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A Compendium of Thermoplastic Polymer Pyrograms

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Defence R&D Canada

Technical Memorandum

DRDC Atlantic TM 2002-116

July 2002

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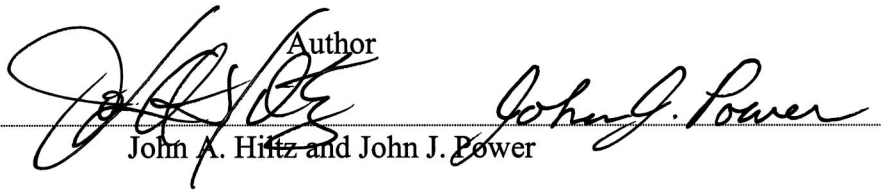

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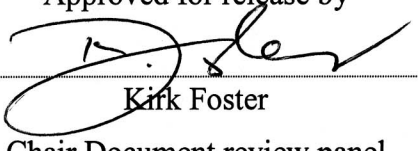

Kirk Foster

Chair Document review panel

Abstract

The identification of polymeric materials is important from several perspectives. The first is that the knowledge of the structure of a polymer yields a great deal of information on the properties of that polymer. This information is critical in determining if a polymer is suitable for a particular application. Identification of a polymer can also indicate changes in a polymer arising from in-service conditions. That is, have additives such as plasticizers or antioxidants been depleted or has the polymer absorbed compounds that alter its properties? Polymer identification is also critical in failure analysis.

In this Technical Memorandum pyrograms of commodity and engineering thermoplastics are presented. Pyrograms are chromatograms arising from a pyrolysis gas chromatography/mass spectrometry analysis. The pyrograms are discussed with emphasis on pyrolytic degradation products that are characteristic of the individual polymers. Often these can be related back to the structure of the polymer and can be used to differentiate between series of polymers with similar chemistry or identify the components of polymer blends.

Résumé

L'identification des matériaux polymériques est importante à plus d'un point de vue. Tout d'abord, la connaissance de la structure d'un polymère donné fournit un grand nombre de renseignements sur ses propriétés. Ces renseignements sont essentiels pour déterminer si un polymère peut être utilisé dans une application particulière. L'identification d'un polymère peut aussi révéler les modifications subies par celui-ci dans des conditions d'utilisation précises. Ainsi, on peut établir si la teneur du polymère en additifs, par exemple des plastifiants ou des antioxydants, a été épuisée, ou s'il a absorbé des composés qui ont modifié ses propriétés. L'identification des polymères constitue aussi un élément clé de l'analyse des défaillances.

Le présent document technique contient des pyrogrammes de thermoplastiques de grande consommation et de thermoplastiques industriels. Les pyrogrammes sont des chromatogrammes obtenus lors de l'analyse par pyro-chromatographie en phase gazeuse couplée à la spectrométrie de masse. La discussion portant sur les pyrogrammes met l'accent sur les produits de dégradation pyrolytique qui sont caractéristiques des différents polymères. Dans de nombreux cas, la nature de ces produits de dégradation permet de déterminer la structure du polymère d'origine et elle permet de différencier des familles de polymères ayant des structures chimiques semblables ou d'identifier les composants de mélanges de polymères.

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Executive summary

Introduction

The identification of polymeric materials is important from several perspectives. The first is that the knowledge of the structure of a polymer yields a great deal of information on the properties of that polymer. This information is critical in determining if a polymer is suitable for a particular application. Identification of a polymer can also indicate changes in a polymer arising from in-service conditions. That is, have additives such as plasticizers or antioxidants been depleted or has the polymer absorbed compounds that alter its properties? Polymer identification is also critical in failure analysis.

Pyrolysis-gas chromatography/mass spectrometry is a technique that has found widespread application to the identification of polymeric materials. In this technique the polymer to be identified is heated rapidly and reproducible in an inert atmosphere to an operator selected temperature. The resulting thermal degradation (pyrolysis) releases compounds that are characteristic of the structure of the polymer. These are used to identify and/or differentiate between polymers.

Principal Results

Twenty thermoplastics polymers and three thermoplastic polymer blends have been analysed using pyrolysis gas chromatography/mass spectrometry. The resulting pyrograms are discussed with respect to degradation products that are characteristic of the polymer or components of the polymer blends. The pyrograms and the characteristic degradation products form a compendium that can be used to identify thermoplastic polymers and their blends.

The pyrograms of the three polymer blends consist of the degradation products that are characteristic of the polymers that make up the blend.

The pyrograms of the thermoplastics with aromatic rings incorporated into the main polymer chain are characterized by degradation products arising from the cleavage of non aromatic main polymer chain bonds. The thermal/pyrolytic stability of the aromatic rings leads to preferential cleavage of the polymer chain at non-aromatic main chain bonds.

Pyrolysis can identify or differentiate between polymers of a particular type. Three poly(sulfone) samples, prepared from different starting materials, were distinguished on the basis of their pyrolytic degradation products. Poly(phenylene oxide)s could also be differentiated on the basis of their degradation products.

Nylons based on diacid/diamine chemistry can be easily distinguished from those based on cyclic lactam chemistry. The cyclic monomers used to prepare Nylon 6, Nylon 11, and Nylon 12 are major degradation product of these lactam based poly(amide)s.

The diacid/diamine poly(amide)s released series of compounds that were characteristic of these nylons and could be used to identify the constituent diacids and diamines used to prepare them.

Significance of Results

A compendium of thermoplastic pyrograms has been prepared. The pyrograms and degradation products analysis form a data base of well characterized polymers that can be used to identify unknowns. This is particular significant when the accurate and rapid identification of polymeric materials is critical in failure analysis or scientific consulting leading to the selection of materials for a particular application.

Hiltz, J. A., Power, J. J. 2002. A Compendium of Thermoplastic Polymer Pyrograms. TM 2002-116. Defence R&D Canada Atlantic.

Sommaire

Introduction

L'identification des matériaux polymériques est importante à plus d'un point de vue. Tout d'abord, la connaissance de la structure d'un polymère donné fournit un grand nombre de renseignements sur ses propriétés. Ces renseignements sont essentiels pour déterminer si un polymère peut être utilisé dans une application particulière. L'identification d'un polymère peut aussi révéler les modifications subies par celui-ci dans des conditions d'utilisation précises. Ainsi, on peut établir si la teneur du polymère en additifs, par exemple des plastifiants ou des antioxydants, a été épuisée, ou s'il a absorbé des composés qui ont modifié ses propriétés. L'identification des polymères constitue aussi un élément clé de l'analyse des défaillances.
La pyro-chromatographie en phase gazeuse couplée à la spectrométrie de masse est une technique qui est actuellement largement utilisée pour identifier des matériaux polymériques. Elle consiste à chauffer rapidement, sous atmosphère inerte, le polymère devant être identifié, jusqu'à une température choisie par l'opérateur. La dégradation thermique (ou pyrolyse) subie par le polymère entraîne un dégagement de composés caractéristiques de la structure de celui-ci. Ces produits de dégradation servent à identifier des polymères distincts et à différencier des polymères ayant des structures semblables.

Principaux résultats

On a analysé vingt polymères thermoplastiques et trois mélanges de polymères thermoplastiques à l'aide de la pyro-chromatographie en phase gazeuse couplée à la spectrométrie de masse. Les pyrogrammes obtenus sont l'objet d'une discussion portant sur les produits de dégradation qui sont caractéristiques du polymère d'origine ou des composants du mélange de polymères. Les pyrogrammes et les produits de dégradation caractéristiques identifiés forment un abrégé qui peut être utilisé pour identifier des polymères thermoplastiques et des mélanges de ceux-ci.
Les pyrogrammes des trois mélanges de polymères contiennent les renseignements permettant d'identifier les produits de dégradation qui sont caractéristiques des polymères composant les différents mélanges.
Les pyrogrammes des thermoplastiques dont la chaîne polymérique principale contient des noyaux aromatiques se caractérisent par la présence de produits de dégradation qui proviennent de la rupture de liens non aromatiques dans la chaîne principale du polymère. La rupture préférentielle des liens non aromatiques de la chaîne principale du polymère est attribuable à la stabilité thermique/pyrolytique des noyaux aromatiques.
La pyrolyse permet d'identifier et, de ce fait, de différencier des polymères appartenant à une même catégorie de macromolécules. On a réussi à distinguer trois échantillons de polysulfones préparés à partir de différentes substances de départ en se basant sur la nature de leurs produits de dégradation pyrolytique. Il est aussi possible de différencier des oxydes de polyphénylène de la même manière.
De plus, on peut facilement distinguer les nylons dont la structure chimique est à base de diacides et de diamines et ceux dont la structure chimique repose sur des lactames cycliques. Les monomères cycliques utilisés pour préparer le nylon 6, le nylon 11 et le nylon 12 constituent des produits de dégradation importants de ces polyamides à base de lactames. Les polyamides à base de diacides et de diamines ont dégagé des séries de composés

caractéristiques de ces nylons, qui peuvent servir à identifier les constituants de nature diacide et diamine qui sont utilisés pour préparer les polymères.

Importance des résultats

On a organisé un abrégé des pyrogrammes des thermoplastiques. Les pyrogrammes et les résultats de l'anal yse des produits de dégradation constituent une base de données de polymères nettement caractérisés, qui peut servir à identifier des échantillons inconnus. Cette capacité est particulièrement utile dans les cas où il est essentiel d'identifier rapidement et sans erreur des matériaux polymériques, notamment en analyse des défaillances ou dans le cadre d'études scientifiques visant à sélectionner des matériaux pour une application particulière.

Hiltz, J.A., Power, J.J. 2002. A Compendium of Thermoplastic Polymer Pyrograms. TM 2002-116. CRDA.

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Introduction

Pyrolysis gas chromatography (py-GC) and pyrolysis gas chromatography/mass spectrometry (py-GC/MS) are routinely used to identify polymeric materials. Py-GC analysis yields retention time and intensity data for the polymer pyrolytic degradation products. This data, referred to as the fingerprint, can be used to identify or differentiate between polymers. When the py-GC is coupled with MS detection, the amount of information in the pyrogram increases significantly. Mass spectrometric detection allows the identification of the individual compounds that give rise to the fingerprint. These compounds can be used to positively identify the polymer if they can be linked through degradation mechanisms to the structure of the polymer.

Pyrolysis can be used to differentiate between polymers that are generically the same but differ in structure. Poly(ethylene) is an example. The pyrograms of straight chain and branched poly(ethylene) samples are similar. However, chain branching leads to fine structure in the pyrogram that is not observed for straight chain poly(ethylene). Pyrolysis can also be used to study differences in polymer formulation. For instance, differences in additives, such as plasticizers and antioxidants, will be reflected in the pyrograms. If MS detection is used the additives can be identified.

In the Emerging Materials Section DRDC Atlantic, py-GS/MS is used on a daily basis. The information derived is used to identify polymers and assure that the polymer has the required chemistry for a particular application, to monitor changes in the polymer including loss of additives or the absorption of solvents that may make it unsuitable for use in a particular environment, and to aid in polymer failure investigations.

Polymers degrade by four major mechanisms: 1) depolymerization, 2) random chain scission followed by a) depolymerization from radical ends, b) disproportionation or c) cyclization, 3) cleavage of side groups and main chain fragmentation and 4) interchain condensation. Many polymers consist of blends of two or more polymers or are the product of copolymerization reactions. Copolymers can be random, alternating or block. These factors complicate the analysis of pyrolytic degradation products. When one adds to this the frequent requirement that the material be identified in a very short time, the analyst needs to have an in-depth knowledge of polymers, their degradation pathways, and characteristic degradation products to identify them.

One approach to gaining this knowledge is to construct libraries (compendia) of pyrograms of well-characterized polymers. Degradation pathways and products, and even fingerprints of these compounds are then available to aid in the analysis of unknowns. In this report the pyrograms of a number of thermoplastic polymers are reported and discussed with respect to characteristic degradation products, degradation pathways, and the effect of changes in composition on the types and relative concentrations of degradation products.

Experimental

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

All pyrolysis were carried out in a platinum coil pyroprobe (Pyroprobe 2000, Chemical Data Systems, Oxford, PA). The polymer sample (0.05 mg to 0.15 mg) was centered in a 25 mm quartz tube and heated with the temperature ramp off (maximum heating rate) to a final temperature of 700^{o}C. The hold time at the final temperature was 20 seconds.

GC/MS analysis was carried out on a Fisons Platform II quadrupole GC/MS with a Fisons Model 8000 GC. The pyroprobe/GC interface temperature was 300^{o}C. The pyrolysis products were separated on a 30m long X 0.25 mm inside diameter capillary column with a 0.25μm thick 5% phenyl-95% dimethylpolysiloxane stationary phase (Alltech Econo-Cap EC-5). The GC was operated in the pressure control mode using Helium (linear flow rate 0.3m/s at 40^{o}C) as the carrier gas.

The GC oven was programmed to hold at 40^{o}C for 5 minutes, then increase to 300^{o}C at a rate of 10^{o}C/min, and finally hold at 300^{o}C for 10 minutes. The total run time was 41 minutes.

Materials

The high density poly(ethylene), medium density poly(ethylene), poly(phenylene sulfide), poly(2,6-dimethyl-p-phenylene oxide), poly(styrene), poly(sulfone), poly(p-phenylene ether sulfone), Nylon 6,6, Nylon 6,9, Nylon 6,10, Nylon 6,12, Nylon 6,T, Nylon 6, Nylon 11, Nylon 12, poly(ethylene terephthalate), and poly(carbonate) samples were purchased from Scientific Polymer Products, Ontario, New York.

Montel PDC 1234 and Union Carbide 5E89 poly(propylene) samples were supplied by Montel and Union Carbide respectively.

Torlon™ poly(amide-imide), Radel™ R poly(arylsulfone), and Xydar™ aromatic poly(ester) liquid crystal polymer were supplied by BPAmoco.

Prevex® poly(phenylene ether) was supplied by GE Plastics.

Makroblend® poly(carbonate)/poly(ethylene terephthalate) blend was supplied by Bayer.

Results and Discussion

The retention time of degradation products are listed to aid the reader in finding them in the pyrograms. Retention times will vary with column pressure (flow), age of the column, and changes in length of the column following maintenance. However, the structure and relative concentrations of degradation products vary little for a particular polymer. Because pyrolysis products are identified using mass spectrometry, the applicability of this technique to the identification of polymers is not dependent on retention times.

Poly(ethylene)

The chemical structure of poly(ethylene) is shown in Figure 1.

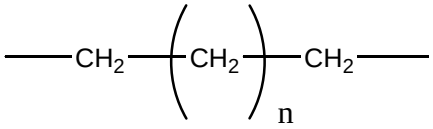

Figure 1. Chemical structure of poly(ethylene).

Poly(ethylene) degrades by a random chain scission mechanism followed by disproportionation. The pyrogram of a high density poly(ethylene) sample is shown in Figure 2.

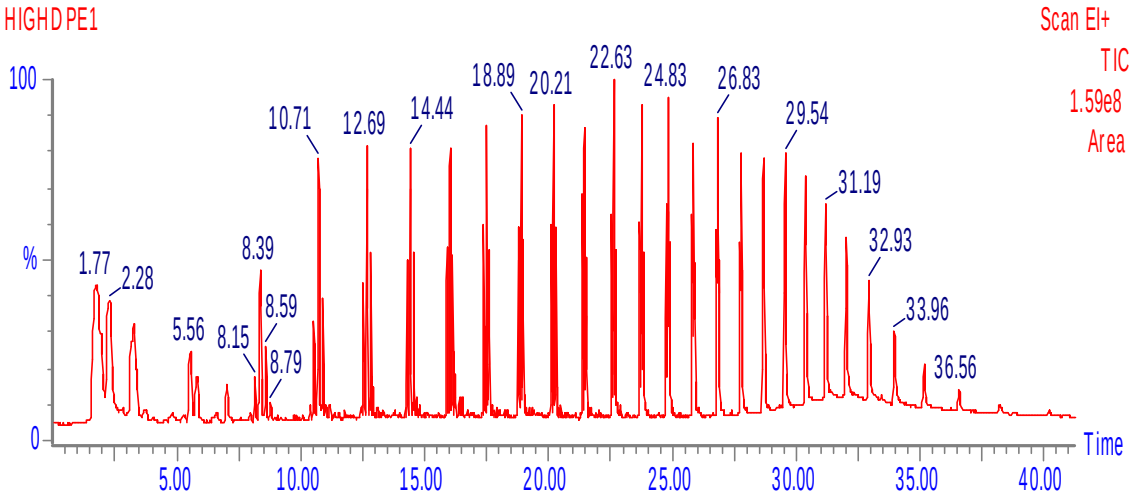

Figure 2. Pyrogram of a sample of high density poly(ethylene).

The pyrogram of poly(ethylene) is characterized by a series of triplets corresponding to an alkadiene, an alkene, and an alkane containing the same number of carbons. For instance the

peaks of the triplet centered at 8.39 min correspond to nonadiene (8.15 min), nonene (8.39 min), and nonane (8.59 min) and the peaks of the triplet centered at 10.71 min correspond to decadiene (10.53 min), decene (10.71 min) and decane (10.90 min).

One method of controlling the density of poly(ethylene) is through the introduction of chain branching. Small amounts of alkenes, such as 1-butene, 1-hexene or 1-octene, are copolymerised with ethylene. Chain branching is reflected in the pyrogram of the sample[1]. That is, chain branching promotes cleavage of the polymer chain at carbons adjacent to, (α), and two bonds from (β) the branch site. Cleavage of the polymer chain at carbons β and γ (three bonds) from the chain branch results in formation of methyl and ethyl substituted alkanes respectively. These compounds give rise to the peaks between the alkadiene/alkene/alkane triplets.

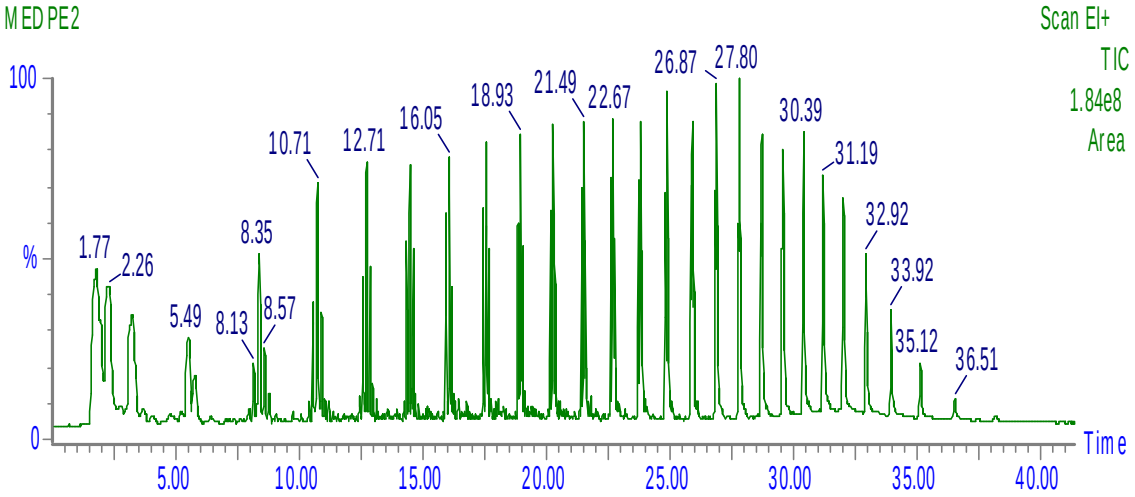

Figure 3. Pyrogram of a sample of medium density poly(ethylene).

The pyrogram of a medium density poly(ethylene) sample is shown in Figure 3. Comparison of this pyrogram with that of high density sample indicates that they are similar (see Figure 4). However, the peaks between the major triplets are slightly more intense for the medium density sample than for the high density sample. This suggests that the level of chain branching in the medium density sample polymer is greater than in the high density sample. It should be noted that parameters such as molecular weight and processing also have an effect on poly(ethylene) density.

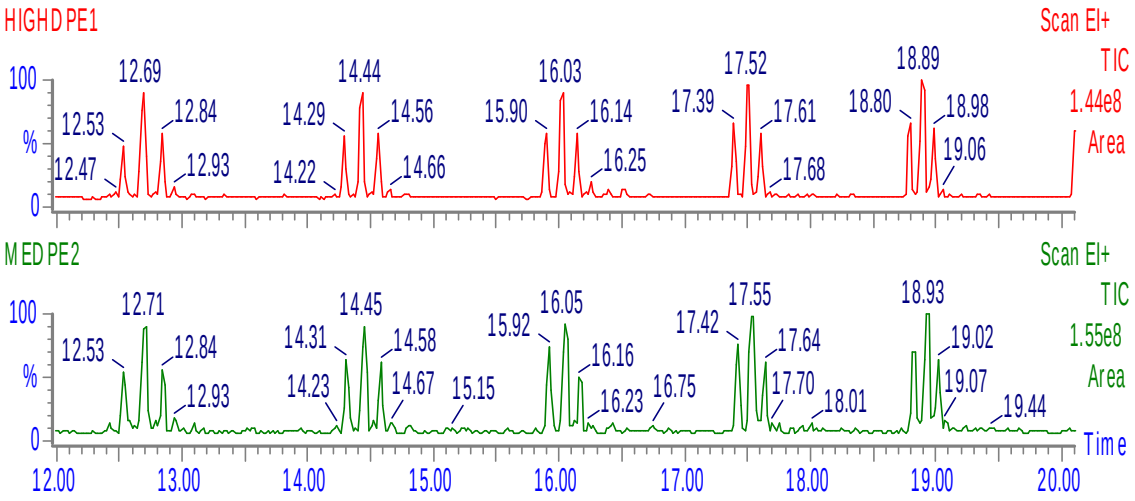

Figure 4. Expansions of pyrograms of high (top) and medium density (bottom) poly(ethylene) samples between 12 and 20 minutes..

Poly(propylene)

The chemical structure of poly(propylene) is shown in Figure 5. The major degradation mechanism of poly(propylene) is random chain scission mechanism followed by disproportionation.

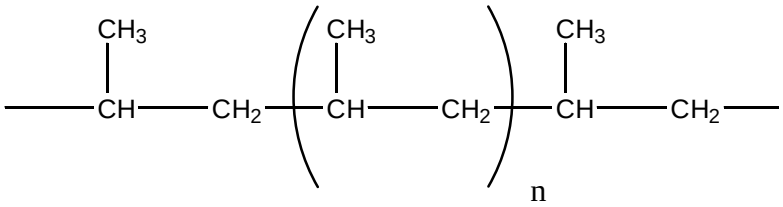

Figure 5. Chemical structure of poly(propylene).

Pyrograms of two poly(propylene) samples, Montel PDC 1234 and Union Carbide 5E89, are shown in Figures 6 and 7.

Comparison of the programs indicates that the degradation products are similar although the relative amounts of degradation products vary from one sample to the other. Characteristic degradation products of poly(propylene) are a series of hydrocarbons corresponding to propylene oligomers. Referring to the pyrogram shown in Figure 6, these include the trimer of propylene (5.75 min) with a molecular weight (MW) of 126, isomeric tetramers of propylene (11.56 min and 11.63 min) with a MW of 168, and isomeric pentamers of propylene (15.34 min, 15.44 min, and 15.58 min) with a MW of 210.

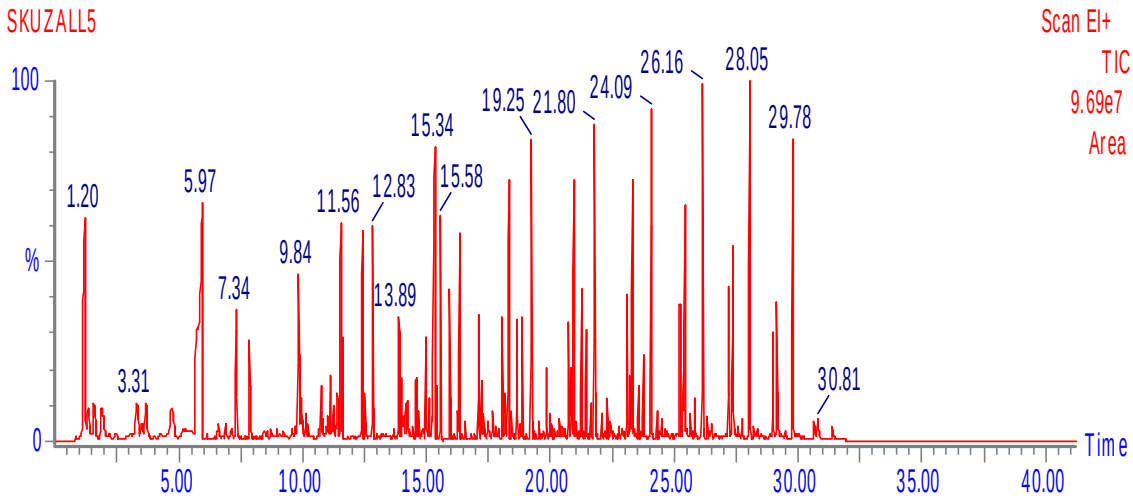

Figure 6. Pyrogram of a sample of Montel PDC 1234 poly(propylene).

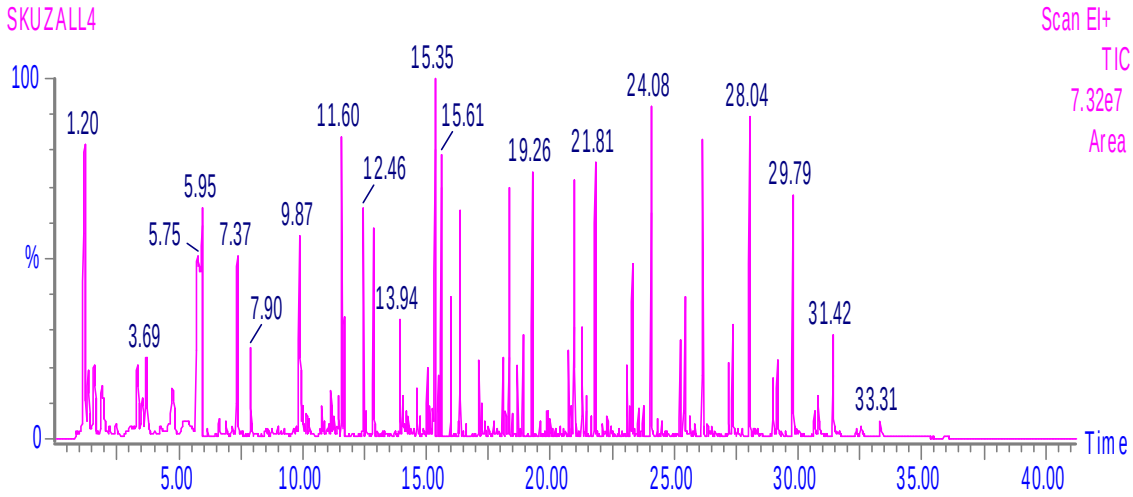

Figure 7. Pyrogram of a sample of Union Carbide 5E89 poly(propylene).

Poly(Ethylene/Propylene) Blend (30% ethylene)

It is difficult to distinguish between the programs of poly(ethylene)/poly(propylene) blends and copolymers[2]. However the programs do contain compounds that are related to the pyrolytic degradation of the poly(ethylene) and poly(propylene) portions of the polymer. The pyrogram of an ethylene/propylene blend containing 30% ethylene is shown in Figure 8.

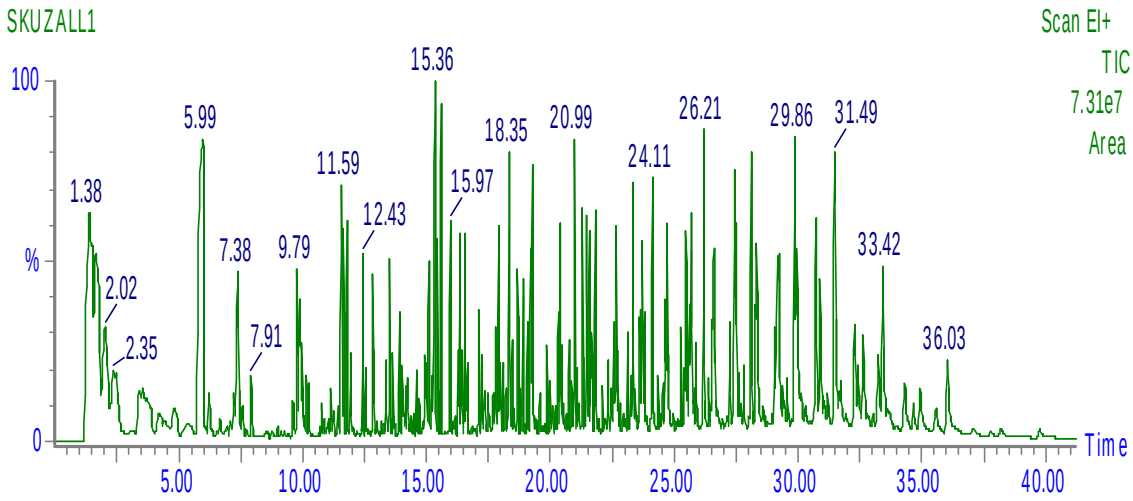

Figure 8. Pyrogram of a poly(ethylene/propylene) blend (30% poly(ethylene)).

Expansions of the pyrograms of the poly(ethylene/propylene) blend, poly(ethylene) and poly(propylene) between 5 and 18 minutes are shown in Figure 9. Comparison of the pyrograms of the blend and poly(ethylene) samples indicates that the characteristic poly(ethylene) triplets (for instance, the triplets centered at 7.32 min, 9.80 min, and 11.80 min in top trace of Figure 9) are present in the blend pyrogram (triplets centered at 7.32min, 9.79 min, and 11.59 min in the bottom trace of Figure 9). The characteristic poly(propylene) degradation products are also present. For instance, the trimer (5.75 min), tetramer (11.59 min) and pentamer of propylene (15.36 min) seen in the middle trace of Figure 9 are also found in the blend pyrogram.

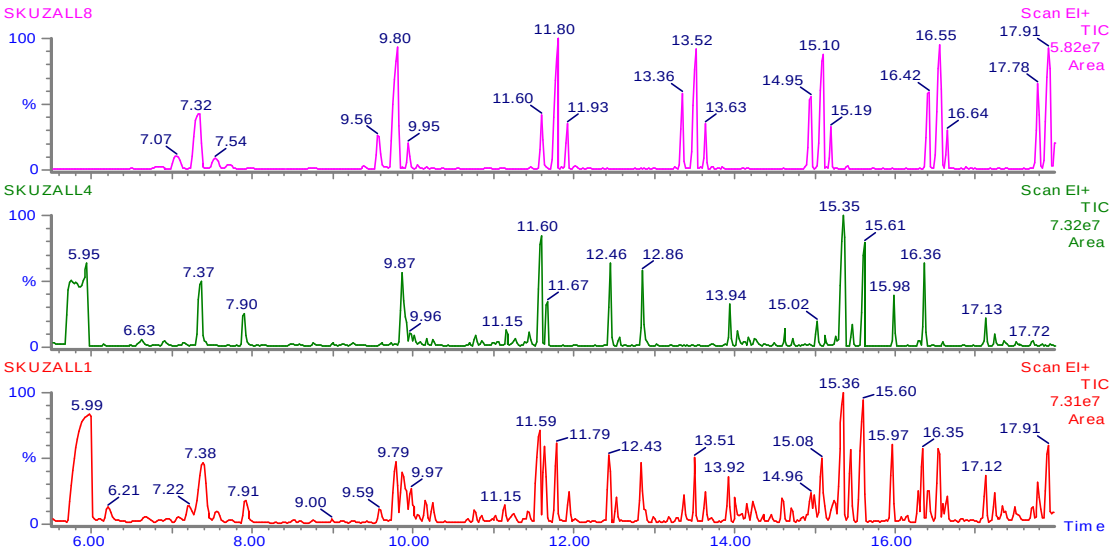

Figure 9. Expansions of pyrograms of top) poly(ethylene), middle) poly(propylene) and bottom) poly(ethylene/propylene) blend (30% poly(ethylene)) between 5 and 18 minutes.

Poly(phenylene sulfide) or Poly(thio-1,4-phenylene)

Poly(phenylene sulfide) is prepared from the condensation of 1,4-dichlorobenzene and sodium sulfide. The chemical structure of poly(phenylene sulfide) is shown in Figure 10.

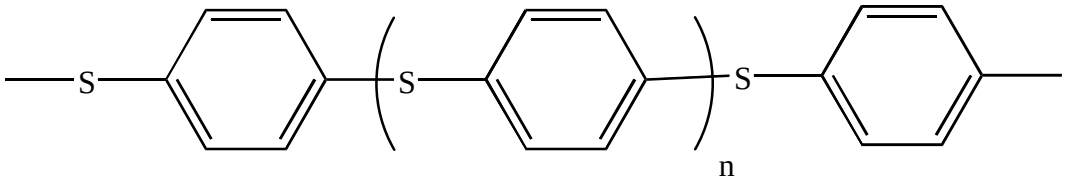

Figure 10. Chemical structure of poly(phenylene sulfide).

The pyrogram of a sample of poly(phenylene sulfide) is shown in Figure 11.

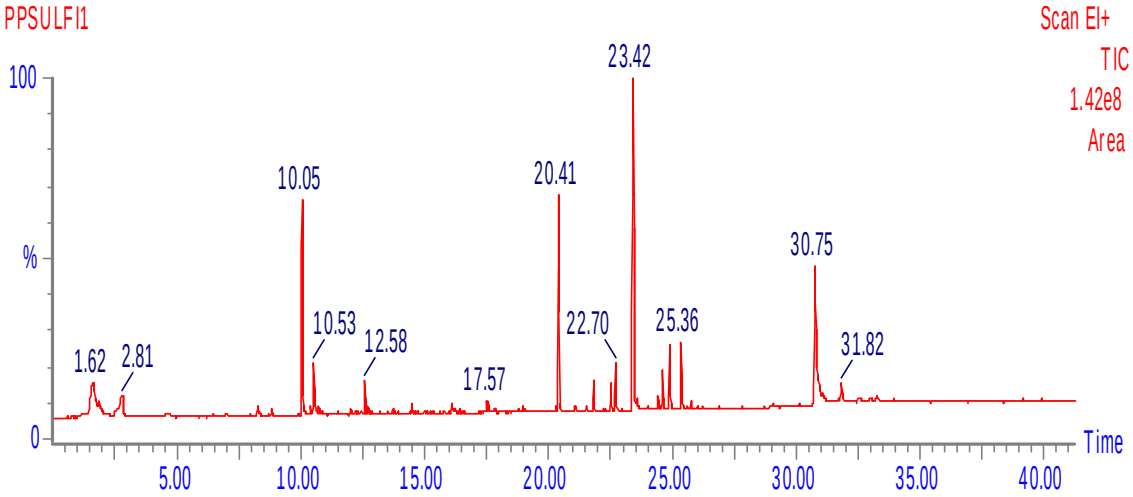

Figure 11. Pyrogram of a sample of poly(phenylene sulfide).

The major degradation products arise from main chain scission, i.e., the cleavage of bonds between sulfur atoms and benzene rings. These include benzene (2.81 min), benzenethiol (10.05 min), diphenyl sulfide (20.41 min), phenyl 4-thiophenyl sulfide (23.42 min), and 4-(phenylthio)phenyl phenyl sulfide (30.75 min). Two degradation products, (4-chlorophenyl) phenyl sulfide (22.70 min) and (4-thiophenyl)(4-chlorophenyl) sulfide (25.36 min), contain chlorine. These compounds arise from partially reacted or residual 1,4-dichlorobenzene, one of the starting materials used in the synthesis of Poly(phenylene sulfide). Other pyrolytic degradation products, such as benzothiophene (22.52 min) and thianthrene (24.88 min), result from secondary reactions of degradation products arising from main chain scission.

Poly(2,6-dimethyl-p-phenylene oxide)

Poly(2,6-dimethyl-p-phenylene oxide) is prepared by the oxidative coupling of 2,6-dimethylphenol. The chemical structure of poly(2,6-dimethyl-p-phenylene oxide) is shown in Figure 12. The pyrogram of a sample of poly(2,6-dimethyl-p-phenylene oxide) is shown in Figure 13.

Pyrolytic degradation products arising from the scission of main polymer chain bonds include xylene (7.67 min), 2,6-dimethylphenol and 3,5-dimethylphenol (13.10 min and 13.83 min), 2,6-dimethylphenyl 3,5-dimethylphenyl ether (24.02 min) and three compounds with molecular weights of 242 at 24.94 min, 26.79 min and 27.14 min respectively. A molecular weight of 242 is consistent with dimethylphenyl dimethylhydroxyphenyl ethers. Degradation products arising from reactions following scission of main chain bonds include toluene (4.57 min), phenol (10.55 min), 2-methylphenol and 3-methylphenol (12.09 min and 12.46 min), 3,5-dimethylphenyl 4-hydroxy-2-methylphenyl ether (26.35 min).

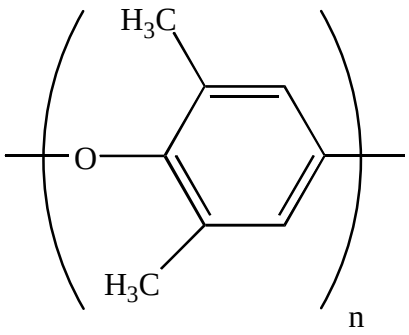

Figure 12. Chemical structure of poly(2,6-dimethyl-p-phenylene oxide).

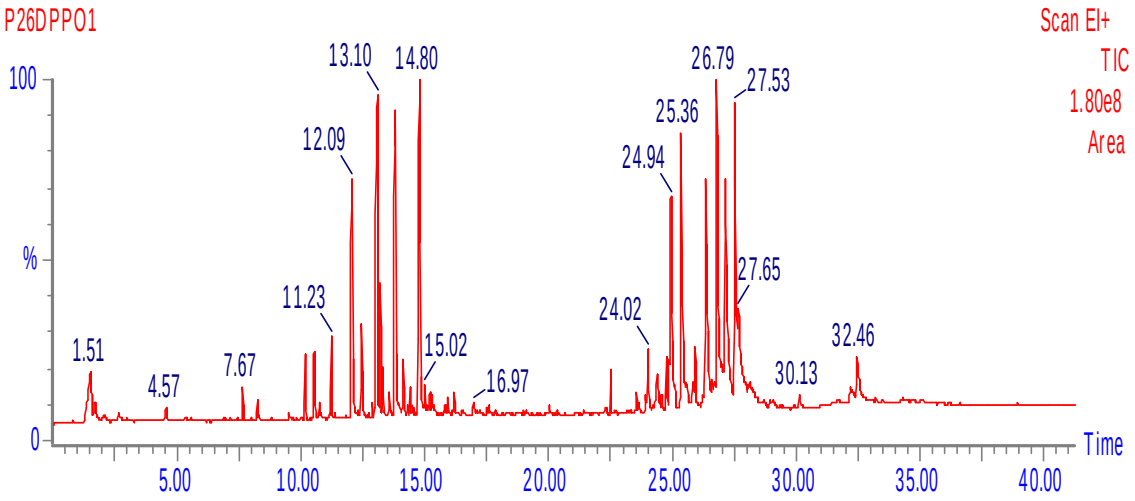

Figure 13. Pyrogram of a sample of poly(2,6-dimethyl-p-phenylene oxide).

Poly(phenylene oxide)/Poly(styrene) blend - Prevex™

Prevex™ is a blend of poly(phenylene oxide) prepared from 2,6-dimethylphenol and 2,3,6-trimethylphenol and poly(styrene). The chemical structure of the poly(phenylene oxide) portion of this polymer is shown in Figure14.

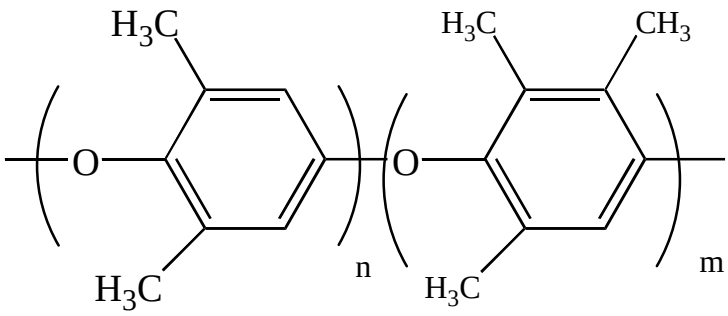

Figure 14. Chemical structure of co-poly-(oxy-2,6-dimethyl-1,4-phenylene)-(oxy-2,3,6-trimethyle-1,4-phenylene). This is the poly(phenylene oxide) portion of the poly(phenylene oxide)/poly(styrene) blend.

The pyrogram of a sample of Prevex™ is shown in Figure 15. The large number of degradation products in the pyrogram of this sample result from two factors. The first is that the poly(phenylene oxide) portion of the polymer is a copolymer of dimethyl- and trimethylphenols. The second is that it is a blend of poly(phenylene oxide) and poly(styrene).

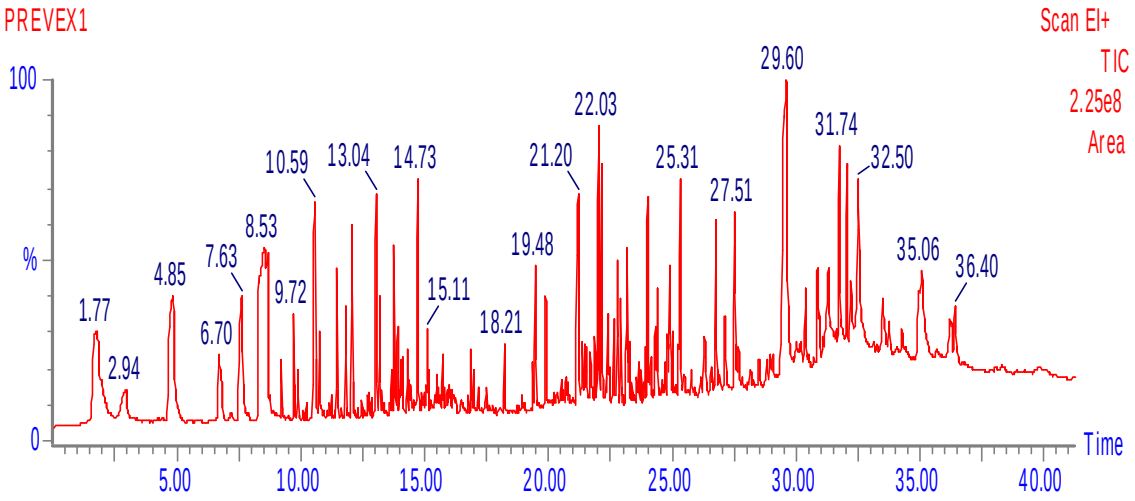

Figure 15. Pyrogram of a sample of Prevex™. This plastic is a blend of poly(phenylene oxide) and poly(styrene).

There are a number of degradation products arising from the scission of main polymer chain bonds of the poly(phenylene oxide) portion of the polymer. These include dimethylbenzene (7.63 min), trimethylbenzene (9.21 min), phenol (10.57 min), dimethylphenols (13.04 min and 13.78 min), 2,3,6-trimethylphenol (14.73 min), and 2,6-dimethyl-4-hydroxyphenyl 2,6-dimethylphenyl ethers (24.87 min, 26.74 min, and 27.11 min). Degradation products arising from the cleavage of bonds in addition to those in the polymer chain include benzene (2.10 min) and 2-methylphenol (11.47 min).

Pyrograms of poly(styrene) and Prevex™ are shown in Figure 16. Comparison of the degradation products of poly(styrene) and Prevex™ indicate that a number of the major degradation products of Prevex™ arise from the poly(styrene) part of the copolymer. These include styrene (8.53 min), the dimer of styrene (22.03 min) and the trimer of styrene (29.60 min.)

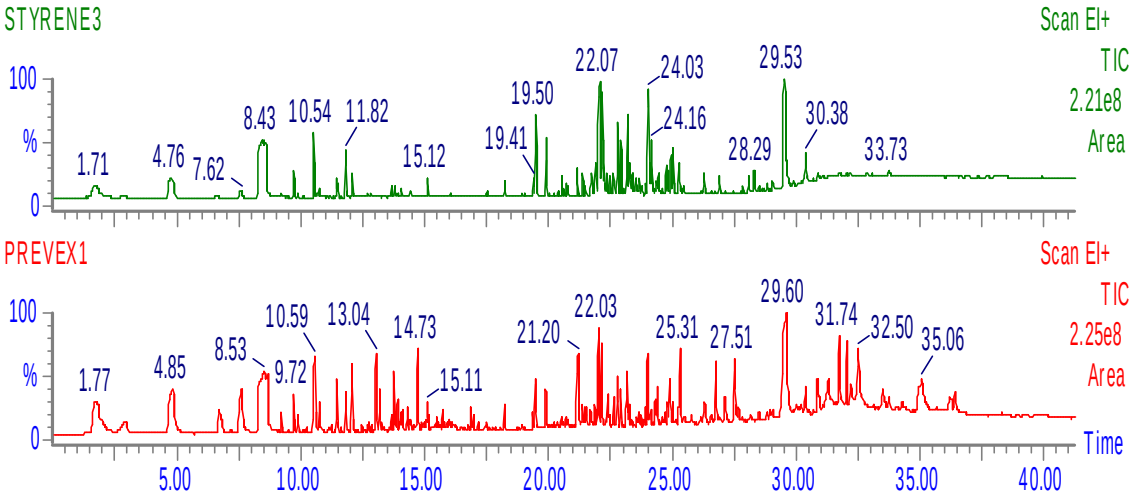

Figure 16. Pyrograms of bottom) Prevex™ and top) poly(styrene).

Poly(amide-imide) - Torlon™

Poly(amide imide)s are prepared from trimellitic anhydride (benzene-1,2,4-tricarboxylic acid-1,2-anhydride) and a diamine. The chemical structure of a poly(amide-imide) prepared using 4,4'-oxybis-benzenamine as the diamine is shown in Figure 14.

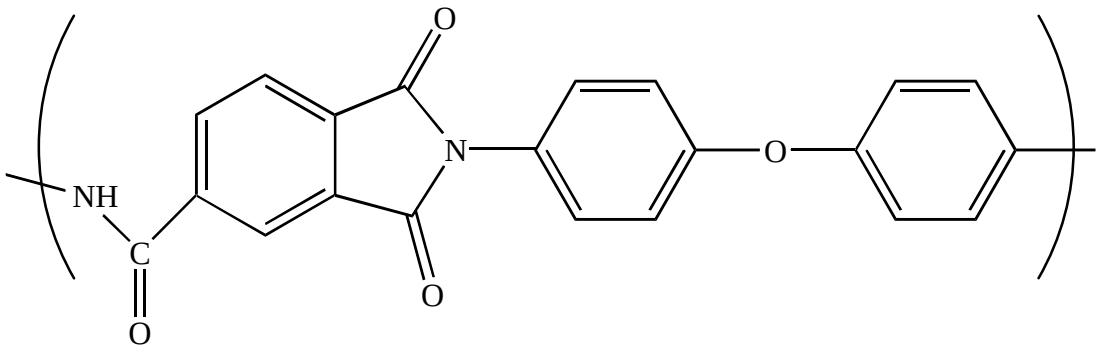

Figure 17. Chemical structure of a poly(amide-imde). The diamine is 4,4'-oxybis-benzenamine.

This polymer degrades through the loss of small molecules and interchain condensation. The pyrogram of a sample of Torlon® is shown in Figure 17.

Pyrolysis products that can be attributed to the loss of small molecules from this polymer include aniline (9.37 min), phenol (9.90 min), 4-aminophenol (15.64 min), 1H-isoindole-1,3(2H)-dione (17.73 min), diphenyl ether (18.14 min), 4-phenoxybenzenamine (21.07 min), 2-phenyl-1H-isoindole-1,3(2H)-dione (24.24 min), and 4,4'-oxybis-benzenamine (24.94 min). As was observed for poly(phenylene sulfide) and poly(phenylene oxide), these degradation products arise from the scission of bonds along the polymer backbone. For instance 1H-isoindole-1,3(2H)-dione, which contains the imide functionality, is released when the nitrogen/benzene ring and the benzene ring/C(O)NH- bonds are broken and 2-phenyl-1H-isoindole-1,3(2H)-dione is released when the benzene ring/oxygen and the benzene ring/ C(O)NH- bonds are broken.

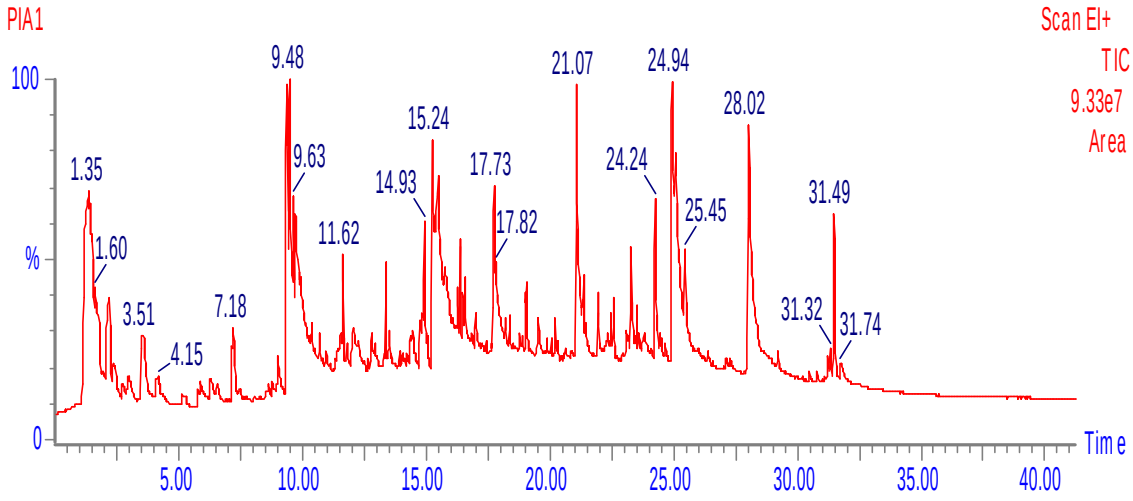

Figure 18. Pyrogram of a sample of Torlon®, a commercial poly(amide-imide).

Poly(imide)

Poly(imide)s are prepared from aromatic tetracarboxylic acids or aromatic tetracarboxylic acid dianhydrides and a diamine. A typical poly(imide) based on benzene tetracarboxylic acid dianhydride and methylene-bis-benzenamine is shown in Figure 19. Poly(imide)s degrade through the loss of small molecules and interchain condensation. The pyrogram of a sample of Solimide™, a high temperature poly(imide) insulating foam, is shown in Figure 20.

Pyrolysis products that can be attributed to the loss of small molecules from this polymer include benzene (2.19 min), toluene (3.62 min), aniline (9.58 min), benzonitrile (9.62 min), 1,4-dicyanobenzene 15.30 min), 1H-isoindole-1,3(2H)-dione (17.85 min), fluorene (19.19 min), benzophenone (19.78 min), 2-phenyl-1H-isoindole-1,3(2H)-dione (24.42 min), and 2-(4-methylphenyl)-1H-isoindole-1,3(2H)-dione (25.61 min).

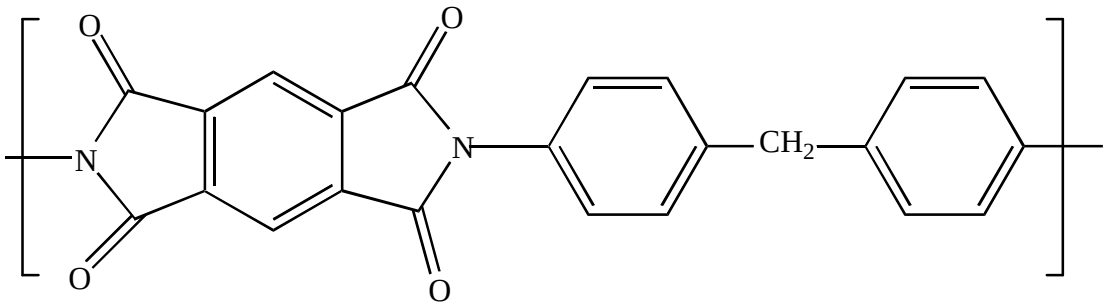

Figure 19. Chemical structure of a polyimde.

As was observed for poly(amide-imide), the majority of the major degradation products arise from the scission of main polymer chain bonds. For instance, 1H-isoindole-1,3(2H)-dione and 2-(4-methylphenyl)-1H-isoindole-1,3(2H)-dione, which contain the imide functionality are both released from Solimide. However, the formation of cyanobenzene and dicyanobenzene requires secondary reactions.

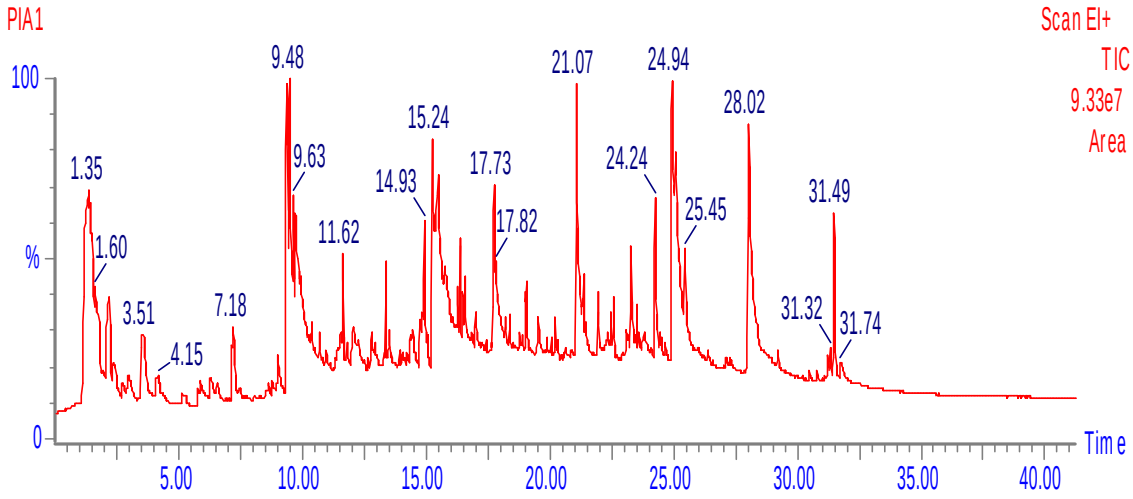

Figure 20. Pyrogram of a sample of Solimide™, a poly(imide) based insulating foam.

Poly(sulfone)

The chemical structure of a poly(sulfone) prepared from bisphenol A and 4,4'-dichlorodiphenylsulfone is shown in Figure 21.

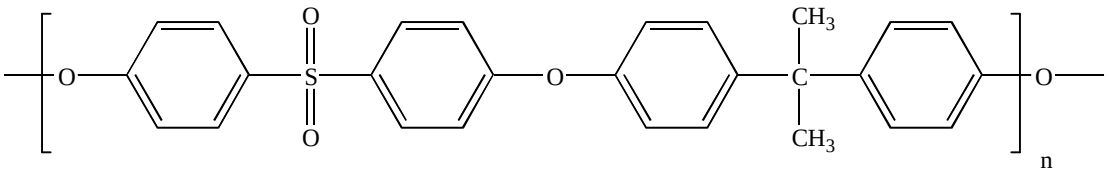

Figure 21. Chemical structure of a poly(sulfone).

The pyrogram of a sample of poly(sulfone) is shown in Figure 22.

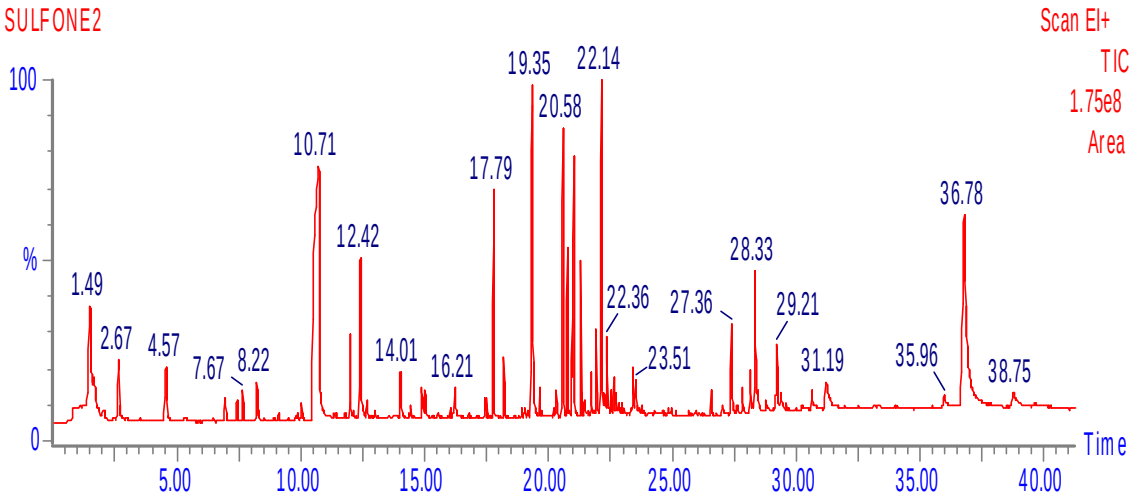

Figure 22. Pyrogram of a sample of poly(sulfone).

A large number of the pyrolytic degradation products arise from the cleavage of polymer main chain bonds. These include benzene (2.67 min), phenol (10.71 min), 4-(1-methylethyl)phenol (15.02 min), diphenyl ether (17.79 min), 2-phenyl-2-(4-hydroxyphenyl)propane (21.31 min), and diphenylsulfone (24.30 min). No bisphenol A was found in the degradation products. This would seem to indicate that bisphenol A was not used to prepare this polymer. However, there are a number of degradation products that are consistent with bisphenol A being incorporated into this polymer. For instance, 4-(1-methylethyl)phenol (15.02 min) and 2-phenyl-2-(4-hydroxyphenyl)propane (21.31 min) would arise from the degradation of the bisphenol A portion of the polymer.

Chlorobenzene (6.94 min) arises from residual or partially reacted dichlorodiphenylsulfone used to prepare this polymer.

Poly(p-phenylene ether sulfone)

The chemical structure of a poly(p-phenylene ether sulfone) is shown in Figure 23. This polymer is prepared from diphenylene oxide sulfonyl chloride via a Friedel-Crafts self condensation.

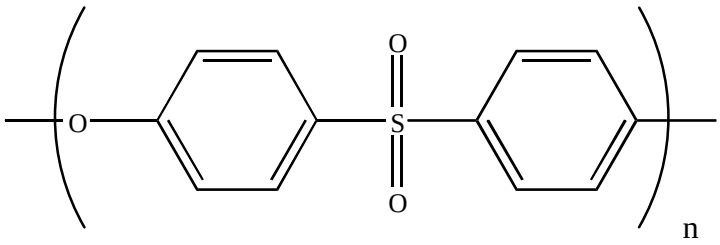

Figure 23. Chemical structure of a poly(p-phenylene ether sulfone).

The pyrogram of a sample of poly(p-phenylene ether sulfone) is shown in Figure 24.

The major degradation products of this polymer include phenol (10.66 min), diphenyl ether (17.83 min), dibenzofuran (19.44 min) and diphenylsulfone (24.34 min). All but dibenzofuran arise from the scission of main polymer chain bonds. Dibenzofuran is formed by a secondary reaction of diphenyl ether. Chlorobenzene (6.99 min) is also found in the degradation products of this polymer and arises from degradation of residual starting material (diphenylene oxide sulfonyl chloride).

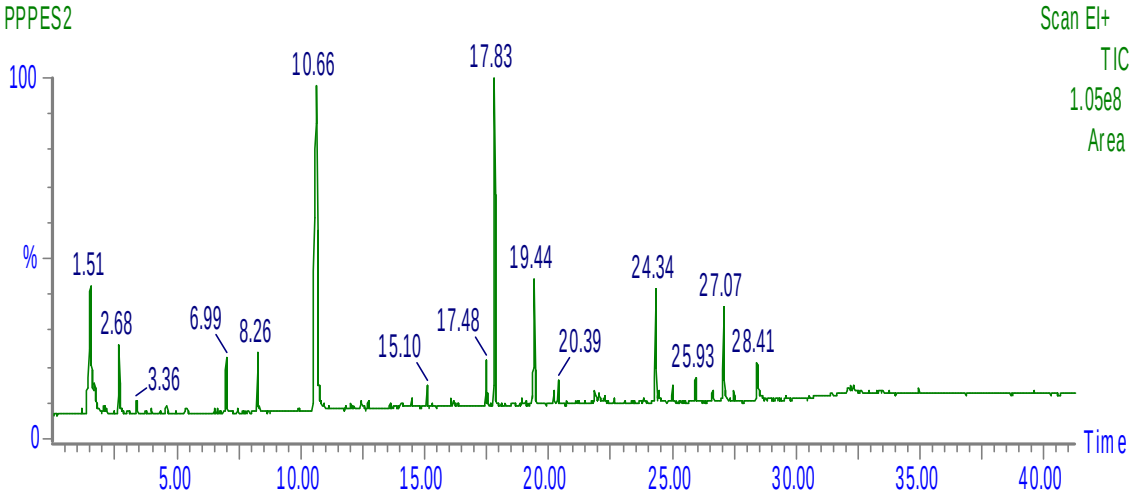

Figure 24. Pyrogram of a sample of poly(p-phenylene ether sulfone).

It is interesting to compare the pyrograms of the poly(sulfone) annd poly(p-phenylene ether sulfone) samples. There are no degradation products in the poly(p-phenylene ether sulfone) sample that are consistent with bisphenol A being used to prepare this polymer. For instance, neither 4-(1-methylethyl)phenol (15.02 min) nor 2-phenyl-2-(4-hydroxyphenyl)propane (21.31 min), which were found in the degradation products of the bisphenol A–based

poly(sulfone) (Figure 22), were found in the pyrolysis products of the poly(p-phenylene ether sulfone) sample.

Poly(arylsulfone) Radel R®

The structure of a typical poly(arylsulfone) is shown in Figure 25. It is the condensation product of bis(4-chlorophenyl)sulfone and 4,4'-dihydroxybiphenyl.

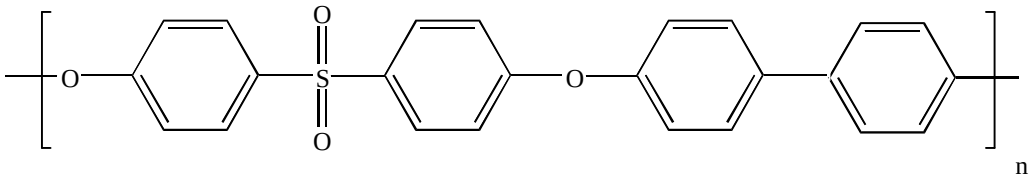

Figure 25. Chemical structure of a poly(arylsulfone).

The pyrogram of a sample of Radel R®, a commercial poly(arylsulfone), is shown in Figure 26.

Pyrolysis products include phenol (11.03 min), biphenyl (17.75 min), diphenyl ether (18.14 min), dibenzofuran (19.72 min), 4,4'-dihydroxybiphenyl (22.25 min), diphenylsulfone (24.54 min), phenoxybiphenyl (25.20 min) and 4,4'-phenoxyhydroxybiphenyl (27.23 min).

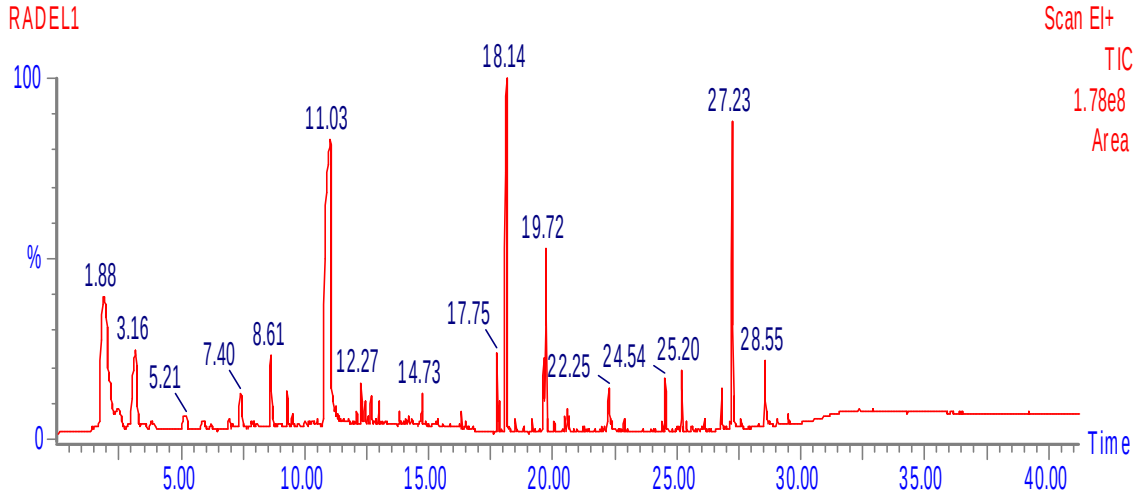

Figure 26. Pyrogram of a sample of Radel™, a commercial poly(arylsulfone).

With the exception of dibenzofuran, these degradation products are released following the scission of main polymer chain bonds. For instance, the release of diphenylsulfone requires

the breaking of two benzene ring/oxygen bonds. Dibenzofuran is formed by a secondary reaction of diphenyl ether.

The presence of pyrolytic degradation products containing the biphenyl moiety indicates that Radel R® is prepared using 4,4'-dihydroxybiphenyl as the diol. Poly(arylsulfone)s are also prepared using 2,2'-di(4-hydroxyphenyl)propane (bisphenol A) as the diol. Poly(arylsulfone)s prepared using bisphenol A would not release pyrolytic degradation products containing the biphenyl moiety.

Aromatic Poly(ester) Liquid Crystal Polymer - Xydar™

The structure of an aromatic poly(ester) liquid crystal polymer (LCP), prepared from 1,4-benzenedicarboxylic acid (terephthalic acid), 4-hydroxybenzoic acid, and 4,4'-dihyroxybiphenyl, is shown in Figure 27.

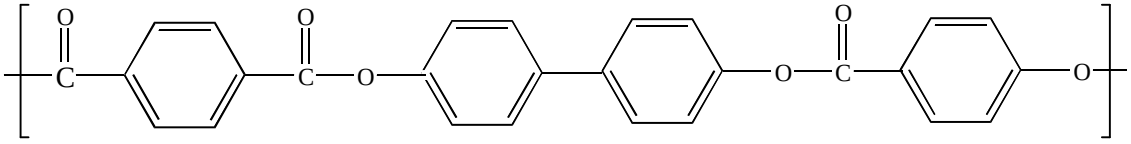

Figure 27. Chemical structure of an aromatic poly(ester) liquid crystal polymer.

The pyrogram of a sample of Xydar™, a commercial aromatic poly(ester) LCP, is shown in Figure 28.

Pyrolytic degradation products of Xydar™ include benzene (3.14 min), phenol (10.92 min), benzoic acid (14.64 min), 4-hydroxybenzaldehyde (17.13), biphenyl (17.74 min), diphenylether (18.05 min), hydroxybenzoic acid (19.51 min), 2-hydroxybiphenyl (19.64 min), dibenzofuran (19.70 min), phenylbenzoate (21.46 min), 4-hydroxybiphenyl (22.10 min), 2-hydroxybenzophenone (22.38 min), xanthone (23.93 min), the phenyl ester of hydroxybenzoic (25.62 min), and 4,4'-dihydroxybiphenyl (25.69 min).

The majority of these degradation products are released following the scission of polymer chain bonds. For instance, two of the three compounds used to prepare this LCP, hydroxybenzoic acid and 4,4'-dihydroxybiphenyl, are found in the pyrolytic degradation products of this polymer and are released after scission of carbon-oxygen/carbonyl carbon-oxygen and two carbonyl carbon-oxygen bonds respectively. Other degradations products, such as benzofuran and xanthone, are formed by secondary reactions that follow the scission of the main polymer chain bonds.

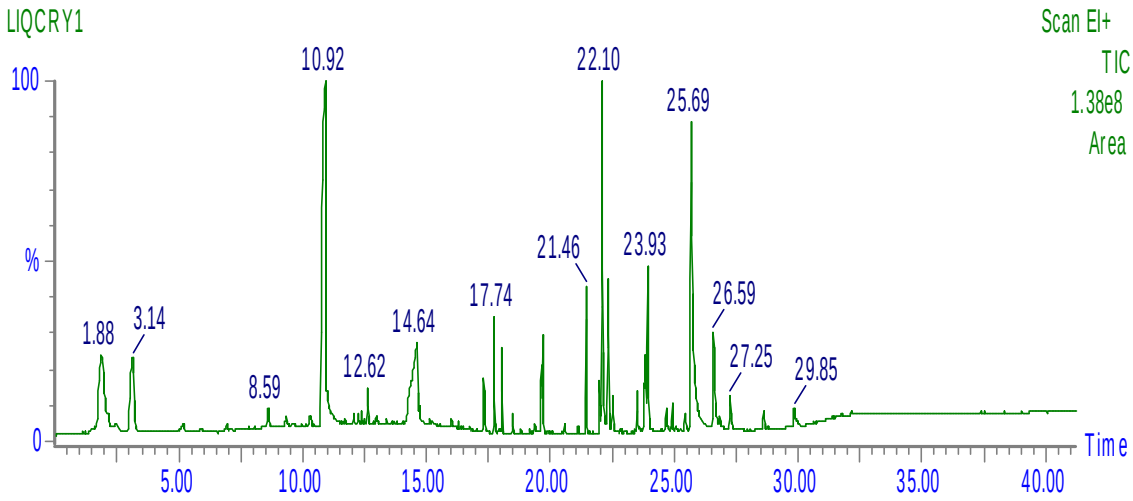

Figure 28. Pyrogram of a sample of Xydar™, a commercial aromatic poly(ester) liquid crystal polymer.

Polyamides

Polyamides are prepared from the condensation of diamines and diacids or by the polymerization of cyclic amides (lactams). For instance Nylon 6,6 is synthesized from 1,6-hexanediamine and 1,6-hexanedioic acid while Nylon 6 is synthesized from caprolactam. The diamine/diacid based polyamides will be discussed separately from the lactam based polyamides.

The diamine/diacid polyamides are named using the number of carbons in the diamine followed by the number of carbons in the diacid. For instance, Nylon 6,10 is prepared from 1,6-hexanediamine and 1,10-decanedioic acid.

The lactam based polyamides are named using the number of carbons in the monomeric lactams.

Polyamides degrade by a random chain scission mechanism.

Nylon 6,6

The chemical structure of Nylon 6,6 is shown in Figure 29. Nylon 6,6 is the condensation product of 1,6-hexanediamine and 1,6-hexanedioic acid.

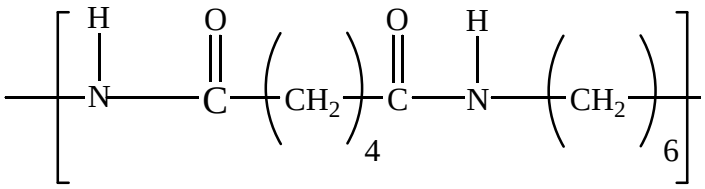

Figure 29. Chemical structure of a sample of Nylon 6,6.

A pyrogram of a Nylon 6,6 sample is shown in Figure 30.

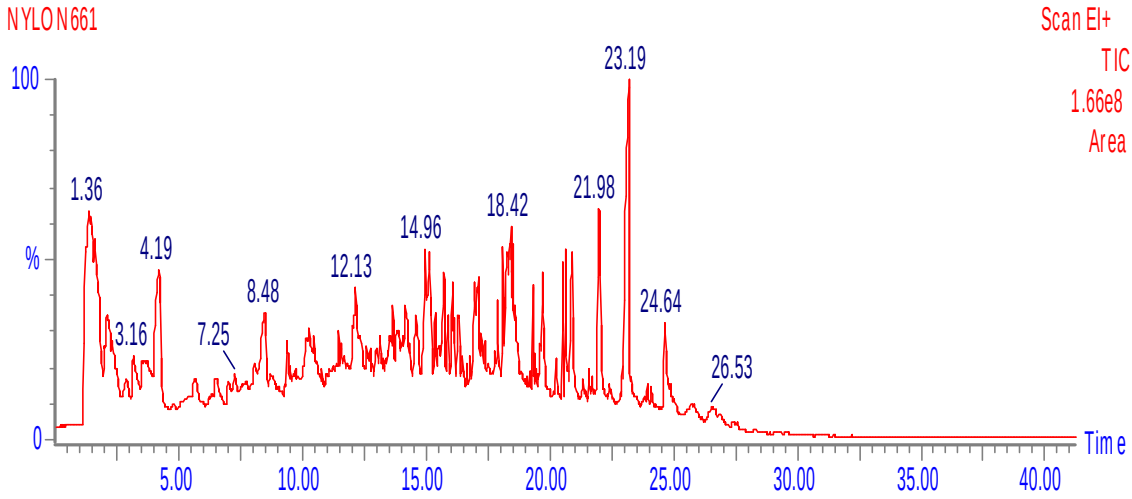

Figure 30. Pyrogram of a sample of Nylon 6,6.

Cyclopentanone (4.19 minutes) is a characteristic degradation product of Nylon 6,6[3]. Cleavage of a CH_2-C=O bond followed by CH_2 attack on the adjacent CH_2-C=O produces cyclopentanone.

Nylon 6,9

The chemical structure of Nylon 6,9 is shown in Figure 31. The polyamide is the condensation product of 1,6-hexanediamine and 1,9-nonanedioic acid.

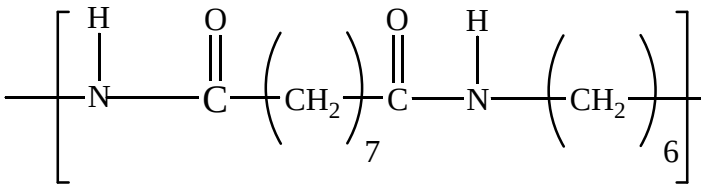

Figure 31. Chemical structure of a sample of Nylon 6,9.

The pyrogram of a sample of Nylon 6,9 is shown in Figure 32. The pyrogram of Nylon 6,9 is characterized by series of compounds with general formulas $C_nH_{2n-1}CN$ (n=6 and 7), $C_6H_{13}NHCO$-R (R= C_4H_9 to C_7H_{15}), and $RNHCO(CH_2)_7CN$ (R= C_4H_9, C_5H_9, C_6H_{11}, and C_6H_{13}). The retention times of the compounds in these three series are listed in Tables 1, 2, and 3 respectively.

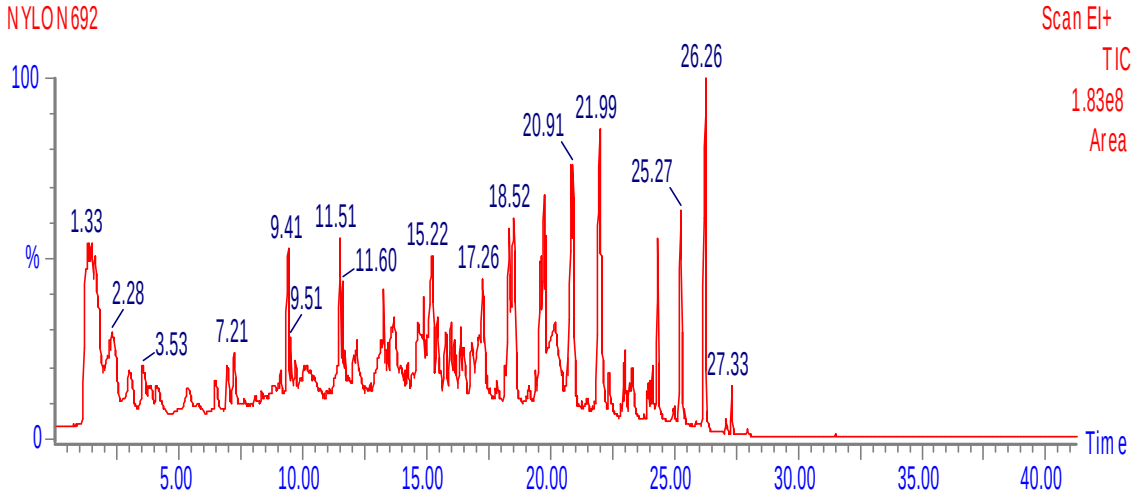

Figure 32. Pyrogram of a sample of Nylon 6,9.

Nylon 6,10

The chemical structure of Nylon 6,10 is shown in Figure 33. Nylon 6,10 is the condensation product of 1,6-hexanediamine and 1,10-decanedioic acid.

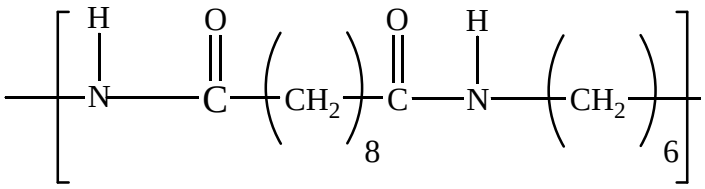

Figure 33. Chemical structure of a sample of Nylon 6,10.

The pyrogram of a sample of Nylon 6,10 is shown in Figure 34. As was observed for Nylon 6,9, the pyrogram of Nylon 6,10 is characterized by series of compounds with the general formulas $C_nH_{2n-1}CN$ (n=6 to 8), $C_6H_{13}NHCO$-R (R= C_4H_9 to C_8H_{17}), and $RNHCO(CH_2)_8CN$ (R= C_4H_9, C_5H_9, C_6H_{11}, and C_6H_{13}). The retention times of these three series of compounds are listed in Tables 1, 2, and 3 respectively.

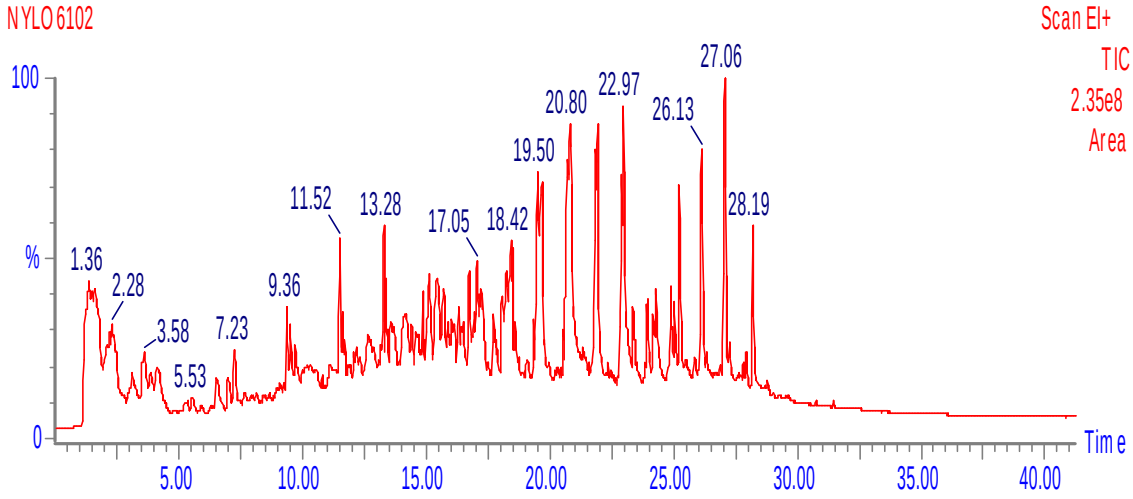

Figure 34. Pyrogram of a sample of Nylon 6,10.

Nylon 6,12

The chemical structure of a sample of Nylon 6,12 is shown in Figure 35. Nylon 6,12 is the condensation product of 1,6-hexanediamine and 1,12 dodecanedioic acid.

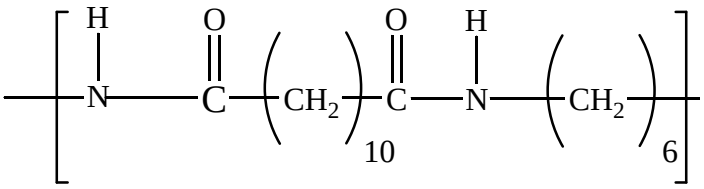

Figure 35. Chemical structure of a sample of Nylon 6,12.

The pyrogram of a sample of Nylon 6,12 is shown in Figure 36. The pyrogram of Nylon 6,12 is similar to both that observed for Nylon 6,9 and Nylon 6,10 in that it is characterized by three series of compounds with the general formulas $C_nH_{2n-2}CN$ (n=6 to 10), $C_6H_{13}NHCO$-R (R= C_4H_9 to $C_{10}H_{21}$), and $RNHCO(CH_2)_{10}CN$ (R= C_3H_5, C_3H_7, C_4H_9, C_5H_9, C_6H_{11}, and C_6H_{13}). The retention times of these three series of compounds are listed in Tables 1, 2, and 3 respectively.

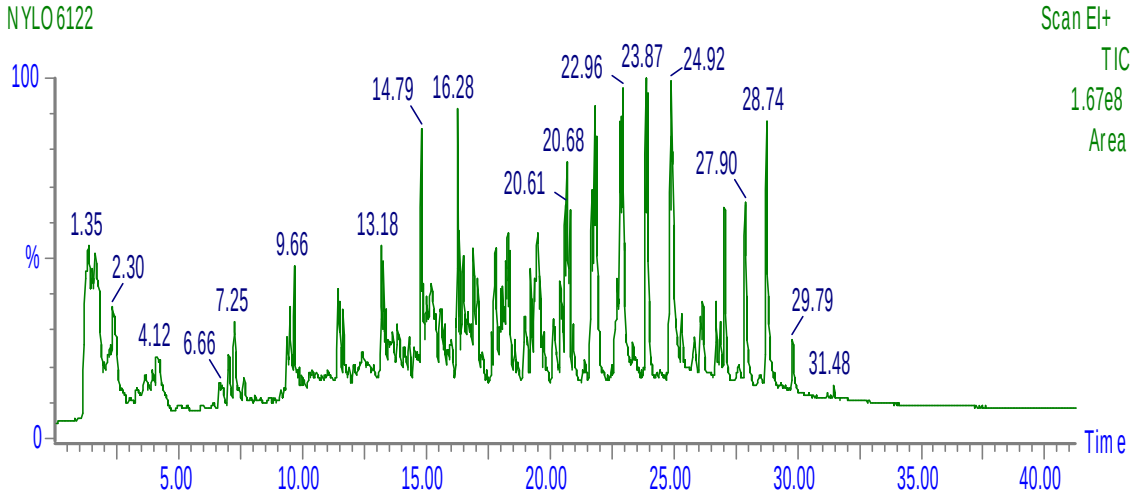

Figure 36. Pyrogram of a sample of Nylon 6,12.

Nylon 6,T

The chemical structure of Nylon 6,T is shown in Figure 37. This polyamide differs from the preceding diamine/diacid based polyamides in that an aromatic dicarboxylic acid is used in its preparation. The aromatic dicarboxylic acid used to synthesize Nylon 6,T is 1,4-benzenedicarboxylic acid (terephthalic acid).

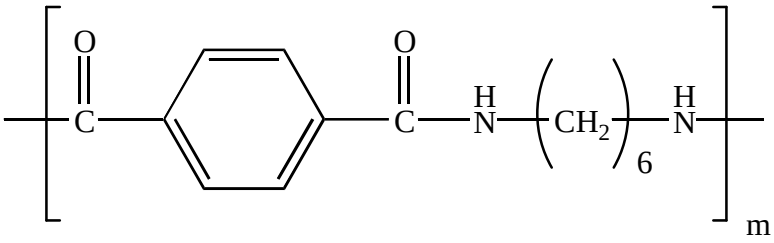

Figure 37. Chemical structure of Nylon 6,T.

The pyrogram of a sample of Nylon 6,T is shown in Figure 38.

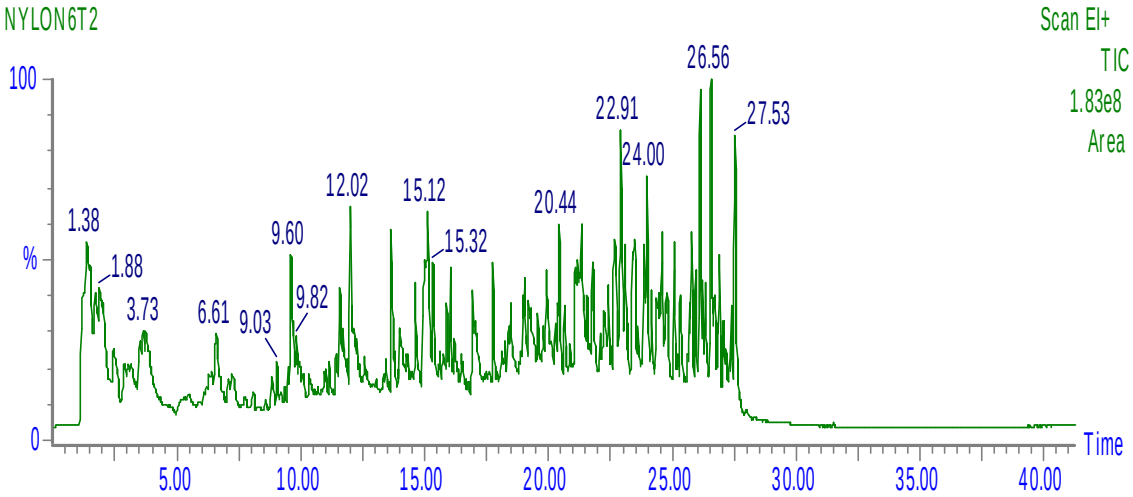

Figure 38. Pyrogram of a sample of Nylon 6,T.

There are several pyrolytic degradation products that arise from secondary reactions of compounds resulting from the cleavage of main chain bonds. These include benzonitrile (9.60 min), isoquinoline (14.00 min), and dicyanobenzene (14.92 min).

Nylon 6

The chemical structure of Nylon 6 is shown in Figure 39.

The pyrogram of a sample of Nylon 6 is shown in Figure 40. The major degradation product of this polymer is caprolactam (broad peak between 14.7 min and 15.8 min), the monomer used in its synthesis. Pyrolytic formation of the monomer is in contrast to the diamine/diacid polyamides discussed above and is indicative of the difference in the degradation mechanisms of polyamides prepared from cyclic amides and diamines and diacids. Depolymerization and the release of the cyclic monomer is a major pyrolytic degradation pathway of the polyamides prepared from cyclic amides. Another characteristic pyrolytic degradation product is $C_5H_9C(O)NH(CH_2)_5CN$ (24.67 min).

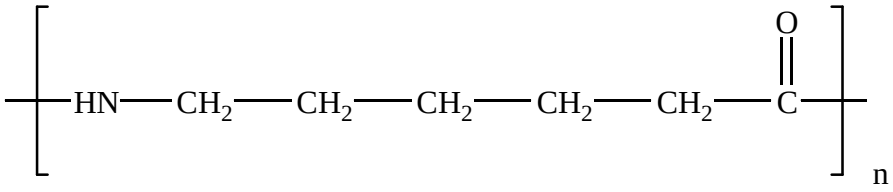

Figure 39. Chemical structure of Nylon 6.

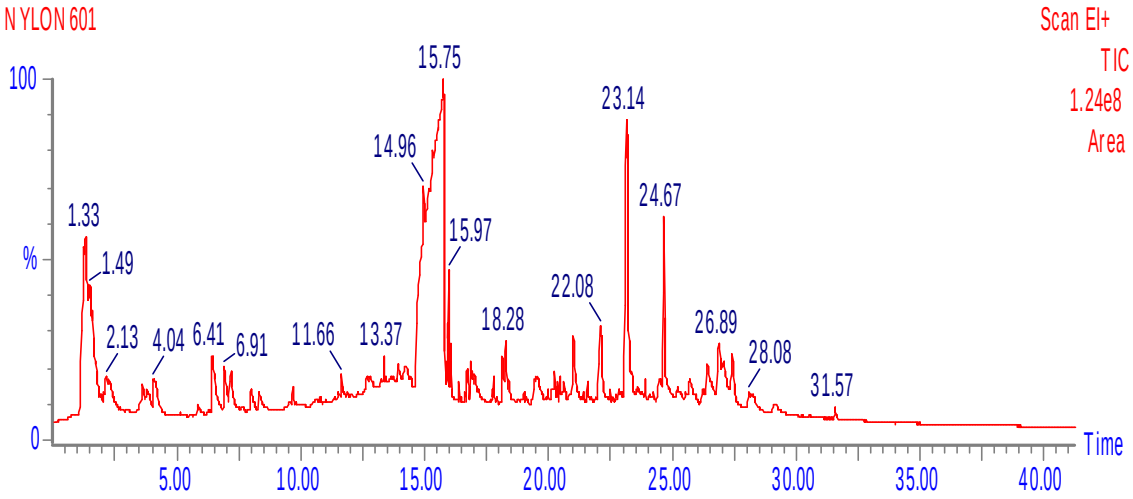

Figure 40. Pyrogram of a sample of Nylon 6.

Nylon 11

The chemical structure of Nylon 11 is shown in Figure 41.

The pyrogram of a sample of Nylon 11 is shown in Figure 42. The cyclic monomer used to prepare this polyamide, azacyclododecan-2-one, is a major degradation product (20.75 min).

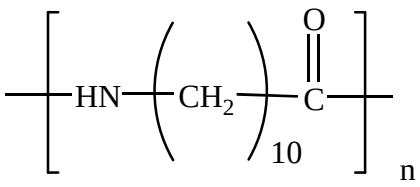

Figure 41. Chemical structure of Nylon 11.

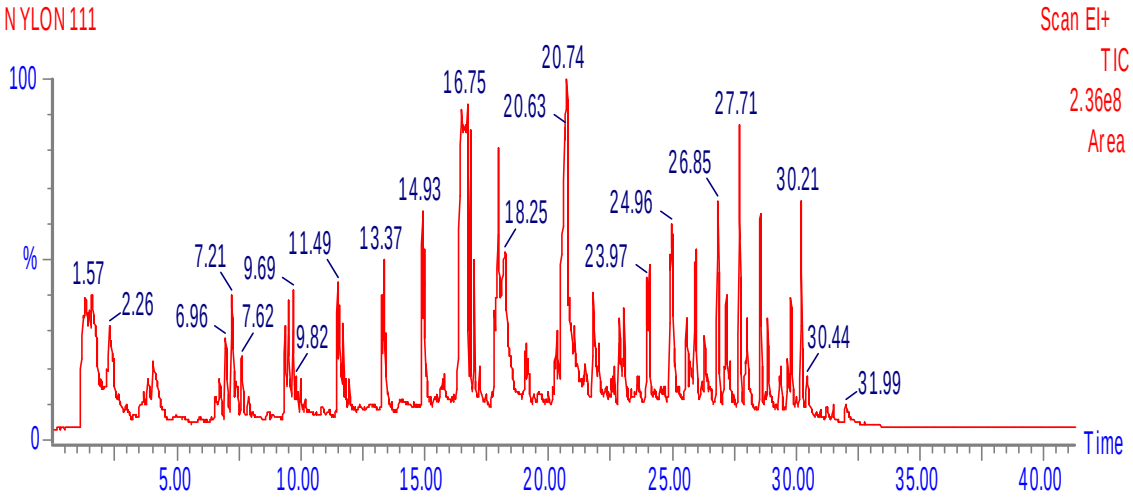

Figure 42. Pyrogram of a sample of Nylon 11.

Compounds with the general formulas $C_{10}H_{19}C(O)NHC_nH_{2n+1}$ and $C_{10}H_{19}C(O)NHC_nH_{2n-1}$ are also found in the degradation products. For instance, compounds with molecular weights of 321 and 323 give rise to the peak at 28.56 min and compounds with molecular weights 307 and 309 give rise to the peak at 27.71 min. The retention times and molecular weights of these two series of compounds are show in Table 4.

Nylon 12

The chemical structure of Nylon 12 is shown in Figure 43.

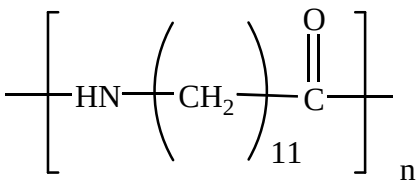

Figure 43. Chemical structure of Nylon 12.

The pyrogram of a sample of Nylon 12 is shown in Figure 44. The pyrolytic degradation of Nylon 12 releases a significant amount of the cyclic monomer, azacyclotridecan-2-one, used to prepare this polyamide (21.70 min). There are also a series of peaks from degradation products with the general formulas $C_{11}H_{21}C(O)NHC_nH_{2n+1}$ and $C_{11}H_{21}C(O)NHC_nH_{2n-1}$ (n = 2 to 10). For instance, compounds with molecular weights of 337 and 335 give rise to the peak at 29.35 min, compounds with molecular weights 323 and 321 give rise to the peak at 28.62 min and so on. The molecular weights and retention times of these two series of compounds are shown in Table 4.

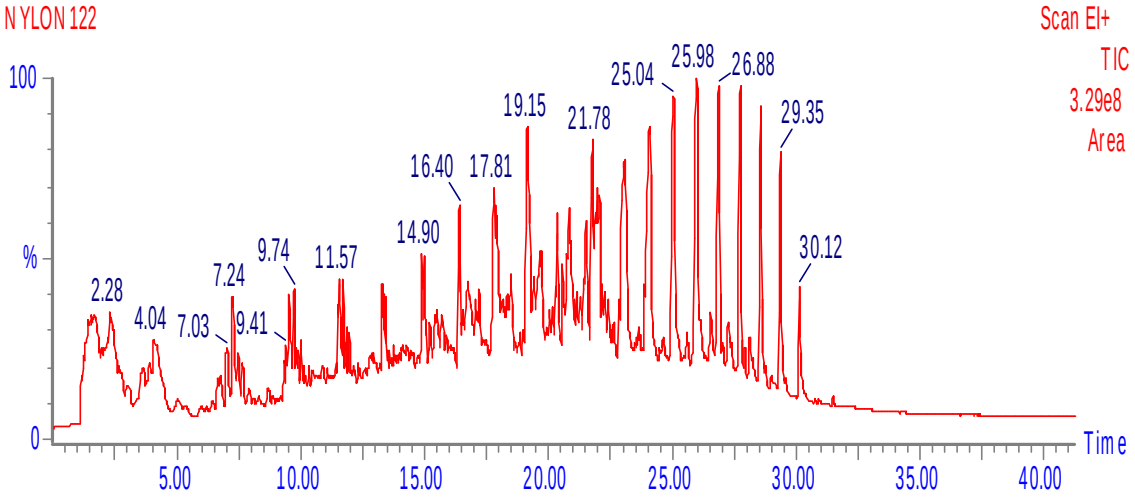

Figure 44. Pyrogram of a sample of Nylon 12.

Poly(ethylene terephthalate)

The chemical structure of poly(ethylene terephthalate) is shown in Figure 45. Poly(ethylene terephthalate) is prepared from a condensation reaction of terephthalic acid or dimethyl terephthalate and ethylene glycol.

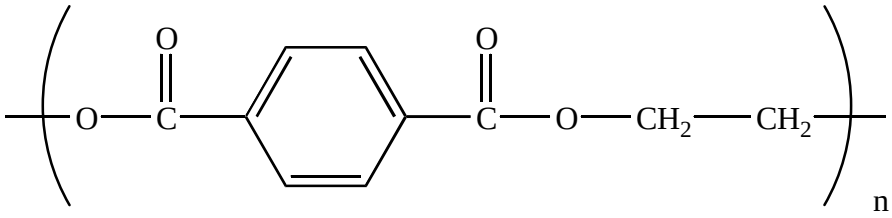

Figure 45. Chemical structure of a sample of poly(ethylene terephthalate).

The pyrogram of a sample of poly(ethylene terephthalate) is shown in Figure 46.

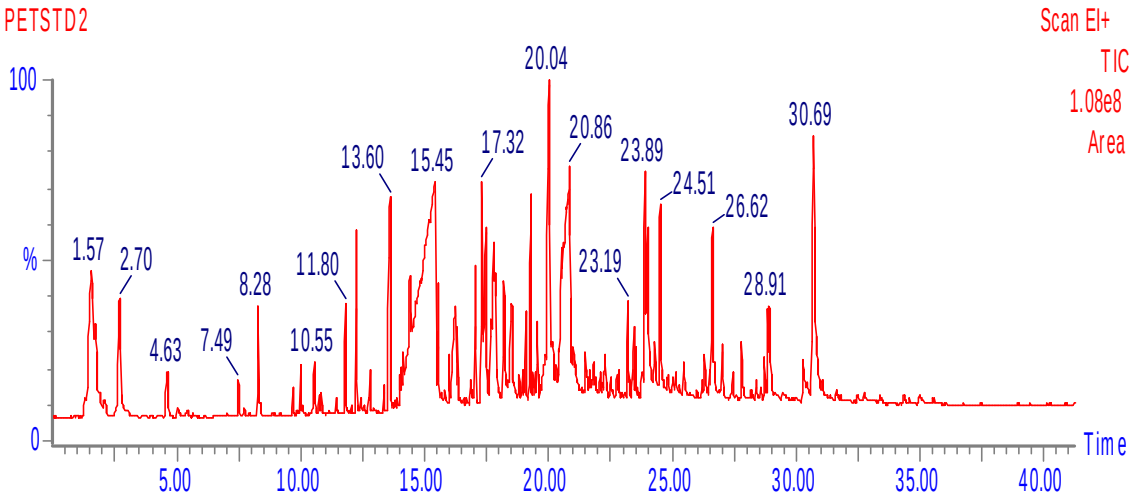

Figure 46. Pyrogram of a sample of poly(ethylene terephthalate).

One of the major pyrolytic degradation products of poly(ethylene terephthalate) is benzoic acid (large peak between 14.00 and 15.45 min). Benzene (2.70 min), benzaldehyde (9.98 min), ethenyl benzoate (13.60 min), the diethenyl ester of 1,4-benzenedioic acid (20.04 min), the monoethenyl ester of 1,4-benzenedioic acid (20.70 min) are other degradation products released following the scission of main polymer chain bonds. The mono (MW 192) and diethenyl (MW 218) esters of 1,4-benzenedioic acid are degradations products that reflect the monomeric compounds (1,4-benzenedioic acid or terephthalic acid and 1,2-ethanediol) used to synthesize this polymer.

Poly(carbonate)

The chemical structure of a bisphenol A-based poly(carbonate) is shown in Figure 47.

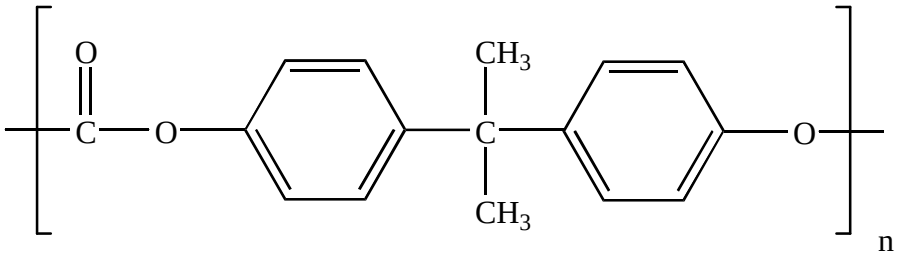

Figure 47. Chemical structure of a sample of poly(carbonate).

The pyrogram of a sample of poly(carbonate) is shown in Figure 48.

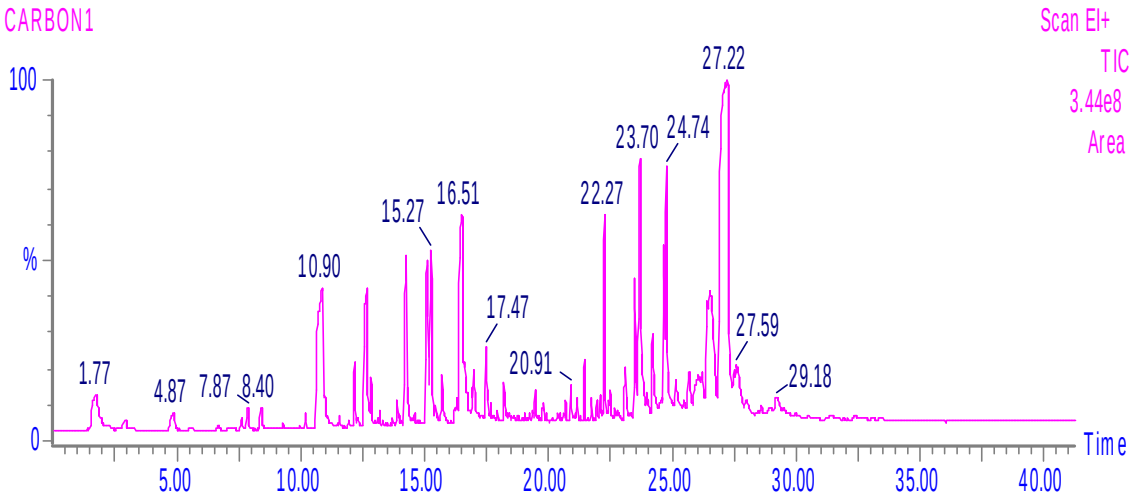

Figure 48. Pyrogram of a sample of poly(carbonate).

Pyrolytic degradation products that are indicative of the main polymer chain scission are phenol (10.90 min), 4-(isopropyl)phenol (15.27 min), 4-(2-propenyl)phenol (16.51 min), diphenyl carbonate (21.72 min), 2-(4-hydroxyphenyl)-2-phenylpropane (23.70 min), and bisphenol A (2,2-di(4-hydroxyphenyl)propane) (27.22 min). Many degradation products arise following secondary reactions of products formed from main polymer chain scission. These include methyl, dimethyl, and ethyl substituted phenols (between 12. 00 and 14.50 min), and benzofuran (15.10 min).

Poly(carbonate)/Poly(ester) Blend (Makroblend®)

The structures of the polymers that constitute this blend are shown in Figures 45 and 47. The pyrogram of a sample of Makroblend is shown in Figure 49.

The major degradation products of Makroblend include phenol (10.64 min), methylphenols (12.29 and 12.46 min), ethenyl benzoate (13.60 min), benzoic acid (broad peak between 14.00 min and 15.50 min), 4-(1-methylethyl)phenol (15.11 min), 4-(1-methylethenyl)phenol (16.32 min), the mono and diethenyl esters of 1,4-benzenedioic acid (20.70 min and 20.10 min), diphenylcarbonate (21.72 min), 2-(4-hydroxyphenyl)-2-phenylpropane (23.66 min), and bisphenol A (27.10 min).

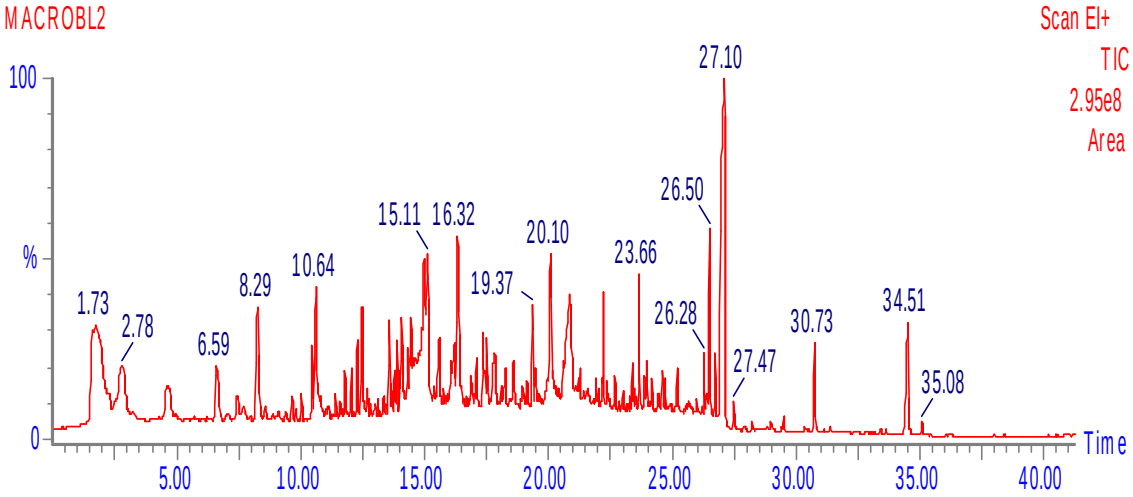

Figure 49. Pyrogram of a sample of a poly(carbonate)/poly(ester) blend.

Pyrograms of Makroblend, bisphenol A based poly(carbonate), and poly(ethylene terephthalate) samples are shown in Figure 50. As was observed for the poly(ethylene)/poly(propylene) and poly(phenylene oxide)/poly(styrene) blends, the pyrogram of the Makroblend sample is composed of degradation products characteristic of its constituent polymers, poly(carbonate) and poly(ethylene terephthalate). For instance, degradation products such as 4-(isopropyl)phenol, 4-(2-propenyl)phenol, diphenyl carbonate, 2-(4-hydroxyphenyl)-2-phenylpropane, and bisphenol A (2,2-di(4-hydroxyphenyl)propane) which are characteristic of bisphenol A based poly(carbonates), and benzoic acid, ethenyl benzoate, the diethenyl ester of 1,4-benzenedioic acid, the monoethenyl ester of 1,4-benzenedioic acid , which are characteristic of poly(ethylene terephthalate) are found in the pyrolytic degradation products of Makroblend.

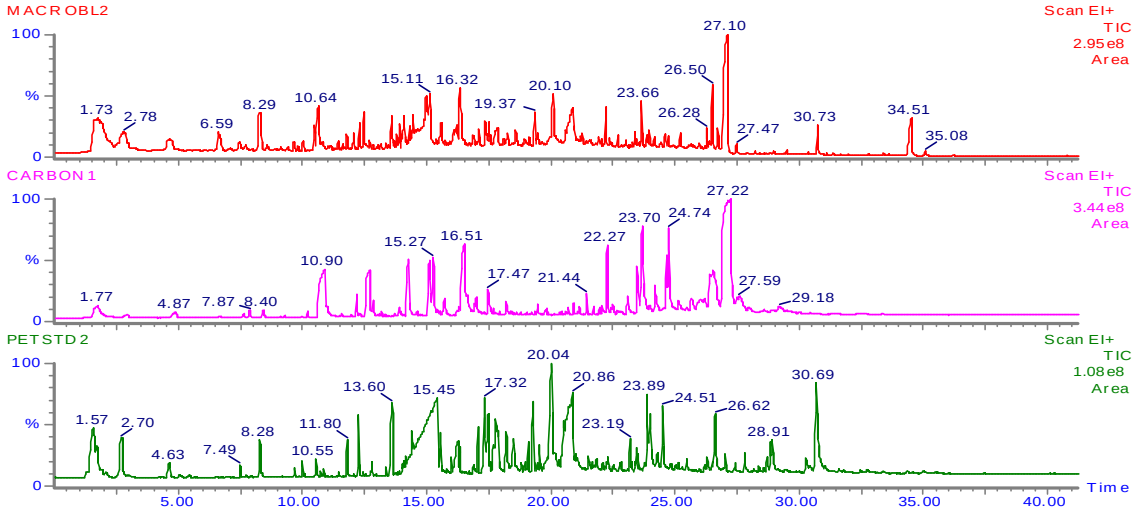

Figure 50. Pyrograms of top) Macroblend (poly(carbonate)/poly(ester) blend),middle) poly(carbonate), and bottom) poly(ethylene terephthalate).

Conclusions

There are a number of general observations that can be made about the polymers and their pyrograms discussed in this memorandum.

The pyrograms of the three polymer blends; poly(ethylene)/poly(propylene), Prevex™ - poly(phenylene oxide)/poly(styrene), and Makroblend™ - poly(carbonate)/poly(ethylene terephthalate), consist of the degradation products that are characteristic of the polymers that make up the blend. For instance, the pyrogram of the poly(ethylene-propylene) blend has the alkadiene/alkene/alkane triplets characteristic of the pyrolytic degradation of poly(ethylene) and the dimer, trimer, tetramer and so on of propylene characteristic of the pyrolytic degradation of poly(propylene). Similarly, the pyrograms of Prevex™ and Makroblend™ consist of degradation products that are characteristic of their constituent polymers.

The pyrograms of the thermoplastics with aromatic rings incorporated into the main polymer chain; poly(phenylene sulfide), poly(amide-imide), aromatic liquid crystal poly(ester), poly(imide), poly(arylsulfone), poly(sulfone), poly(phenylene oxide) and poly(carbonate), are characterized by degradation products arising from the cleavage of non aromatic main polymer chain bonds. The thermal/pyrolytic stability of the aromatic rings leads to preferential cleavage of the polymer chain at non aromatic main chain bonds. For instance, pyrolytic degradation of poly(phenylene sulfide) releases benzene thiol, diphenyl sulfide, phenyl 4-thiophenyl sulfide, and so on. These products arise from the cleavage of sulfur/benzene ring bonds. The pyrolytic degradation products of poly(amide-imide) can also be directly related to the cleavage of non aromatic main chain bonds. Referring to Figure 17 it can be seen that the release of aniline, phenol, 4-aminophenol, 1H-isoindole-1,3-(2H)-dione, diphenyl ether, 4-phenoxybenzenamine, and 2-phenyl-1H-isoindole-1,3(2H)-dione arise from the cleavage of non aromatic main chain bonds.

The three samples of poly(sulfone) , referred to as poly(sulfone), poly(p-phenylene ether sulfone) and poly(aryl sulfone), can be distinguished on the basis of their pyrolytic degradation products. For instance, the poly(sulfone) sample releases pyrolytic products characteristic of bisphenol A, while poly(p-phenylene ether sulfone) and Radel™ do not. Although the degradation products of poly(p-phenylene ether sulfone) and Radel™ are similar, Radel™ releases dihydroxybiphenyl while poly(p-phenylene ether sulfone) does not.

Nylons based on diacid/diamine chemistry can be easily distinguished from those based on cyclic lactam chemistry on the basis of the presence of cyclic monomer as a major degradation product of the lactam based poly(amide)s. Azacycloheptan-2-one (caprolactam), azacyclododecan-2-one, and azacyclotridecan-2-one are major degradation products of Nylon 6, Nylon 11, and Nylon 12 respectively.

The pyrolytic degradations products of diacid/diamine based poly(amide)s released series of degradations products whose structures were similar. For instance, Nylon 6,9, Nylon 6,10, and Nylon 6,12 released unsaturated nitriles of the general formula $C_nH_{2n-1}CN$ that arose from the degradation of the acid portion of the polymer. The maximum value of n increased from 7 (Nylon 6,9) to 8 (Nylon 6,10 and to 10 (Nylon 6,12). Nylon 6,6, Nylon 6,9, Nylon 6,10, and

Nylon 6,12 also released a series of n-hexylamides with the general formula $C_6H_{13}NHC(O)R$ where R was a saturated (C_nH_{2n+1}) or unsaturated (C_nH_{2n-1}) hydrocarbon. The maximum value of n in for any of the Nylons was two less than the number of carbons in the diacid used to prepare that poly(amide), for instance, n had a maximum value of 10 for Nylon 6,12. These same Nylons also released a series of N-alkenyl or N-alkyl nitrile amides of the general formula $RNHC(O)(CH_2)_nCN$ with n = 4, 7, 8, and 10 for Nylon 6,6, Nylon 6,9, Nylon 6,10 and Nylon 6,12 respectively.

Nylon 11 and Nylon 12 released series of N-alkyl or N-alkenyl amides with the general formulas $C_{10}H_{19}C(O)NHR$ and $C_{11}H_{21}C(O)NHR$ respectively.

Table 1. *Retention times of unsaturated nitriles released from the pyrolytic degradation of Nylon 6,9, Nylon 6,10, and Nylon 6,12.*

$C_NH_{2N-1}CN$	**MOLECULAR WEIGHT**	**NYLON 6,9**	**NYLON 6,10**	**NYLON 6,12**
n	***g/mol***	***Retention Time (min)***	***Retention Time (min)***	***Retention Time (min)***
5				
6	109	9.40	9.33	9.34
7	123	11.45	11.51	11.42
8	137		13.27	13.18
9	151			14.79
10	165			16.28

Table 2. *Retention times of hexyl amides of the general formula* ***$C_6H_{13}NHC(O)R$*** *released by the pyrolytic degradation of Nylon 6,6, Nylon 6,9, Nylon 6,10, and Nylon 6,12.*

$C_6H_{13}NHC(O)R$	**MOLECULAR WEIGHT**	**NYLON 6,6**	**NYLON 6,9**	**NYLON 6,10**	**NYLON 6,12**
R	***g/mol***	***Retention Time (min)***	***Retention Time (min)***	***Retention Time (min)***	***Retention Time (min)***
C_3H_5	169	17.10	17.05	17.07	17.06
C_4H_7	183	18.51	18.50	18.44	18.46
C_5H_9	197		19.73	19.67	19.67
C_6H_{11}	211		20.91	20.88	20.86
C_7H_{13}	225		21.99	22.00	21.99
C_8H_{15}	239			23.04	23.06
C_9H_{17}	253				24.08
$C_{10}H_{19}$	267				25.08

Table 3. *Retention times of the compounds with the general formula* ***RNHC(O)-$(CH_2)_N$CN*** *released from the pyrolytic degradation of Nylon 6,6, Nylon 6,9, Nylon 6,10, and Nylon 6,12.*

RNHC(O)-$(CH_2)_n$CN	**NYLON 6,6**		**NYLON 6,9**		**NYLON 6,10**		**NYLON 6,12**	
n	***4***		***7***		***8***		***10***	
R	***R T (min)***	***MW (g/mol)***	***R T (min)***	***MW (g/mol)***	***R T (min)***	***MW (g/mol)***	***R T (min)***	***MW (g/mol)***
C_3H_5							26.16	250
C_3H_7							26.30	252
C_4H_7				222		236		
C_4H_9	20.86	182	24.28	224	25.36	238	27.15	266
C_5H_9			25.20	236	26.16	250	28.04	278
C_5H_{11}	21.96	196		238		252	28.04	280
C_6H_{11}			26.19	250	27.08	264	28.82	292
C_6H_{13}	23.04	210	26.19	252		266		

Table 4. Retention times and molecular weights of the compounds with the general formulas C10H19C(O)NHR and C11H21C(O)NHR released from the pyrolytic degradation of Nylon 11 and Nylon 12 respectively.

SAMPLE	NYLON 11		NYLON 12	
R	***$C_{10}H_{19}C(O)NHR$***		***$C_{11}H_{21}C(O)NHR$***	
	Molecular Weight	***Retention time (min)***	***Molecular Weight***	***Retention time (min)***
C_4H_7	237	23.06	251	24.08
C_4H_9	239	23.06	253	24.08
C_5H_9	251	23.97	265	25.06
C_5H_{11}	253	24.04	267	25.06
C_6H_{11}	265	24.93	279	26.00
C_6H_{13}	267	25.02	281	26.00
C_7H_{13}	279	25.95	293	26.91
C_7H_{15}	281	25.95	295	26.91
C_8H_{15}	293	26.85	307	27.77
C_8H_{17}	295	26.85	309	27.77
C_9H_{17}	307	27.71	321	28.62
C_9H_{19}	309	27.71	323	28.62
$C_{10}H_{19}$	321	28.56	335	29.42
$C_{10}H_{21}$	323	28.56	337	29.42

References

1. David H. Ahlstrom, "Microstructure of Synthetic Polymers", pages 216-222 of Chapter 5 in **Pyrolysis and GC in Polymer Analysis**, Volume 29, Chromatographic Science Series, edited by S. J. Liebman and E. J. Levy, Marcel Dekker Inc. New York (1984). page 259-262 polylactams

2. ibid., page 226.

3. ibid., page 260.

List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
DRDC	Defence Research and Development Canada
Py	pyrolysis
GC	gas chromatography
MS	Mass spectrometry
Py-GC/MS	Pyrolysis gas chromatography/mass spectrometry
^{o}C	Degrees Celsius or Centigrade
min	minute
mg	milligram
m	meter
mm	millimeter
μm	micrometer
s	second
MW	molecular weight

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The identification of polymeric materials is important from several perspectives. The first is that the knowledge of the structure of a polymer yields a great deal of information on the properties of that polymer. This information is critical in determining if a polymer is suitable for a particular application. Identification of a polymer can also indicate changes in a polymer arising from in-service conditions. That is, have additives such as plasticizers or antioxidants been depleted or has the polymer absorbed compounds that alter its properties? Polymer identification is also critical in failure analysis.

In this Technical Memorandum pyrograms of commodity and engineering thermoplastics are presented. Pyrograms are chromatograms arising from a pyrolysis gas chromatography/mass spectrometry analysis. The pyrograms are discussed with emphasis on pyrolytic degradation products that are characteristic of the individual polymers. Often these can be related back to the structure of the polymer and can be used to differentiate between series of polymers with similar chemistry or identify the components of polymer blends.

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