelve carbon atoms such as  $C_{12}H_{24}$  (scan 328 in Figure 4, and scan 327 in Figures 5 and 6) which arise from the trimeric unit of the butadiene.

The Buna N rubber released several compounds that can be attributed to the acrylonitrile portion of the elastomer. These include the compounds at scan 373 ( $C_8H_9N$ ), scan 427 (benzothiazole), and scan 462 ( $C_9H_{11}N$ ). Similarly, the white nitrile rubber released compounds at scan 410 ( $C_9H_{11}N$ ) and scan 429 (benzothiazole) and the black nitrile rubber released compounds at scan 280 ( $C_6H_7N$ ), scan 405 ( $C_9H_{11}N$ ), and at scan 424 (benzothiazole).

The pyrograms also showed differences in additives used in the preparation of the white nitrile, black nitrile, and Buna N rubbers. Dioctylphthalate (scan 878), hexadecanoic acid (scan 715) and octadecanoic acid (scan 775) were found in the pyrolysis products of the white nitrile rubber sample, while dioctylphthalate (scan 901) and hexadecanoic acid (scan 714) were released by the black nitrile rubber, and dioctyladipate (scan 846) and dioctylsebacate (scan 1082) were released by the Buna N rubber. Dioctylphthalate, dioctylsebacate, and dioctyladipate are plasticizers while octadecanoic acid (stearic acid) and hexadecanoic acid (palmitic acid) are used as dispersants and softeners.

The black nitrile rubber also released some 1-chloro-4-chloroethenylcyclohexene (scan 434) which is the dimer of 1-chloro-1,3-butadiene and some 1-methyl-2-methylethenylcyclohexene which is the major degradation product of natural rubber and poly(isoprene) rubber. As was noted in Section 3.3, 1-chloro-4-chloroethenylcyclohexene is a characteristic of the degradation of poly(chloroprene) rubber. This might indicate that 2-chloro-1,3-butadiene might have been used in the formulation of the rubber or that polychloroprene has been blended in the nitrile formulation. The 1-methyl-2-methylethenylcyclohexene (scan 327) indicates that some 2-methyl-1,3-butadiene might have been used in the preparation of the rubber or that some natural or polyisoprene rubber has blended into the nitrile rubber formulation.

The nitrile rubbers that release the dimers of 2-chloro-1,3-butadiene or the dimer of 2-methyl-1,3-butadiene can be differentiated from polychloroprene or natural rubber by the presence of alkyl nitriles in their degradation products. Also the acrylonitrile-butadiene rubbers release degradation products containing nitrogen that are not released during the pyrolysis of polychloroprene or natural rubber.

#### **4.0 SUMMARY AND CONCLUSIONS**

Py-GC/MS is an analytical technique that can be used identify elastomeric materials. In some instances the elastomer type can be identified on the basis of a characteristic degradation product. For instance, the release of the dimer of 2-methyl-1,3-butadiene, in conjunction with groupings of compounds containing 15, 20, and 25 carbons atoms, is characteristic of the thermal degradation of natural rubber. Similarly, the release of 2-methylpropene, in conjunction with compounds corresponding to the dimer, trimer, tetramer, etc. of 2-methylpropene, is characteristic of the degradation of butyl rubber, while the dimer of 2-chloro-1,3-butadiene is characteristic of the pyrolytic degradation of polychloroprene rubber.

In contrast to natural rubber and polychloroprene rubber, the nitrile rubbers cannot be characterized by the release of a single degradation product. However, there are degradation products from these rubbers that are characteristic of the acrylonitrile and butadiene portions of the rubber and together can be used to identify this elastomer. Alkyl nitrile degradation products in the vicinity of scans 690 and 750 and aromatic heterocycles containing nitrogen were observed for all three nitrile rubbers and are released by the

acrylonitrile portion of the nitrile rubbers. Similarly, 1,3-butadiene and compounds containing 8 and 12 carbon atoms, such as methylenecyclohexene, are characteristic degradation products of the butadiene portion of these rubbers.

Py-GC/MS analysis of rubbers also provides information concerning additives, such as plasticizers and extenders, that are present in a formulated elastomer. This information can be used to differentiate between rubbers of the same type that were compounded differently, or to study the effect of exposure of the elastomers to certain chemical environments. For instance, the loss of an additive from an elastomer as the result of the leaching of the additive from the polymer can be monitored using this technique.

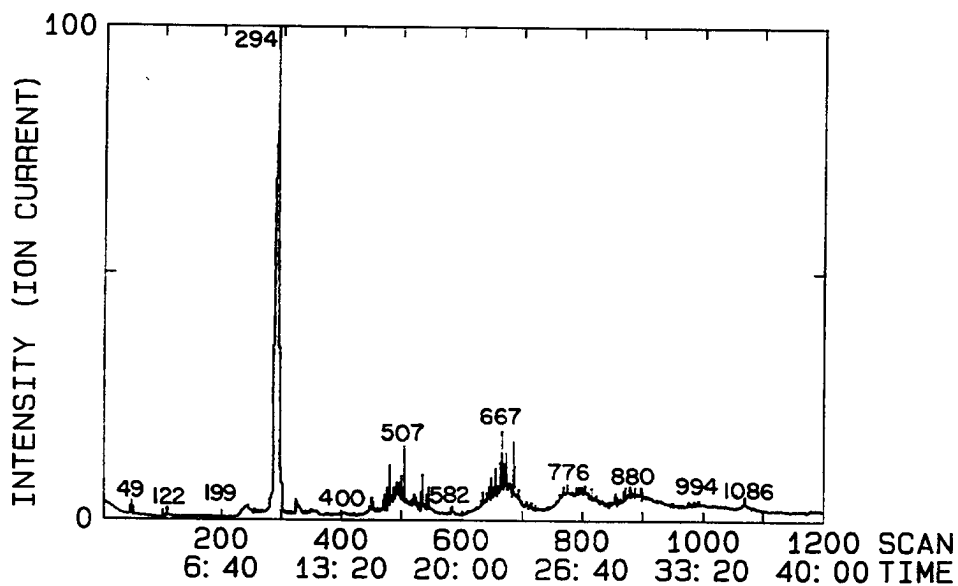


Figure 1 - Reconstructed ion chromatogram (RIC) of a sample of natural rubber following pyrolysis at 700°C.

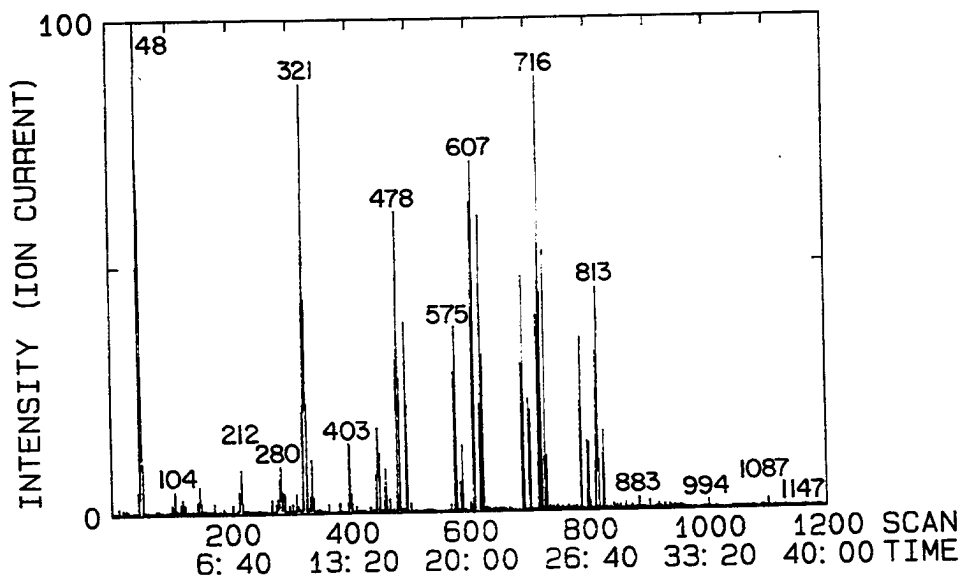


Figure 2 - RIC of a sample of butyl rubber following pyrolysis at 700°C.

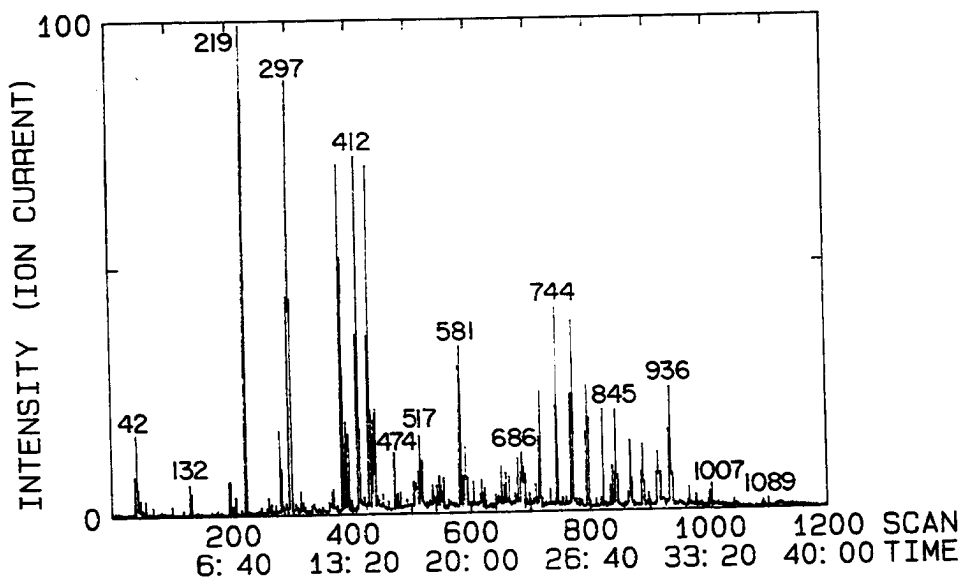


Figure 3 - RIC of a sample of poly(chloroprene) rubber following pyrolysis at 700°C.

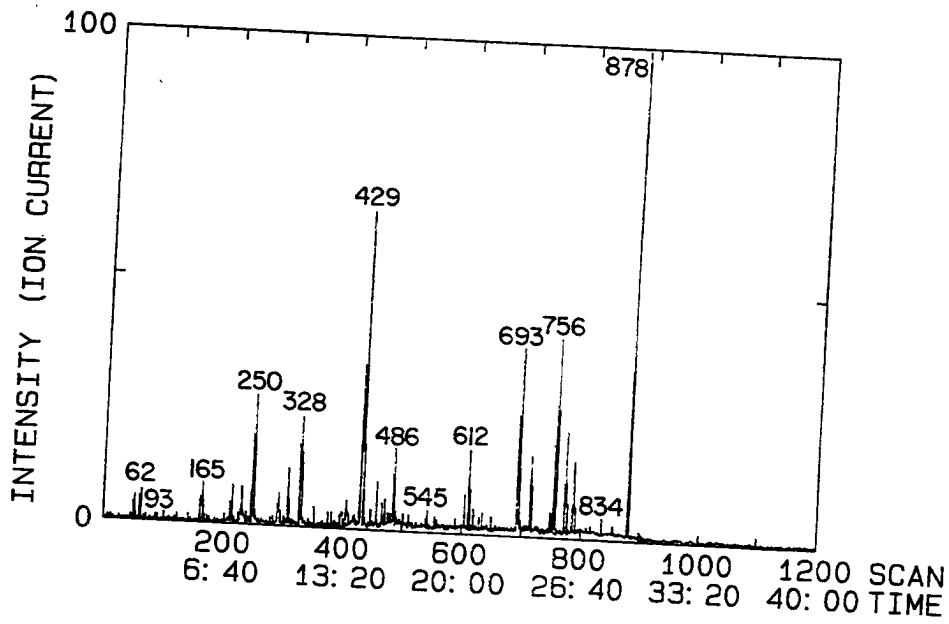


Figure 4 - RIC of a sample of white nitrile rubber following pyrolysis at 700°C.

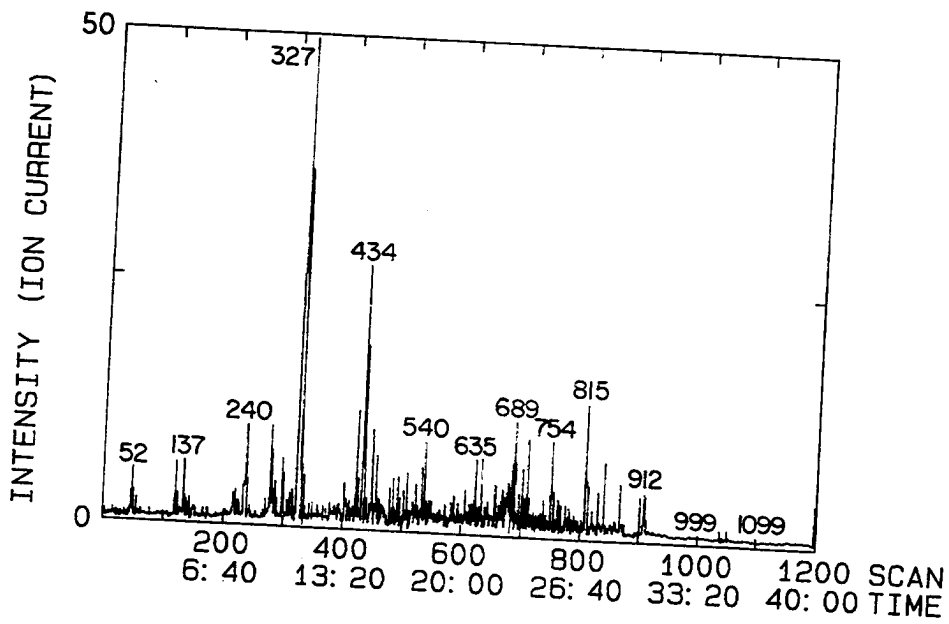


Figure 5 - RIC of a sample of black nitrile rubber following pyrolysis at 700°C.

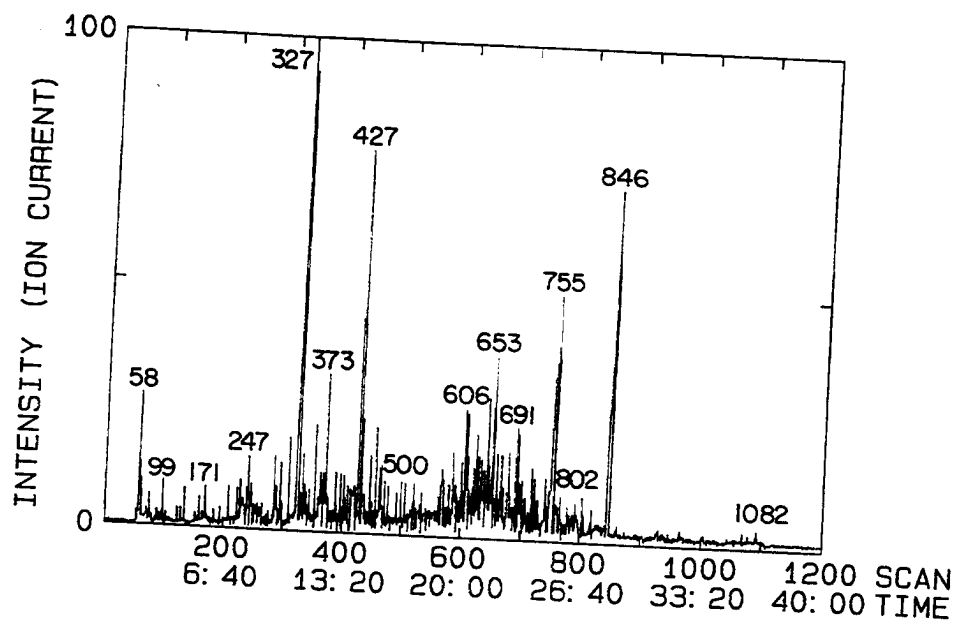
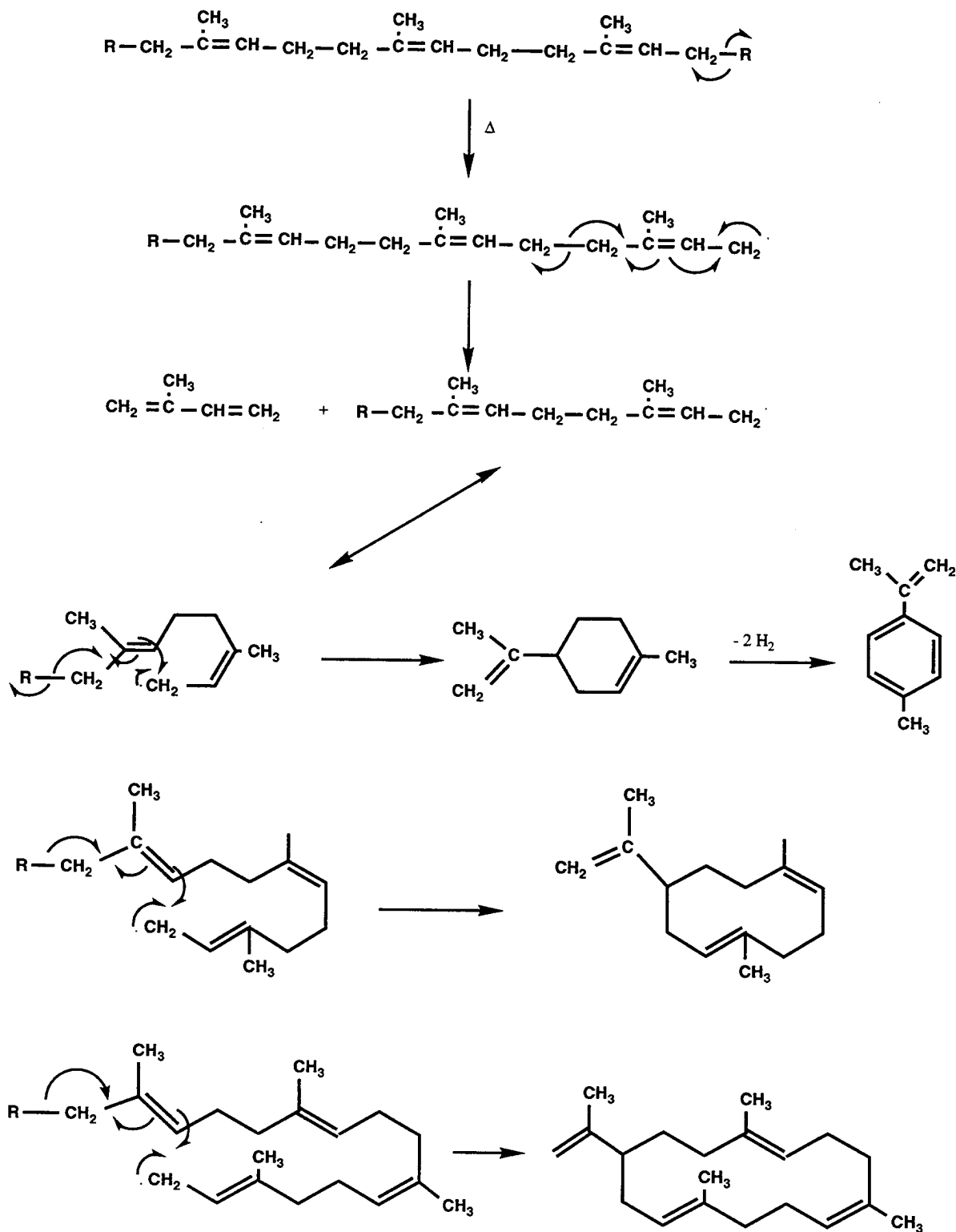
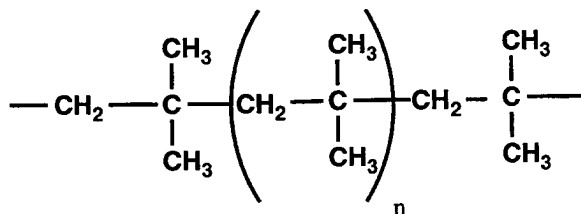


Figure 6- RIC of a sample of Buna N rubber following pyrolysis at 700°C.

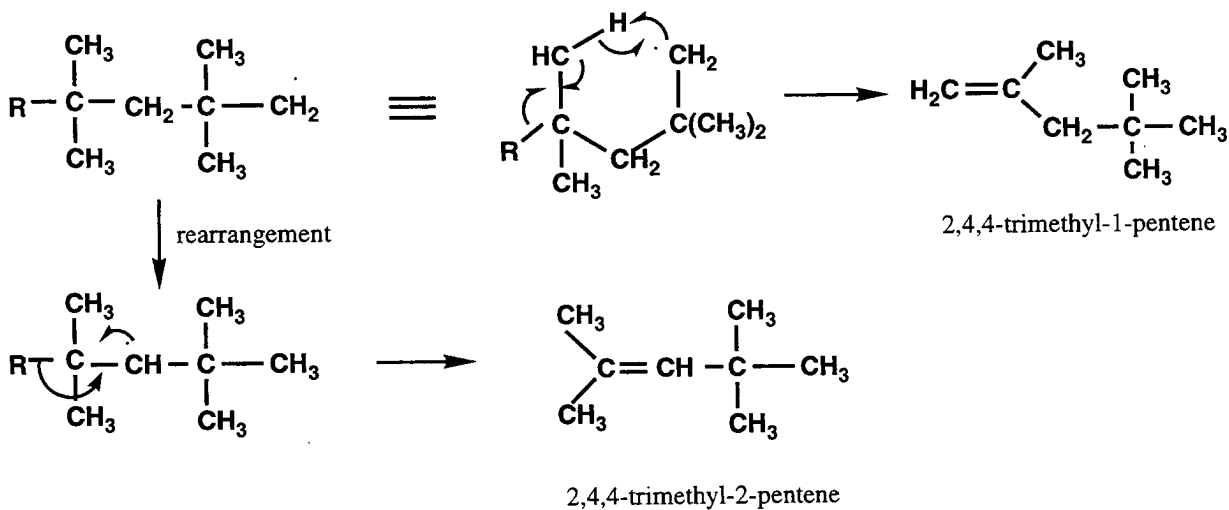
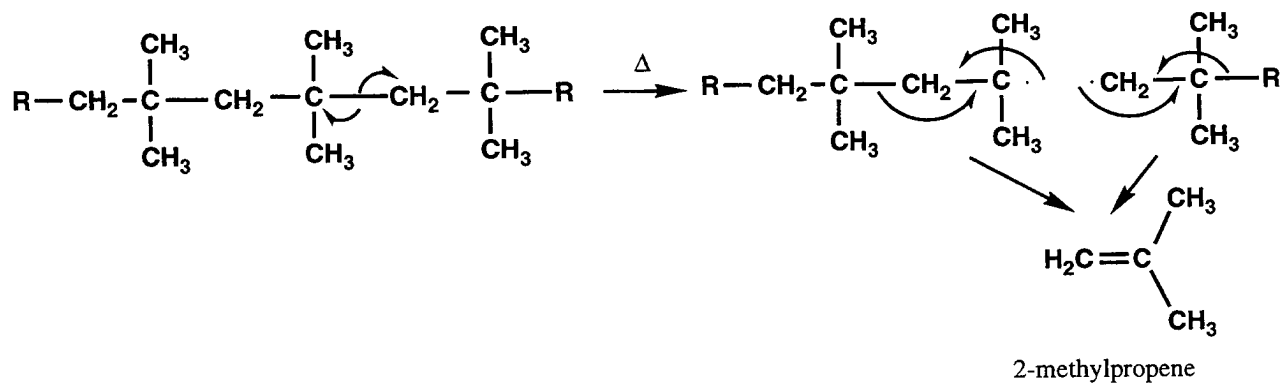
Scheme 1 - Pathways leading to the formation of several of the major thermal degradation products of natural rubber.



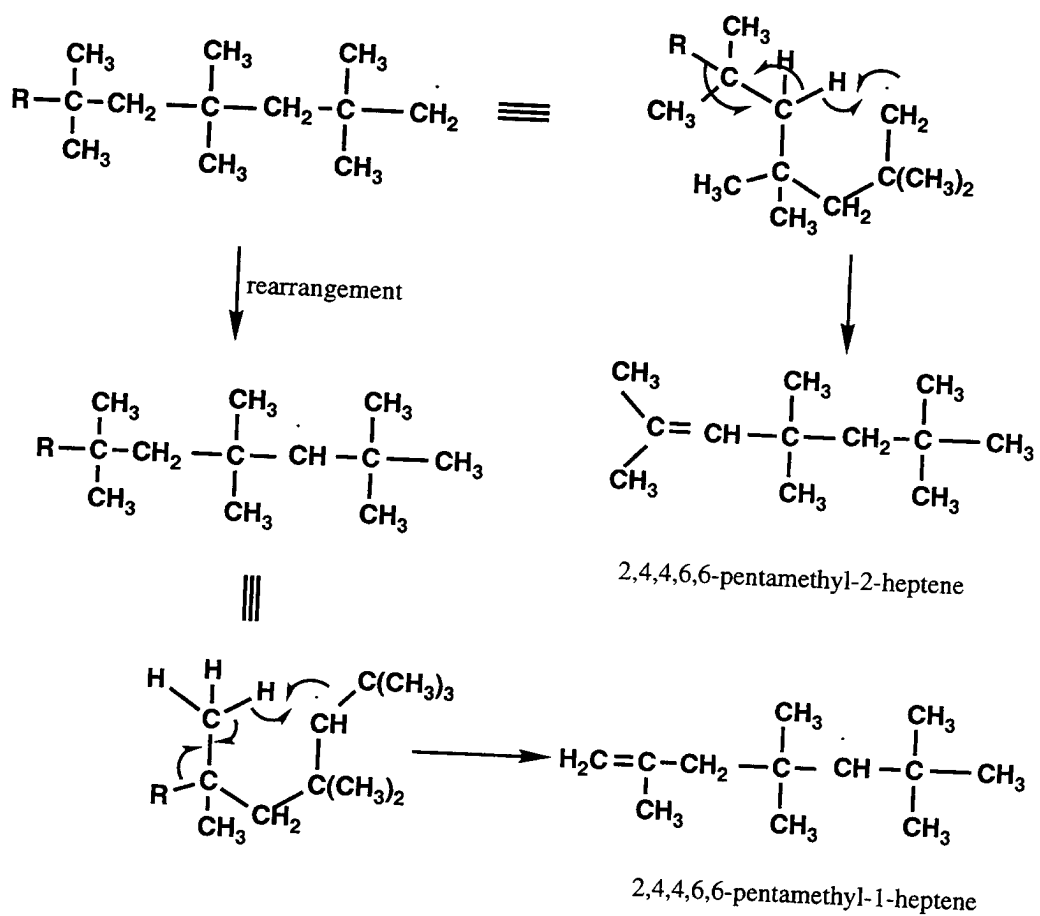
Scheme 2 - Thermal degradation of butyl (poly(2-methylpropene)) rubber. The formation of 2-methylpropene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2,4,4,6,6-pentamethyl-2-heptene and 2,4,4,6,6-pentamethyl-1-heptene are shown.



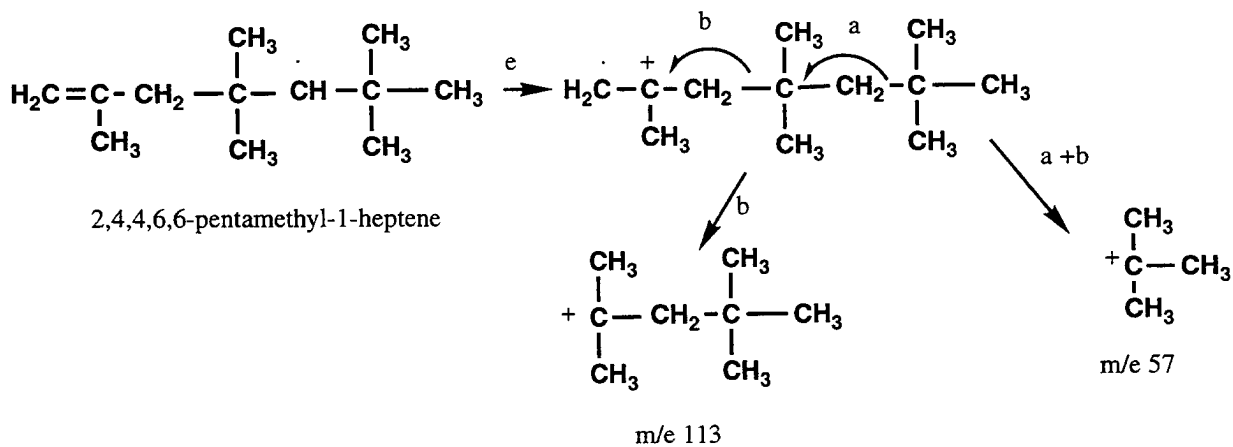
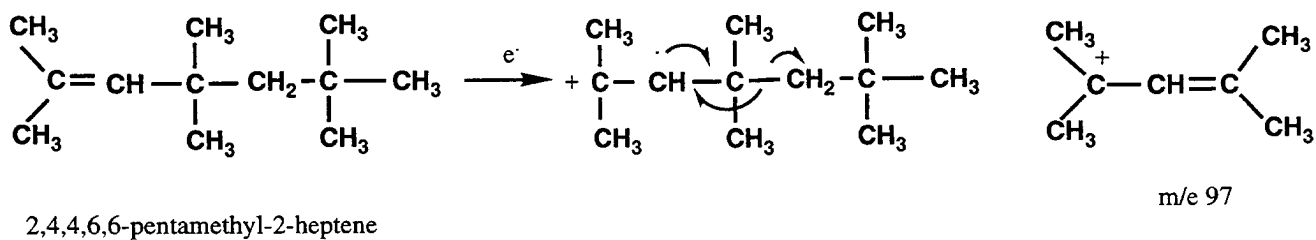
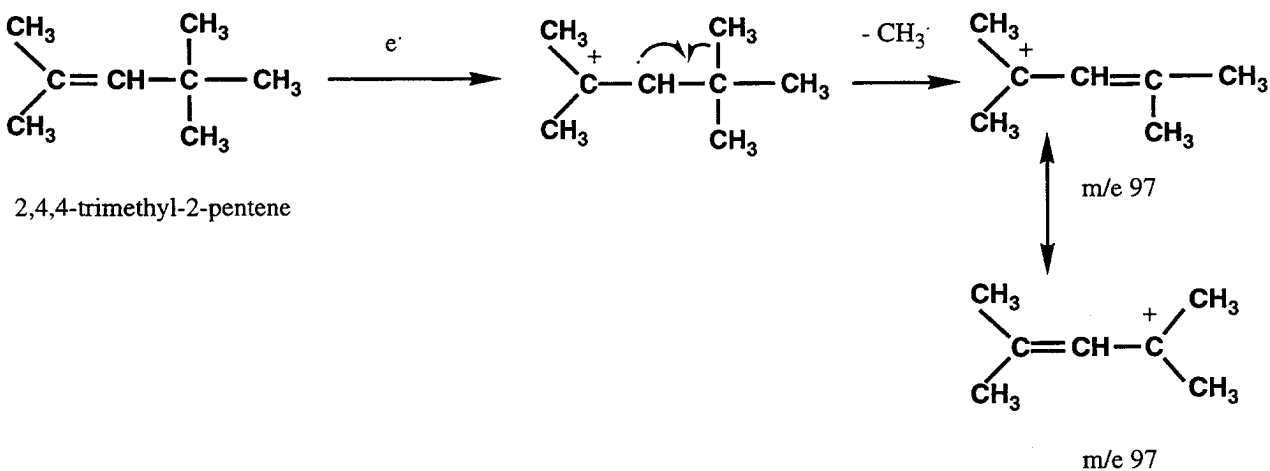
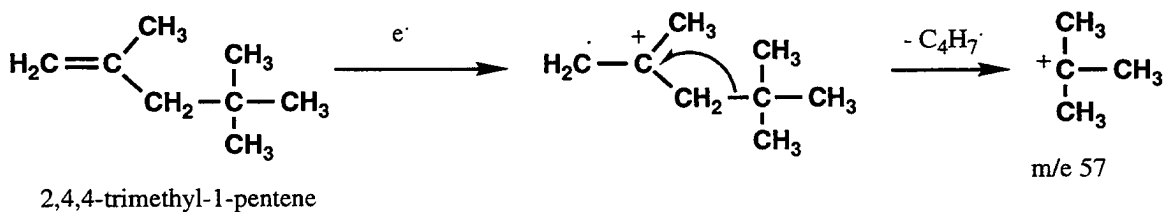
poly(2-methylpropene)



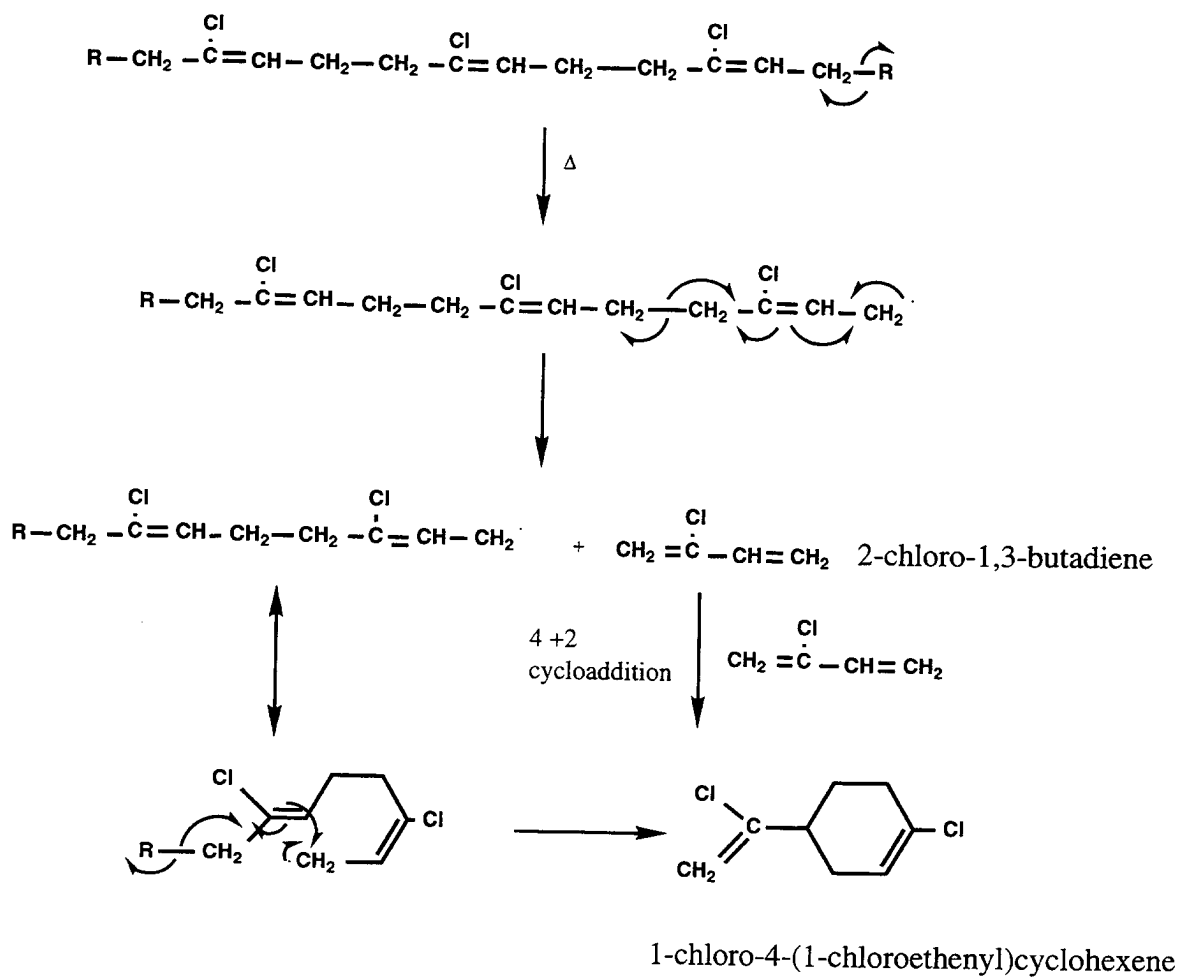
Scheme 2 (continued)



Scheme 3 - Mass spectral degradation pathways of 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2,4,4,6,6-pentamethyl-2-heptene, and 2,4,4,6,6-pentamethyl-1-heptene showing formation of ions that allow differentiation of the pairs of structural isomers.



Scheme 4 - Thermal degradation pathways of polychloroprene leading to the formation of 2-chloro-1,3-butadiene and 1-chloro-4-(1-chloroethenyl)cyclohexene.



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Elastomers and thermoset polymers can be difficult to identify as a result of their cross-linked structure. Techniques such as transmission infrared spectroscopy have limited application to these materials because of difficulty in preparing thin films. Surface infrared techniques including multiple internal reflectance and total attenuated reflectance are more useful but their application can be hampered by the presence of additives such as carbon and plasticizers. Pyrolysis coupled with gas chromatographic separation and mass spectrometric identification of degradation products provides a rapid reproducible method of degrading cross-linked materials and identifying their degradation products. As the degradation products are related to the structure of the polymer, these can be used to identify the polymer. In this paper, the pyrolysis products of samples natural rubber, butyl rubber, polychloroprene rubber, and three samples polyacrylonitrile-butadiene rubber are studied to identify degradation products that are characteristic of each type of elastomer. Knowledge of characteristic degradation products allows the rapid, unambiguous identification of elastomer types. This information is critical in the selection of elastomers for use in a particular application or in determining why an elastomer failed in a particular environment.

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