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Review

Recent trends and developments in pyrolysis-gas chromatography

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Abstract

Pyrolysis-gas chromatography (Py-GC) has become well established as a simple, quick and reliable analytical technique for a range of applications including the analysis of polymeric materials. Recent developments in Py-GC technology and instrumentation include laser pyrolysis and non-discriminating pyrolysis. Progress has also been made in the detection of low level polymer additives with the use of novel Py-GC devices. Furthermore, it has been predicted that future advances in separation technology such as the use of comprehensive two-dimensional gas chromatography will further enhance the analytical scope of Py-GC.

Keywords: Pyrolysis; GC; Polymers; Laser pyrolysis; Non-discriminating pyrolysis; Polymer additives

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15 **1. Introduction**

17 Pyrolysis has been used extensively over the last 20 to 30 years as an analytical technique in which
18 large molecules are degraded into smaller volatiles species using only thermal energy. The ultimate
19 objective of analytical pyrolysis is to use the chromatographic information of pyrolysis products to
20 determine the composition or structure of the original sample. The complexity of polymeric materials
21 can vary extensively and they can be very challenging to analyse. Pyrolysis, combined with modern
22 analytical methods, such as gas chromatography and/or mass spectrometry (Py-GC/MS) has become a
23 quick, convenient and powerful tool for characterising polymers from involatile, complex
24 heterogeneous samples. Previous reviews on Py-GC instrumentation, methods and applications were
25 published by Wampler [1] and Wang [2] in 1999 and Moldoveanu [3] in 2001. Since this time there
26 have been major instrumental developments in laser pyrolysis systems and non-discriminating
27 pyrolysis techniques as well as progress in the use of Py-GC for the detection of low level additives in
28 polymers. This review mainly covers the period from 1999 to 2007 but also included are references to
29 literature before this period that appear not to have been covered in previous reviews.

32 **2. Pyrolysis-GC technique**

34 *2.1 Instrumental configuration*

36 The standard configuration of a pyrolysis-GC instrument has been discussed previously and largely
37 remains the same in that the pyrolysis device, or pyrolyzer, is interfaced with the analytical column of
38 the GC via the injection port [2]. A flow of inert gas, such as nitrogen or helium, flushes the
39 pyrolyzates into the column, where components are separated. As discussed by Wampler, capillary
40 columns offer the advantage over packed columns of higher resolution [1]. The detection method used
41 is typically mass spectrometry but other GC detectors have also been employed depending on the
42 intentions of the analysis. Nevertheless, instrument configuration is often varied. Newly developed
43 thermal analysis equipment designed to enhance performance may replace existing ones or be
44 incorporated in order to meet specific applications. Such developments include the use of lasers as a
45 fragmentation source and more recently a technique called in-column or non-discriminating pyrolysis,
46 all of which are discussed in detail below. This constant refinement of instrumental devices and
47 parameters during the past 20 years provides an expansive record on the pyrolysis of polymers.

1 2.1.1 *Types of pyrolyzers*

2
3 The three most commonly used and recognised pyrolyzers for GC are the microfurnace, Curie-point
4 and resistively heated filament [1-2,4-6].

5 The microfurnace rapidly raises the temperature of the sample until the pyrolysis temperature is
6 reached and then maintains this temperature for the desired pyrolysis time. The samples are either
7 injected or dropped into the pyrolysis zone by liquid syringe, solid plunger syringe or by using a small
8 cup. The desired characteristics of this type of pyrolyzer, such as reproducibility, have always been
9 difficult to develop [4]. Although much improved, most available furnaces still suffer from the relative
10 drawback of rise times of several seconds [7]. Tsuge et al. developed a multifunctional microfurnace
11 pyrolyzer for pyrolysis-GC and evolved gas analysis of various synthetic and natural materials [5,8].
12 The system was composed of a double shot microfurnace pyrolyzer with a sophisticated temperature-
13 control device; a GC equipped with an ultrahigh-temperature metal, chemically inert capillary
14 separation column; and a quadrupole MS with an electron impact (EI) and/or chemical ionization (CI)
15 source. It proved to be a very effective tool for a wider range of applications including, the structural
16 characterisation of copolymer-type polycarbonates (PCs), the determination of flame-retardant
17 mechanisms of PC, trace determination of stabilizers, the rapid characterisation of natural products, and
18 forensic identification of various drugs and oils.

19 Curie-point pyrolyzers accurately reproduce pyrolysis conditions using ferromagnetic metals. The
20 sample, which is positioned on to the end of a pyrolysis wire made from an appropriate ferromagnetic
21 alloy, is inserted into the pyrolyzer and rapidly heated using a high frequency induction coil. The
22 temperature ceases to rise when the Curie-point of the metal has been reached; that is the exact
23 reproducible temperature at which the ferromagnetic material loses its magnetism. At this point the
24 temperature remains constant until the coil is switched off [7]. In contrast to the microfurnace, the rise
25 time of Curie-point pyrolyzers is much quicker from 0.2 to 0.4 seconds. However, the choice of
26 different pyrolysis temperatures is limited since they are determined by the Curie-points of available
27 materials [9]. Buco et al. used Curie-point Py-GC/MS for the determination of polyaromatic
28 hydrocarbons (PAHs) in contaminated soil [10]. The technique proved particularly effective for low-
29 molecular-mass PAHs but lacked in sensitivity for quantification of high-molecular-mass PAHs. It
30 demanded a short operating time and required no extraction solvent. In addition, the results showed
31 good accuracy for the measured PAHs when compared with a certified soil.

32 Filament pyrolyzers can acquire a controlled pyrolysis temperature extremely quickly by using a
33 piece of resistive metal. An initial pulse of heating at a high voltage produces a current through the
34 metal causing the filament to heat rapidly until the programmed pyrolysis temperature is reached. The
35 pyrolysis temperature is maintained by reducing the voltage. Various commercial models of the
36 Pyroprobe appear to be the most widely used filament pyrolyzer. Samples that are soluble in a volatile
37 solvent are pyrolysed using a ribbon probe, those that are not are heated using a coil probe [4]. Whilst
38 samples are added directly onto the ribbon probe, quartz tubes are used to hold the samples before
39 being inserted into the coil probe. With regards to the latter, the exact pyrolysis reaction time is
40 difficult to determine since the sample never comes into direct contact with the filament [9].
41 Reproducibility with this system is very good providing that care is taken to ensure consistency with
42 sample size and positioning [4,11].

43 Heated filament and Curie-point pyrolysis result in less secondary pyrolysis products compared to
44 furnace pyrolysis and thus, the resulting pyrograms are easier to interpret. A major disadvantage exists
45 with all three conventional pyrolyzers in that because they are mounted external to the GC system, they
46 are prone to the deposition of higher-boiling point pyrolyzates and condensation of reaction products in
47 the transfer line. This often results in sample losses and discrimination of high-molecular weight
48 components [9,12].

1
2 *2.1.2 Importance of pyrolysis-GC interface*
3

4 The rapid and efficient transfer of pyrolysis products from the pyrolysis zone to the GC column is
5 vital in order to attain good peak resolution. The interfacing of these two devices is therefore very
6 important. Several parameters for the pyrolyzer have been identified in order to achieve this [1]. The
7 pyrolyzer needs to heat the sample as instantaneously as possible to prevent drawn out transfer of the
8 pyrolyzates through the injection port. It also needs to have a small internal volume and a rapid carrier
9 flow to make sure all of the volatiles are swept out and onto the column and are not left in the hot zone
10 to undergo secondary pyrolysis. Finally, a small sample size is essential to ensure that all of it degrades
11 rapidly, and that the column capacity is not exceeded. At too large a sample size, parts of the sample
12 may pyrolyze before others affecting reproducibility. As a result of these operating conditions,
13 interfacing between the pyrolyzer and the GC injection port should be kept minimal to reduce the
14 surface area and volume through which the pyrolyzate compounds travel. It should also be kept hot
15 and insulated to eliminate cold spots and prevent condensation reactions.

16 The above conditions are not always attainable or suitable for particular experiments and variations
17 always occur. For example, lower temperatures are often used to study the degradation kinetics of a
18 material i.e. its thermal stability and degradation mechanisms.
19
20

21 *2.1.3 Types of detectors*
22

23 The purpose of a detector used in conjunction with pyrolysis-GC is to monitor the carrier gas as it
24 leaves the column and respond to changes in its composition as solutes are eluted. Ideally a detector
25 should show a rapid response time, a wide range of linear response and high sensitivity. Mass
26 Spectrometry continues to be the most widely used detector in qualitative and quantitative polymer
27 analysis. The main advantage with MS is that it preserves the complex patterns of the initial sample by
28 means of a mass spectrum corresponding to each peak in the GC profile, therefore allowing for the
29 characterisation of polymers, the identification of additives and contaminants in polymeric samples and
30 the determination of degradation mechanisms. The different methods of sample ionization available
31 for MS allow for different degrees of fragmentation of the sample. Electron impact ionization involves
32 the bombardment of sample molecules with high energy electrons and is the usual choice for the
33 identification and structural analysis of complex macromolecules because it results in a higher degree
34 of dissociation. Chemical ionization has also been used in polymer analysis for much gentler, more
35 selective ionization whereby much less dissociation into ions of smaller mass occurs. Recently an
36 alternative selective ionization method, metastable atom bombardment, has been reported [13-15]
37 allowing the direct and fast insertion of samples into the mass spectrometer reducing analysis time.
38 Quadrupole MS analysers, in particular, offer different modes by which mass spectra can be acquired
39 depending on the purpose of the investigation. Selected ion monitoring (SIM) compared to total ion
40 monitoring is a much more sensitive scanning mode for target compound identification. Instead of
41 completing full scans of the chromatogram and collecting all of the ion fragments, SIM only measures
42 and records pre-selected ions for a given retention time window. Thus if fragments were created at m/z
43 values other than those selected, data regarding those ions would not be recorded. SIM requires the
44 retention data of compounds to perform a scan and in the case of co-eluting pyrolysis products; it is not
45 able to distinguish between two compounds with the same mass ions and retention time.

46 Magnetic, quadrupole, ion trap and time-of-flight mass spectrometers have all been successfully
47 coupled to conventional Py-GC instruments. The rapid analysis of polymers has specifically been
48 achieved using time-of-flight mass spectrometry (TOF-MS) [11,13]. TOF-MS can acquire high-
49 density data across narrow GC peaks and has proven to be a suitable detection system for fast GC

1 separations without compromising the chromatographic peak information. There is an extensive
2 amount of literature available on the use of Py-GC/MS for a wide range of applications, some of which
3 will be mentioned throughout this review and some of which have been reviewed in a recent paper by
4 Peacock and McEwen [16].

5 Isotope-ratio mass spectrometry (IRMS) has also been successfully combined with Py-GC. IRMS
6 allows for the highly precise analysis of the stable-isotopic composition of organic compounds
7 separated by GC. All IRMS instruments work in EI mode, use a single magnetic-sector analyzer, and
8 multiple Faraday detectors for analog measurement of ion currents. A more detailed overview and
9 evaluation of IRMS is provided in a recent paper by Sessions [17]. Although not yet a widely used
10 technique, Py-GC/IRMS has proven to be useful for some applications. Pel et al. performed cytometric
11 cell sorting and compound-specific Py-GC/IRMS analysis to determine population-specific isotopic
12 signatures and growth rates in cyanobacteria-dominated lake plankton [18]. They reported that Py-
13 GC/IRMS was able to analyse very small samples and reduced the chances of contamination and
14 sample loss during handling. Impressed with the resolution achieved, they also recognized the
15 potential of Py-GC/IRMS in the future analysis of plankton dynamics. A similar study used Py-
16 GC/IRMS to determine planktonic community structure and trophic interactions and further
17 recommended the technique for carbon isotope-based food web studies [19]. In a more unusual study,
18 Py-GC/IRMS was used to obtain isotopic and structural information from the macromolecular material
19 in meteorites [20]. The results highlighted the ability of the technique to analyse milligram-sized
20 samples without compromising the resolution. Gleixner et al. studied the individual turnover rate of
21 specific carbohydrates, lignin, lipids and N-containing compounds from French arable soil using Curie-
22 point Py-GC/IRMS [21]. Again its potential as a technique to analyse organic compounds was
23 highlighted.

24 Differential mobility spectrometry (DMS) [22] and ion mobility spectrometry (IMS) [23-25] are
25 recognized methods for the detection of chemical and biological agents (gases, vapors and aerosols) in
26 field settings. As advanced portable instruments they are small, highly sensitive, require little power
27 and are capable of fast analysis times. Py-GC/IMS has proved particularly useful for the detection and
28 identification of certain degradation compounds resulting from the pyrolysis of biological material,
29 such as bacterial spores which could be used as biological warfare agents. Open and closed sample
30 introduction tubes have been used in the Py-GC/IMS system for the detection of biological aerosol
31 particulates and chemical compounds in water respectively. A study in 2001 made improvements to an
32 existing Py-GC/IMS system in order to increase the amount of pyrolyzate compound information
33 reaching the IMS detector [23]. The airflow enhancement through the pyrolysis tube allowed for an
34 increase in the previously observed biomarkers for aerosols. The altered Py-GC/IMS instrument was
35 subjected to several outdoor aerosol trials in which it was shown to provide information regarding the
36 biological or non-biological nature of an aerosol and more specifically discriminate between aerosols
37 of a gram-positive spore, a gram-negative bacterium, and a protein. Yinon provides a comprehensive
38 review on instrumental advances and developments in IMS and further assesses its ability as a fast,
39 general analytical measurement device [24]. A recent study compared both open tube and closed tube
40 sample introduction Py-GC/IMS systems for the analysis of water contaminated with a surrogate
41 chemical warfare agent [25]. Results showed that the limit of detection for the VX nerve agent
42 surrogate was lowered by two orders of magnitude for the closed injector compared to the open tube
43 system, making the closed tube Py-GC/IMS system more suitable for detecting chemicals in liquids.

44 Besides MS [26-30] and mobility spectrometers, other Py-GC detection methods have been reported
45 for a wide variety of applications. These include, flame ionization detection (FID) [31-36] and atomic
46 emission detection (AED) [37-40].

47 48 49 2.2 Sample preparation

1
2 Often, time consuming pre-treatments of the sample are required to make it amenable for Py-GC/MS
3 analysis. Depending on the nature of the sample, this can involve a simple hydrolysis or dissolution
4 step and/or a more complex derivatization process.
5

6 7 *2.2.1 Derivatization*

8
9 Derivatization involves the conversion of non-volatile polar or thermally sensitive compounds into
10 related more volatile derivatives. It is a well established technique in pyrolysis-GC, extending the
11 capabilities of pyrolyzate analysis by improving the behaviour of the analyte during separation in the
12 column, modifying the thermal degradation pathway or enhancing detectability of the analyte.
13 Different methods of derivatization have been reported, namely hydrogenation, methylation and
14 silylation, whereby the hydroxyl, carboxyl and amino functional groups in polar compounds are
15 converted into much less polar methyl, trimethyl or trifluoroacetyl derivatives of greater volatility using
16 appropriate reagents. The most commonly used derivatising reagent is tetramethylammonium
17 hydroxide (TMAH) although other quaternary ammonium hydroxides have also been reported as
18 effective reagents. Haffenden and co-workers developed a novel Py-GC/MS based methodology to
19 analyse the composition of non-volatile residues of Maillard reaction products in two separate studies
20 [41,42]. Both studies involved a post-pyrolytic in-situ derivatization technique, the first using
21 hexamethyldisilazane (HMDS) and the second using trimethylsilyldiethylamine as silylating reagents.
22 The application of the technique indicated the formation of several derivatives in both cases. The
23 analytical characterisation of diterpenoid and acrylic resins employed in art works has been achieved
24 using an on-line derivatization method using HMDS reagent and Py-GC/MS [43,44]. Results obtained
25 were compared with previously reported results from in-situ thermally assisted hydrolysis and
26 methylation with TMAH. Several non-reported trimethylsilylated derivatives of compounds present in
27 the diterpenoid resins were identified. In both cases, improved sensitivity, better resolution of the most
28 representative peaks and more simplified, well-resolved chromatograms were obtained by using HMDS
29 as a derivatizing reagent.

30 Thermally assisted hydrolysis and methylation (THM) is an alternative on-line derivatization
31 technique for Py-GC/MS, which is much simpler and faster compared to wet chemically derivatization
32 methods. Asperger and co-workers analysed natural waxes using THM in the presence of TMAH,
33 carried out on a filament pyrolyzer [45,46]. They found THM to be a very suitable derivatization
34 method which was able to overcome problems such as the generation of non-specific pyrolyzates
35 observed in conventional Py-GC analysis of waxes. The method enabled both rapid fingerprinting and
36 detailed compositional analysis by means of structural elucidation of the THM products. The effect of
37 TMAH used in THM, in comparison with the effect of sodium hydroxide on the slow pyrolysis of
38 cotton cellulose has been reported [47]. Information regarding the reactive decomposition of cellulose
39 was obtained using Py-GC/MS. In a recent study, Ikeya et al. compared an off-line methylation
40 method using carbanion and methyl iodide reagent with thermally assisted hydrolysis and methylation
41 using TMAH on Py-GC analysis of humic and fulvic acids [48]. The off-line methylation proved to be
42 the better method as it produced additional information on structural unit of humic substances.

43 There are a number of excellent reviews available on derivatization methods. Wang discussed both
44 pre and post-derivatization techniques adapted for Py-GC analysis [2]. Particular focus was placed on
45 the developments in pre-pyrolysis derivatization, which is used to convert the functional group in the
46 polymer to obtain a favourable degradation pathway during pyrolysis. A review on Py-GC/MS by
47 Moldoveanu in 2001 reported advancements in derivatization techniques including methylation and
48 silylation [3]. The same year, a review by Challinor on the development and applications of on-line
49 and off-line thermally assisted hydrolysis and methylation reactions in analytical pyrolysis was

1 published [49]. Trimethylsulphonium hydroxide (TMSH), tetramethylammonium acetate (TMAAc)
2 and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) reagents provided more specific advantages
3 when compared to TMAH where particular applications were required. A recent review by Halket and
4 Zaikin published in 2006 describes on-line derivatization methods employed in mass spectrometry,
5 including Py-GC/MS [50].
6
7

8 *2.3 Instrumental developments*

9

10 Gains in chromatographic sensitivity are continually being made with improved techniques and
11 instrumentation, including the design of sophisticated gas inlet systems and interfaces which improve
12 the efficiency of the trapping and transfer of gaseous products to the GC column. In addition, progress
13 continues to be made with GC detectors including mass spectrometry, which also contributes to the
14 ever increasing power of Py-GC systems. However, details regarding such improvements are beyond
15 the scope of this review. The most significant instrumental improvements in pyrolysis-GC include
16 laser pyrolyzers for the analysis of microscopic samples, and non-discriminating pyrolysis for the
17 analysis of high-molecular weight pyrolysis products.
18
19

20 *2.3.1 Laser pyrolysis-GC*

21

22 Micro analytical techniques that facilitate the separate analysis of distinct regions within complex
23 heterogeneous samples have an increasing application in polymer analysis. Laser pyrolysis-gas
24 chromatography (laser Py-GC), or laser micropyrolysis-GC, is one such technique, however studies
25 which have utilized this method are limited. Although early works involving the analytical technique
26 and its applications date back to the early 1970s, recent studies are still primarily focussed on
27 instrumental development. This lack of progress is due to a number of factors including i) the
28 sensitivity limitations of existing chromatographic technologies required for testing the typically small
29 product concentrations; ii) the inter-disciplinary skills needed; iii) the financial expense of the different
30 instruments; iv) the difficulties involved with interfacing these instruments; v) the lack of
31 understanding of the interactions between laser and material; and vi) the issue that not all samples are
32 compatible with laser radiation to produce pyrolysis products [51,52].

33 The laser pyrolysis or micropyrolysis system (Fig. 1) consists of the laser and associated optical
34 device; the sample chamber and cold trap; and a GC/MS for separation and detailed molecular
35 characterisation of the pyrolysis products (i.e. molecular fingerprinting). Interfacing between the
36 sample chamber and the cold trap inside the GC injection port has been achieved using a heated
37 transfer tube, a sophisticated gas inlet system, or more recently using a specially designed pyrolysis
38 valve interface which can function both on-line and off-line (CDS Analytical, model 1500). Solid
39 polymer samples of small size are mounted in the sample chamber and then viewed through the
40 microscope until a suitable area to be pyrolyzed is located. The laser is focussed through the
41 microscope objective and the targeted area is pyrolyzed using either a continuous wave or a number of
42 high-energy pulses. The size of the crater formed and thus the intensity of pyrolyzate distribution is
43 dependent upon the degree of focussing and the time span and energy setting of the laser. During
44 pyrolysis, a helium carrier gas sweeps the pyrolyzates from the sample cell and (ultimately) onto the
45 cold trap via a heated transfer line. Once collected, components are desorbed onto the GC column for
46 subsequent analysis.

47 The use of a laser and a microscope in place of a conventional pyrolyzer such as those mentioned
48 earlier, facilitates visual observation of the sample and focusing of the laser beam onto a specific area
49 and layer to achieve selective heating. This can therefore provide useful data on the molecular

1 compositional units of macromolecules in situ, something that traditional bulk pyrolysis methods
2 cannot. The short duration laser beam is collimated enabling it to target the isolated components with
3 an immense amount of thermal energy [53]. This thermal interaction between laser and material
4 initiates a shock which in turn produces a range of pyrolysis products [11]. These extreme heating
5 rates are characteristic of laser pyrolysis and also serve a great purpose in minimizing secondary
6 pyrolysis reactions.

7 A variety of different lasers can be used as a fragmentation source depending on the type of material
8 being pyrolysed. Greenwood et al. analysed various organic fossil samples, namely Sydney Basin
9 torbanite, Green River oil shale and Tasmanite oil shale, to test the efficiency and potency of laser
10 micropyrolysis-GC/MS equipped with a continuous wave Nd:YAG laser with a near IR output (1064
11 nm) [51,53]. A pulsed ruby laser (694.3 nm) was used to study the in-situ pyrolysis of individual coal
12 macerals [54]. Thomsen & Egsgaard described an instrumental set-up for the pressurized laser-induced
13 pyrolysis of coal foils using the visible blue-green emission from an argon ion laser (458-515 nm) [55].
14 Choi et al. performed direct chemical analysis of UV laser ablation products of organic polymers using
15 an ArF excimer laser (193 nm) coupled to a Py-GC/MS [56]. Other applications involving all of these
16 laser sources have been briefly reviewed by Meruva and co-workers [11,52]. They themselves
17 designed and developed a novel instrument for rapid characterisation of synthetic polymers using UV
18 laser pyrolysis coupled to fast GC and TOF-MS. The combined Q-switched Nd:YAG laser, frequency
19 quadrupled to 266 nm, was used on a model polymer (polyethylene) in order to measure the production
20 and distribution of pyrolysis products. They provide an excellent discussion evaluating the effects of
21 experimental factors and interactions on the performance of the laser Py-GC/TOF-MS system in
22 comparison to conventional filament pyrolysis.

23 Unlike the filament, Curie-point and furnace pyrolyzer, laser pyrolysis requires very little sample
24 preparation or pre-treatment since analysis is performed directly on the solid polymer matter. The
25 sample is therefore much easier to handle and consequently analysis time is greatly reduced. However,
26 a common problem encountered with using laser radiation is that a specific laser wavelength may not
27 be appropriate for all types of materials. The transparency of some polymers at the laser wavelength
28 makes them more difficult to degrade thermally. To overcome this, researches have found that the
29 sample can be indirectly pyrolysed by embedding it in a strongly absorbing matrix such as powdered
30 carbon [57] or graphite, or by depositing the sample on an absorbing surface such as blue cobalt glass
31 [58]. However, it has been reported that by heating the sample indirectly, both the heating rate and
32 maximum temperature are decreased [59]. Armitage et al. discussed the difficulties in directly
33 analyzing synthetic fibres using near IR laser radiation (1064 nm) due to their transparency at this
34 wavelength [60]. Consequently the fibres were impregnated in a graphite matrix and then pyrolysed.
35 They concluded that the use of additional laser sources such as UV or visible lasers may have enhanced
36 the analytical scope of their method. Metz and co-workers reported that by using a 1064 nm Nd:YAG
37 laser, frequency quadrupled to 266 nm, the addition of carbon or other sample supports could be
38 avoided [52]. Since most organic compounds efficiently absorb UV energy, optically transparent
39 polymers could be directly pyrolysed.

40 The capabilities of laser pyrolysis-GC have been assessed in many areas of research including
41 geochemistry and petrology [61,62], natural and synthetic organic polymers [63,64], and forensic
42 science [60] (Fig. 2). Laser energy continues to be a suitable source to generate pyrolysis for the in-situ
43 molecular investigation of macromolecules.

44 45 46 *2.3.2 Non-discriminating pyrolysis-GC*

47
48 Discrimination of high molecular weight compounds during the pyrolysis of complex mixtures is a
49 significant problem with all types of conventional pyrolyzers [12, 65-67] as these fragments often carry

1 very significant structural information. Efforts have been made using a laser pyrolysis system to
2 analyse both low and high molecular pyrolyzates [52]. A technique called in-column pyrolysis (Fig. 3)
3 established in 2000 was designed to overcome this problem by enabling the pyrolysis step to be
4 performed in-line with the GC column [9]. Samples were introduced by hand into a disposable, inert
5 stainless steel capillary tube, which was then heated rapidly to the pyrolysis temperature using an
6 electric current. The entire assembly was contained within the GC oven to prevent cold spots in the
7 system. Initial experiments demonstrated no discrimination effects of high boiling point compounds
8 and excellent pyrolysis reproducibility. However, limitations of the in-column pyrolysis system
9 included disconnection of the column every time a new sample was analyzed and inaccurate control of
10 sample amount, position and temperature due to manual sample introduction [68]. Beyer et al.
11 developed and evaluated an automated in-column pyrolysis-GC/MS system which they found to offer
12 new opportunities for quantitation of polymers or other high molecular weight materials due to high
13 reproducibility of peak areas [12]. The system included the option to work in normal injection mode
14 and in pyrolysis mode simultaneously, thus facilitating the analysis of compounds such as additives in
15 polymers, and the characterisation of the non-volatile fraction in a single run.

16 Considerations regarding the advantages and disadvantages of in-column pyrolysis have led to the
17 recent development of a new system. Non-discriminating pyrolysis-GC, like in-column pyrolysis, is
18 specifically designed to minimize the transfer losses of larger fragments from the pyrolysis unit to the
19 GC column so that important structural information among other things can be obtained. Several
20 designs have been developed and tested but the general configuration of a non-discriminating pyrolysis
21 system is much like a normal Py-GC/MS in that the pyrolysis step is performed external to the GC and
22 not in-line with the GC column in the GC oven (Fig. 4). Instead of a conventional pyrolyzer, pyrolysis
23 occurs in an inert, Silcosteel capillary tube which is interfaced to the GC through a septumless injector
24 in the GC injection port. The sample is secured inside the capillary tube using fused-silica wool plugs,
25 the narrowness of the tube assuring that the temperature at the sample remains consistent with that at
26 the heating element at all times. Pyrolysis of the sample is achieved using an electric current. The
27 addition of a ceramic shield ensures the capillary pyrolysis temperature is not affected by external air
28 currents. An inert gas supply to the capillary column during pyrolysis flushes the pyrolyzates out of the
29 hot zone thus preventing secondary reactions and allowing for the recovery of higher molecular weight
30 products through post-heating. A more detailed description of the instrumentation is available
31 elsewhere [68]. The technique can be used for any type of material and despite its novelty, has already
32 been used to study samples including synthetic and naturally occurring polymers [69]. In a study by
33 Parsi et al., the performance of non-discriminating Py-GC/MS in the characterisation of natural organic
34 matter (NOM) was assessed [70]. The results were compared to those also obtained using a filament
35 and a Curie-point pyrolyzer. The study showed that the ambiguity caused by mass discrimination
36 against larger fragments was dramatically reduced with non-discriminating Py-GC/MS compared to
37 that of conventional pyrolysis approaches. Larger fragments such as traces of cholesterol in the
38 pyrolysis of chitin were detected, which could not be observed with the commercial pyrolyzers.
39 Furthermore, the macromolecular pyrolyzates showed a greater abundance in the pyrograms of various
40 polyaromatic and long-chain aliphatic compounds obtained via non-discriminating Py-GC/MS. In
41 another study, non-discriminating Py-GC/MS was used for the detection of ergosterol in various
42 samples [70]. As the major sterol constituent in fungi, ergosterol is an essential chemical indicator of
43 fungal contamination. Results showed that it was clearly detected in all of the samples and the authors
44 reported that the benefits of non-discriminating pyrolysis including no sample preparation, small
45 sample size and short analysis time, far outweighed those of other techniques. The profiling of fatty
46 acids in bacterial biomasses using non-discriminating TMAH induced thermochemolysis Py-GC/MS
47 has also been reported [71].

1 On the whole, not only is the performance of the modified non-discriminating pyrolysis system much
2 better than the original in-column pyrolysis system, it is also much easier to use. It offers great
3 potential for the future analysis of high molecular weight pyrolyzates.
4
5

6 **3. Thermal degradation**

7
8 The kinetics of thermal degradation and structure determination of polymers and co-polymers has
9 been covered in great detail in other reviews [2-3,72] and with little development in this area it is best
10 to refer to those papers.
11

12 *3.1. Degradation properties*

13
14 Degradation results from free radical reactions initiated by bond breaking within the molecules; the
15 bond that is more easily broken will be favoured. Thermal and environmental conditions, such as
16 temperature and additional reactants, can affect both the extent and route of degradation of a polymeric
17 material and the nature (physical and chemical) and quantity of molecular species generated by
18 pyrolysis. Molecular degradation of a sample will occur as soon as the temperature is high enough to
19 initiate bond breaking, but at this point will not necessarily yield much useful product [1]. With much
20 higher temperatures, other bonds will break simultaneously, creating very small and non-specific free
21 radicals. Generally, the higher the temperature, the smaller the radicals and molecules produced. The
22 optimum pyrolysis temperature, which will be different for every polymer, is the point at which
23 degradation produces a wide array of chemically useful products. Poly α -methylstyrene for example
24 yields 100% of monomer at 500°C, 88.5% at 800°C and only 37.7% at 1200°C [73]. These products,
25 identified using GC/MS, can provide a fingerprint of the original polymer and copolymer composition
26 and microstructure and help determine the degradation mechanisms.

27 The chemical composition of a polymer can also affect its degradation properties. Stauffer discussed
28 how the substitution of a hydrogen atom with a CH₃ group can alter the point at which the polymer
29 chain breaks, affecting the degradation route and amount of product yielded [73].

30 Low level compounds added to a polymer, intended to alter its physical or chemical properties, are
31 another factor which may influence its degradation properties and make the analysis of its products
32 very challenging. Some additives can be thermally removed from the polymer before they degrade by
33 heating the sample to a sub-pyrolysis temperature. In this instance the polymer undergoes degradation
34 at a set pyrolysis temperature and the pyrogram should only contain peaks from the polymer itself.
35 However, polymer additives present a problem in that they cannot be removed and must be pyrolysed
36 along with the polymer matrix. The degradation behaviour of the original polymer and the additive
37 will differ due to differences in their size, structure and composition therefore products generated from
38 additives are often overshadowed by products generated from the polymer itself. More complex
39 macromolecular additives produce even more degradation products upon pyrolysis, significantly
40 changing the appearance of the pyrogram by reducing the size of other peaks. Recently, a multi-step
41 approach has been used to thermally separate compound families at intervals during pyrolysis in order
42 to simplify the pyrograms [74].
43
44

45 *3.2 Mechanisms*

46
47 Pyrolysis products reflect the molecular structure, free radical stability, substitution and internal
48 rearrangements of the polymers constituting the sample material [1]. Thus, the degradation
49 mechanisms undertaken are dependent upon the structure and bond dissociation energies of the

1 polymers. Consequently a polymer may take multiple degradation routes simultaneously. Identical
2 molecules, heated to the same temperature will break apart and rearrange in the same characteristic
3 way. The understanding of these mechanisms has led to improved interpretations of pyrograms. The
4 three main mechanisms include random scission, side-group scission, and monomer reversion [73].

5 Random scission involves the random breaking of the polymer's C-C bonded backbone as all the
6 bonds are of equal strength, resulting in the formation of products including, alkanes, alkenes and
7 alkadienes of smaller sizes. Figure 5 shows the random scission of polyethylene. Upon pyrolysis the
8 products formed can be seen clearly on a chromatogram as a familiar series of "triplet" peaks.

9 Side-group scission occurs when the side groups attached to the backbone are broken away resulting
10 in the backbone becoming polyunsaturated. Its subsequent rearrangement produces aromatic
11 compounds such as benzene, toluene, ethylbenzene, styrene and naphthalene as shown in Figure 6.
12 Polymers including styrene, vinyl and some rubbers will undergo side-group scission.

13 During monomer reversion, the polymer simply unzips and reverts back to its original monomeric
14 version otherwise referred to as depolymerisation. Usually only one predictable compound is
15 produced. Polymers known to undergo this mechanism include polymethylmethacrylate (Fig. 7),
16 polytetrafluoroethylene, poly α -methylstyrene and polyoxymethylene.

17 Other mechanisms do exist but are not as common as those mentioned above; cross-linking and char
18 formation is one of them. The occurrence of more cross-linking within the polymer molecules during
19 pyrolysis ultimately strengthens the product, creating only a small number of volatiles. Typical
20 polymers undergoing this route include polyacrylonitriles or phenolic resins. The thermal behaviour
21 and degradation mechanisms, or rearrangements, in the pyrolysis of natural and synthetic polymeric
22 materials, as well as other organic compounds, are continually being investigated.

23 It has been noted how, under various temperatures for the pyrolysis of polymers, traditional Py-
24 GC/MS is unable to distinguish the main degradation mechanism and evolved product distribution at
25 specific temperature regions [75]. Whilst studying the pyrolysis of poly(aryl-ether-ether-ketone) and
26 poly(arylene sulfone)s, Perng and co-workers overcame this issue by using stepwise pyrolysis-GC/MS.
27 The method facilitated consecutive heating of the sample at fixed temperature intervals, thus achieving
28 narrow temperature pyrolysis conditions and enabling the dominant pyrolysis mechanisms to be
29 obtained [76,77]. A similar study of the thermal degradation mechanism of poly(ether imide) has also
30 been reported [75]. The major mechanisms determined were two-stage pyrolysis, involving main-chain
31 random scission and carbonization. Guo et al. identified the thermal degradation behaviour of a novel
32 phosphorous-containing aromatic poly(ester amide) (ODOP-PEA) compound using Py-GC/MS [78].
33 Results suggested that bond cleavage of the pendant phosphorous groups occurred initially but
34 maximum decomposition was attributed to the main chain scission at higher temperatures. High
35 resolution Py-GC/MS was applied to analyse the degradation products of benzocyclobutene-terminated
36 imide polymers, a kind of thermoset polymer [79]. Degradation mechanisms including, thermal
37 cleavage, chain transfer, isomerization and cyclizations, were suggested and the relationship between
38 polymer structure and pyrolyzates was discussed.

39 It is important to recognize that the dominant degradation mechanisms or pathways undertaken
40 during pyrolysis of a sample might not necessarily be the same for each type of material. Most
41 examples given above relate to the analysis of synthetic polymers however a significant number of
42 samples analyzed by Py-GC are of natural origin. For example, Sun and co-workers used a
43 microfurnace Py-GC/MS to analyse the thermal behaviour of vitamin D₃ [80]. The study was focussed
44 on understanding what products were formed during the pyrolysis process in an attempt to identify the
45 ingredient variation of the vitamin D₃ that exists as crude and/or additive forms in foods under high
46 temperatures. Furthermore, a number of studies on the analysis of natural organic matter using Py-GC
47 methods have reported the formation of carbonaceous residue through charring as one of the major
48 degradation processes [9].

1 Pyrolysis-GC has also been used to study the influence of additives on the thermal degradation
2 pathways of polymers. Ishikawa et al. studied the thermal degradation and flame retardancy of
3 polycarbonate with the addition of a variety of different flame retardant chemicals using Py-GC/MS
4 [81]. Different mechanisms were observed including hydrolysis, bond cleavage and cross-linking.
5 Another study focused on the thermal degradation of a polycarbonate containing methylphenyl-silicone
6 additive [82]. With the use of Py-GC/MS they deduced the addition of silicone could promote cross-
7 linking and char formation as the mass loss rate of PC in the major degradation step was decreased.
8 Bond scission was another proposed degradation route, thought to have produced the main volatile
9 decomposition products of the PC-silicone blends. Bertini and Zuev investigated the influence of
10 fullerene C60 additives on the thermal behaviour and degradation mechanism of fully aromatic regular
11 polyesters using Py-GC/MS [83]. The presence of fullerene, being an efficient radical acceptor, was
12 found to alter the decomposition from a radical pathway to a non-radical pathway. Jakab and
13 Omastova studied the thermal decomposition of carbon black composites, used as a reinforcing agent
14 and filler, with polyethylene (PE), polypropylene (PP) and polyisobutylene (PIB) [84]. Results of Py-
15 GC/MS experiments determined that the product distribution of polymers was dependent upon the level
16 of volatility of the carbon black. The product distribution of both PE/carbon black composites and
17 PP/carbon black composites indicated that carbon black participated in a hydrogenation process.
18 Moreover, the formation of several other isomers during the degradation of PP composites also
19 indicated that carbon black promoted other mechanisms including, chain scission and radical transfer
20 reactions. Depolymerisation was observed in the decomposition of PIB composites in the presence of
21 carbon black.

24 4. Applications

26 4.1 Art materials

28 The chemical, physical and structural characterization of materials such as glues, paints, pigments,
29 binders and varnishes used to create artistic masterpieces, continues to provide art historians and
30 conservators with precious information. This knowledge enables restoration and conservation work to
31 be carried out properly without causing any damage to the original artifacts [85] and also helps to
32 understand the techniques adopted by the artists. The organic materials used as binders in art media
33 have received considerable attention. A review by Colombini and Modugno discusses the application
34 of chromatographic techniques including Py-GC for the characterisation of proteinaceous binders such
35 as animal skins or bones, egg and milk, or casein in artistic paintings [86]. Ling et al. attempted to
36 characterize the natural binding media used in ancient Chinese artworks including non-proteinaceous
37 materials such as Chinese lacquer, tung oil, deer glue, and peach gum using Py-GC/MS [87]. The
38 kinds of natural resins used as the main ingredients in varnishes and binding media have also been
39 assayed [88], including terpenoid resins [89,90] and triterpenic resins from the *Burseraceae* family
40 [91]. Several studies have focused on the analysis of different artists' paints. Chiavari et al. analysed
41 lipid materials used in paint layers using an in-situ pyrolysis and silylation method [92]. A paper by
42 Bruck & Willard discusses the process of de formulation of paints in order to obtain ingredient and
43 compositional information [93], and a paper by Scalarone & Chiantore reviews separation techniques
44 for the analysis of acrylic emulsion paints [94]. Natural dyes used in works of art, namely madder,
45 curcuma, saffron and indigo, have also been analysed by Py-GC/MS [95], and finally an interesting
46 study by Bonaduce and Colombini used Py-GC/MS to characterize beeswax from a sculpture called
47 "The Plague" (1691-1694) by Gaetano Zumbo [96].

1 *4.2 Biological samples*

2
3 Much work continues to be done in an effort to identify and differentiate biological materials such as
4 microorganisms. A flash Py-GC/MS method was reported for the rapid screening of bacterial species
5 in order to detect the presence of bacteriohopanepolyols [97] and more recently, Py-GC/FID was
6 employed for the quantitative pyrolysis of three different bacterial strains [32]. Goodacre et al. [98]
7 detected a simple biomarker for the rapid detection of Bacillus spores using curie-point Py-GC/MS,
8 whilst Schwarzingler [99] identified specific marker compounds characteristic of fungi type. The
9 development of a miniaturized Py-GC system for the rapid detection and identification of bacteria and
10 other pathogens has also been proposed [100]. Furthermore, the use of analytical pyrolysis in bio-
11 terrorism studies has been evaluated [101]. In an interesting application, Buckley et al. used Py-
12 GC/MS to analyse the complex organic balms on tissues and wrappings from pharaonic animal
13 mummies in an effort to understand the mechanism of preservation in comparison to that observed with
14 human mummies [102]. Other applications of Py-GC in biological studies include the compositional
15 analysis of Copoly(DL-Lactic/Glycolic Acid) used in the medical and pharmaceutical fields when
16 applied to devices for wound closure, orthopedics and controlled drug release [103], and structural
17 investigations of neuromelanin from the human substantia nigra in the brain in an attempt to determine
18 if neuromelanin is involved in cell death in Parkinson's disease [104,105].
19
20

21 *4.3 Environmental*

22
23 Applications of Py-GC in environmental science continue to grow, as the benefits of the analytical
24 technique are still being discovered. This is demonstrated in a paper by White et al. which describes
25 four recent applications of Py-GC/MS fingerprinting of environmental samples [106]. Several studies
26 on the analyses of particulate organic matter (POM) suspended in water have been reported, such as a
27 paper by Yildiz et al. who used Py-GC/MS to investigate suspended POM in open and coastal waters of
28 the southern Black Sea and found evidence in the pyrograms of 23 marker compounds characteristic of
29 chlorophylls, lipids, carbohydrates and proteins formed during pyrolysis [107]. Volkman and Tanoue
30 have reviewed the chemical and biological research carried out on POM in oceans across the globe and
31 in doing so have discussed Py-GC/MS as a new approach [108]. In addition to the characterisation of
32 particulate organic matter, research has been done on the organic matter in marine sediments. Fabbri et
33 al. compared pyrolytic and lipid markers in the Adriatic Sea using semi-quantitative Py-GC/MS and
34 classical GC/MS [109]. Much work has also been published on the analysis of soil [110,111]. A
35 recent review on soil health discusses the progress that has been made in the development of molecular
36 and analytical methods, including Py-GC/MS, and the application of these techniques in determining
37 soil health status [112]. In another application, a Py-GC/MS method for the analysis of the UV-B-
38 absorbing compounds in small numbers of pollen, spores and other microscopic entities was developed
39 in order to allow research toward the effect of increased UV-B radiation on plants [113].
40
41

42 *4.4 Food and agriculture*

43
44 Foodstuffs have been routinely analyzed by Py-GC for decades because of its ability to analyse
45 complex molecules such as proteins, polysaccharides and lipids. Halket and Schulten studied several
46 whole foodstuffs namely ground roast coffee, rosehip tea, wheatmeal biscuit, chocolate drink powder
47 and milk chocolate, and were able to differentiate them all by examining the molecular weight
48 distributions of released volatiles and pyrolysis products in their spectra [114]. The identification and
49 quantification of soy protein in ground beef has also been reported [115]. Several papers have

1 described rapid Py-GC/MS derivatization methods for profiling of fatty acids in vegetable oils and
2 animal fats [116], including a study by Fabbri et al. who used dimethyl carbonate and titanium silicate
3 as non-toxic derivatising agents to analyse soybean, coconut, linseed, walnut and olive oil [117].

4 Agricultural applications of analytical pyrolysis are mostly focused on soil chemistry, more
5 specifically soil structure and soil organic matter (SOM) dynamics and composition. Nierop et al.
6 investigated the differences in the chemical composition of SOM within one soil series from three
7 differently managed fields in The Netherlands [118]. Results using a combination of Py-GC/MS and
8 thermally assisted hydrolysis and methylation with TMAH determined that SOM composition is hardly
9 affected by organic farming compared to conventional management i.e. high tillage intensity and
10 intensive fertilization. Similarly, Marinari and co-workers used carbon fraction pools and pyrolytic
11 indices as an indication of SOM quality under organic and conventional management in central Italy
12 [119]. Furthermore, Rodriguez et al. evaluated chemical-structural properties of SOM under different
13 agronomical practices of the Venezuelan central plains by measuring the relative abundance of volatile
14 organic products produced by pyrolysis [120], and the chemical composition of organic matter in
15 various fresh and composted wastes has been characterized by Dignac et al. [121]. A comparison
16 between organic and mineral fertilization in the investigation of chemical and biochemical changes in
17 SOM has also been reported, in which the detection of high levels of water soluble organic carbon and
18 aliphatic pyrolytic products confirmed that mineral fertilization caused greater alteration of native SOM
19 than the organic amendments [122].

20 21 22 *4.5 Geochemistry and fuel sources*

23
24 Investigations involving petrochemical related materials, of which there are several categories, are
25 not a new phenomenon in Py-GC studies. The structural characterisation and differentiation of
26 kerogens for example has received much attention in previous years but despite great progress, some
27 knowledge of their chemical structure and the mechanism by which they form and change in time on
28 Earth is still limited. González-Vila and co-workers analysed a set of kerogen concentrates using Py-
29 GC/MS both in the presence and absence of TMAH so as to study their structural characteristics [123].
30 Results indicated that considerable amounts of functionalized compounds are bound to the
31 macromolecular structure via ester and ether linkages. Petsch et al. analysed the weathering profiles of
32 organic carbon-rich black shales in order to determine the loss and degradation of organic matter
33 during weathering and its role in the geochemical carbon cycle [124]. A model for kerogen weathering
34 was suggested involving non-selective oxidation and hydration followed by cleavage/dissolution of
35 oxidized kerogen fragments. The chemical structure, source(s), and formation pathway(s) of kerogen-
36 like organic matter in sediments from the northwestern Black Sea has also been investigated [125], as
37 well as the molecular structure of kerogens from source rocks of the Tarim Basin [126]. A review of
38 pyrolysis techniques in the molecular characterisation of environmental kerogen and humic substances
39 and their application to geochemistry has been published by Yamamoto et al. [127].

40 Another area of geochemical research which has been greatly explored includes the compositional
41 analysis of coal materials. The release behaviour of hydrocarbon components of pulverized coal has
42 been investigated using Py-GC [128], as have the pyrolyzates of raw vitrinites and their residues from
43 selected coal samples following a novel binary solvent extraction procedure [129]. The co-pyrolysis of
44 coal and petroleum residues has been studied by Suelves et al. in an attempt to examine the synergetic
45 effects on the yield of the main petrochemical pyrolysis products [130], and the structural
46 characterisation of oil and coal tars using pyrolysis techniques have also been reported [131,132].
47 Other studies include the analysis of byproducts resulting from the combustion of coal, such as flyash
48 [133].

1 Additional research using Py-GC includes the study of both volatile and involatile organic
2 compounds in extraterrestrial environments during planetary missions [134], and the examination of
3 cuticles from fossil arthropods [135].
4
5

6 *4.6 Synthetic polymers* 7

8 Py-GC has developed considerably to become a routine tool for the identification and differentiation
9 of synthetic polymers as well as the quantitative determination of monomers in copolymers. A great
10 deal of research is now focused on the detection of low level chemical compounds in the polymers.
11 There are many publications on this application of Py-GC however here only a brief overview is
12 presented. Many examples have already been provided throughout the scope of this review, but the
13 most frequently analysed synthetic products include plastics, rubbers, coatings and composites. The
14 developments in analytical techniques for the analysis of polyolefins with respect to molar mass and
15 chemical composition distribution have been addressed by Pasch [136]. A very recent study on the
16 composition and microstructure of ethylene and propylene copolymers using Py-GC found it to be a
17 very reliable and reproducible method [137]. Future developments regarding the technique were
18 suggested, including the development of a novel pyrolysis and two-dimensional GC system (Py-GC ×
19 GC) which would further improve accuracy by facilitating enhanced separation of pyrolyzates and thus
20 greatly reducing detection interferences. Wampler et al. have demonstrated a Py-GC/MS method from
21 which monomer ratios in random and block copolymers of polyolefins, especially polyethylene and
22 polypropylene can be obtained [138], and Evans et al. report an approach for the structural analysis of
23 polyester thermosets [139]. The chemical composition of multicomponent acrylic resins, including
24 ethyl acrylate-butyl methacrylate copolymers and ethyl acrylate-styrene-ethyl methacrylate terpolymers
25 has been assayed [140], as well as the quantitative determination of poly(ethylacrylate-
26 methylmethacrylate) layers on drug granules for pharmaceutical use [141]. The compositional and
27 microstructural determination of water-based synthetic polymers in a latex system using a pre-pyrolysis
28 derivatization step has also been described [142]. Furthermore, Learner analyzed the synthetic
29 polymers used in the formulation of paints such as alkyd, polyvinyl acetate and nitrocellulose [143],
30 and many authors have studied the pyrolysis patterns of rubbers using Py-GC [144], including Choi
31 who assayed styrene-butadiene rubbers with differing microstructures [145].
32
33

34 *4.6.1 Detection of additives and contaminants* 35

36 Compounds added to polymeric materials in order to alter their physical or chemical properties in
37 some way consist of fillers, pigments, antioxidants, stabilizers, flame retardants, plasticisers, lubricants,
38 preservatives and other modifiers [74]. The effect additives have on the thermal degradation properties
39 of a polymer has already been addressed. The determination of low level polymer additives in complex
40 pyrograms is a subject briefly discussed by Wang in his earlier review on Py-GC [2], and despite
41 several studies published since then, analytical development in this area has been slow. The key to the
42 successful analysis of additives is to understand the properties they possess and to have knowledge of
43 the polymers and their applications. Volatile and semi-volatile additives can usually be extracted from
44 the matrix and analysed independently using GC methods. A fast Py-GC method has been described
45 for the qualitative identification of plastic additives from samples of recycled and pure acrylonitrile-
46 butadiene-styrene (ABS) originating from electronic waste [146]. The method combines the
47 advantages of thermal desorption and flash pyrolysis by using a novel double-shot pyrolyzer; the low
48 molecular weight additives are desorbed before the polymer chain undergoes decomposition.

1 More complex additives however cannot be extracted, and so pyrolysis of both the additive and the
2 polymer must occur simultaneously. Identification of the pure additive is dependent upon careful
3 interpretation of the intricate array of peaks present on the pyrogram and making distinctions between
4 peaks which are chemically or chromatographically different. Recent investigations have found the
5 selective ion monitoring mode of MS detectors to be the most informative approach in this case as it
6 immediately simplifies the identification process [74]. Wang has published a series of papers
7 analyzing several types of polymer additives, namely plasticizers, flame retardants, lubricants and
8 antioxidants, in order to demonstrate the utility of Py-GC as a good tool for the characterisation of such
9 polymeric systems [147-150]. The advantages of using Py-GC in each case have been discussed.
10 Yang et al. investigated the effects of different inorganic fillers on the natural photo-oxidation
11 degradation of high-density polyethylene (HDPE) using Py-GC/MS [151]. Results showed that whilst
12 some fillers, e.g. CaCO₃ and wollastonite, stabilized HDPE a little, other inorganic fillers including
13 kaolin, diatomite and mica, accelerated the degradation. In an interesting application Py-GC was used
14 to analyse the ABS plastic material used to make faulty Takata press release buttons in automobile seat
15 belts, to determine if a UV stabilizer had been added [152]. A UV stabilizer was detected and validated
16 using mass spectrometry.

17 Additives are also incorporated into natural polymers for the same reasons as they are added to
18 synthetic polymers and they can be detected using the same methods. Techniques for applying internal
19 standards for the quantification of typical chemical paper additives using Py-GC with mass selective
20 detection have been suggested and demonstrated by Odermatt et al [153]. Zhu and co-workers studied
21 the pyrolysis products of cotton and flame retardant cotton fabrics in an attempt to understand their
22 thermal degradation mechanisms and thus the fire-resisting functions of the materials [154].

25 *4.7 Forensic*

27 Pyrolysis-GC is a well established technique in forensic analysis often used by forensic chemists to
28 analyse a vast array of polymeric materials. The literature available is therefore extensive and it
29 includes many different applications. Certainly one of the most investigated areas is document
30 analysis, including the classification and differentiation of photocopy toners and the analysis of inks.
31 Studies on the examination of machine copier toners using Py-GC date back to the 1980's.
32 Zimmerman et al. analysed thirty-five different photocopy toners and respective machine copied
33 documents in an attempt to establish a library of spectra from which an unknown toner extracted from a
34 questioned document may be matched [155]. Levy and Wampler used Py-GC/MS to analyze a variety
35 of photocopies produced by different manufacturers of copying instruments and found specific
36 chemical differences in the toner materials used in each make of copier [156]. Similarly, Munson
37 separated photocopy toner material from photocopies from 62 different machines into 18 classes
38 depending on the presence or absence of peaks in the pyrograms [157] and Chang et al. described a Py-
39 GC/FID method for the differentiation of photocopier toners using a Curie-point pyrolyzer and a
40 computer-assisted library search method [158]. A less damaging technique for the identification of
41 black toner material using Py-GC with mass selective detection has also been reported involving the
42 heat transfer of the toner from the paper to a medium [159]. More recent work includes the forensic
43 discrimination of photocopy and printer toners using multivariate statistics [160], and a study of
44 solvents in inkjet printings which found varying proportions of different solvents in different inks
45 [161]. A review on chromatographic and electrophoretic applications in ink analysis and the
46 components of different types of inks has been published [162].

47 Besides photocopy toners and ink, the forensic analysis of packaging tapes and the adhesives is
48 another area in which literature is readily available. The identification of trace amounts of synthetic
49 adhesives has been achieved by Li et al. who incorporated simultaneous methylation in order to

1 measure the polar compounds [163]. Sakayanagi et al. used Py-GC/MS to identify 20 different
2 products of colourless, transparent, pressure-sensitive adhesive polypropylene tapes, the results of
3 which proved it to be such an effective method that it was applied to the analysis of a real forensic
4 sample [164]. Furthermore, the deteriorated rubber-based pressure sensitive adhesives of three
5 packaging tapes were analysed by Kumooka who determined that tackifiers including Coumarone
6 resins, aromatic petroleum resins and β -pinene resins have higher resistance to oxidation than natural
7 rubbers and aliphatic petroleum resins, and can still be identified by Py-GC/MS even after the
8 deterioration [165]. A multi-step analysis of packaging tape has also been reported by using a
9 Pyroprobe 5150 model which can be programmed to take the same sample material to a variety of
10 temperatures automatically [166].

11 Py-GC has long been recognized as a standard method for the forensic analysis of other materials as
12 well. Several papers have described methods for the identification and differentiation of automotive
13 paint samples [167,168], and for the analysis of fibers [169]. Drugs and their metabolites have also
14 been investigated, including a study by Takayasu and Ohshima who devised a Py-GC/MS method for
15 the rapid analysis of methamphetamine and its analogs [170]. Another study proposed a protocol for
16 the forensic detection and analysis of condom and personal lubricants in sexual assault cases [171,172].
17 Further applications of Py-GC in the field of forensic medicine and toxicology include the postmortem
18 alcohol analysis of the synovial fluid and its availability as a biological specimen for the prediction of
19 blood alcohol concentration and urine alcohol concentration in medico-legal cases [173], and the rapid
20 analysis of pesticide components in blood and urine [174].

23 5. Miscellaneous

25 Future developments regarding Py-GC as a technique have been suggested. In their work on the
26 composition and microstructure of synthetic copolymers, Wang et al. discussed the development of a
27 novel pyrolysis and comprehensive two-dimensional GC system (GC \times GC) designed to further
28 improve the accuracy achieved using conventional GC methods by facilitating enhanced separation of
29 pyrolyzates [137]. Based on orthogonal separation principles, comprehensive GC \times GC relies on a
30 configuration comprising of two columns displaying different separation characteristics. The entire
31 sample is first separated on a normal-bore capillary column under programmed temperature conditions.
32 The effluent is then modulated and each subsequent small portion of eluate is refocused and re-injected
33 onto the second column for further separation. As a result, the resolving power of the chromatograph is
34 increased by over a factor of ten and the probability of coeluting compounds or detection interferences
35 is greatly reduced. Comprehensive GC \times GC not only simplifies sample preparation procedures but
36 also provides higher sensitivity making it extremely well suited for the analysis of complex
37 pyrolyzates. The advantages of this system have been demonstrated in a study by Parsi et al. who used
38 non-discriminating pyrolysis combined with conventional GC/MS and comprehensive GC \times GC/TOF-
39 MS to analyse the organic fraction of airborne particulate matter (PM) [69]. Whilst results obtained
40 using conventional GC/MS provided insufficient chromatographic resolution to enable identification of
41 PM volatiles and semi-volatiles due to many coelutions, those obtained using comprehensive GC \times
42 GC/TOF-MS showed a dramatic improvement in analyte separation and thus identification.

43 Other instrumental techniques involving pyrolysis without the GC separation step also exist but are
44 beyond the scope of this review. Both direct pyrolysis mass spectrometry (DPMS) and direct pyrolysis
45 fourier transform infrared spectrometry (DP/FTIR) involve the direct interfacing of the pyrolysis device
46 to the detector. In both cases, the technique has been used in polymer analysis as a quick way of
47 identifying primary degradation products which avoid secondary pyrolysis reactions, with minimal
48 sample preparation. With DPMS, pyrolysis occurs under high vacuum and the readily volatilised
49 pyrolyzates are immediately ionised and detected, preventing further thermal degradation. This

1 technique has been used in a number of studies in order to obtain characteristic information much faster
2 and to study the primary degradation pathways of polymers [175-181]. With DP/FTIR, the pyrolysis
3 instrument (usually a platinum coil Pyroprobe) is designed to fit into the sample compartment of a
4 standard FTIR detector with the use of a specially designed interface. The filament of the Pyroprobe is
5 placed directly in the light path so that upon pyrolysis, the volatile pyrolyzates diffuse immediately into
6 the beam where they are detected. Rapid analysis in the beam eliminates any chance of condensation.
7 DP/FTIR is therefore a fast and easy method of obtaining a wide range of information on polymeric
8 materials. Several studies have demonstrated its potential [182-184].
9

10 **6. Conclusion**

13 Py-GC has evolved to become a routine analytical tool for the characterisation and differentiation of
14 polymers, both natural and synthetic. Since 1999, several types of thermal analysis equipment have
15 been developed to improve the analytical scope of Py-GC. Besides conventional pyrolyzers, the
16 introduction of laser pyrolysis has become a new phenomenon for Py-GC. Laser energy used as a
17 fragmentation source has facilitated controlled pyrolysis of specific regions on a sample, providing
18 useful data on the molecular compositional units of macromolecules in situ. The very recent
19 development of a non-discriminating Py-GC system has been designed to overcome the problems
20 associated with traditional pyrolyzers relating to sample losses and discrimination of high-molecular
21 weight compounds. Having already been used in a range of applications it offers great potential for the
22 future analysis of macromolecular structures. Furthermore, the development of a novel double-shot
23 pyrolyzer incorporating both thermal desorption and flash pyrolysis, has become a useful instrument
24 for the fast identification of low molecular weight polymer additives. Future developments in Py-GC
25 technology have also been suggested, which include the use of comprehensive GC \times GC for the
26 enhanced separation and detection of pyrolyzates.
27

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29
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32

33 **8. References**

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1 **Figure legends**

2
3 Figure 1. Schematic diagram of a laser pyrolysis-GC system (from ref [11])

4 Figure 2. Pyrograms of blue paint (a) from the laser microprobe pyrolysis GC/MS and (b) from the pyroprobe

5 pyrolysis GC/MS (from ref [60])

6 Figure 3. Schematic diagram of an in-column pyrolysis-GC system (from ref [68])

7 Figure 4. Schematic diagram of a non-discriminating pyrolysis-GC system (from ref [68])

8 Figure 5. Schematic diagram of random scission mechanism (example of polyethylene) (from ref [73])

9 Figure 6. Schematic diagram of side group scission mechanism (example of polyvinyl chloride) (from

10 ref [73])

11 Figure 7. Schematic diagram of monomer reversion mechanism (example of polymethylmethacrylate)

12 (from ref [73])

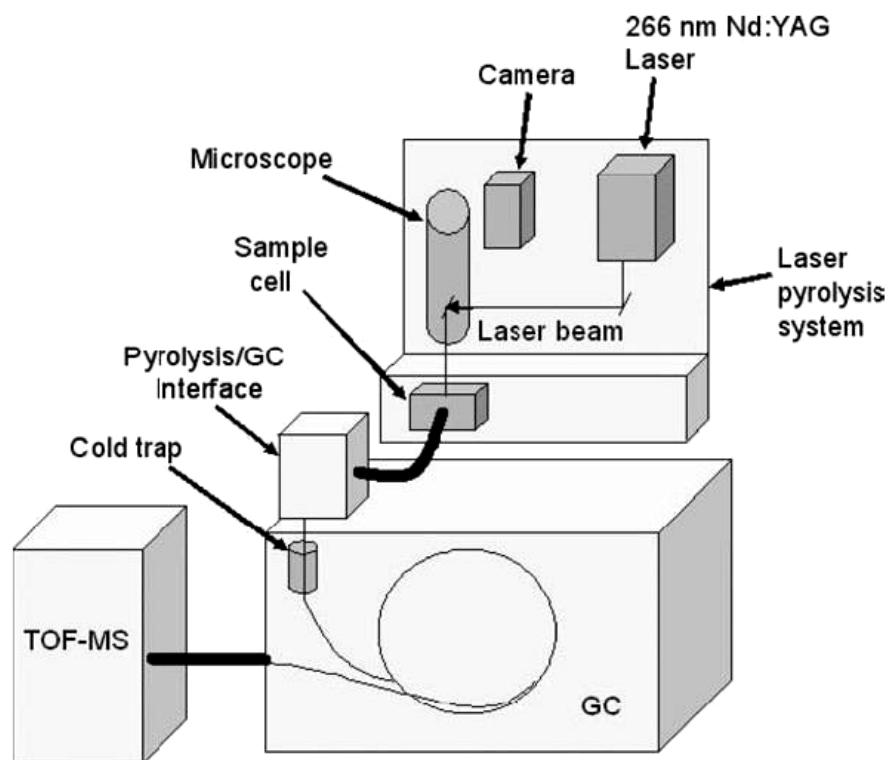
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15 **Figure 1**

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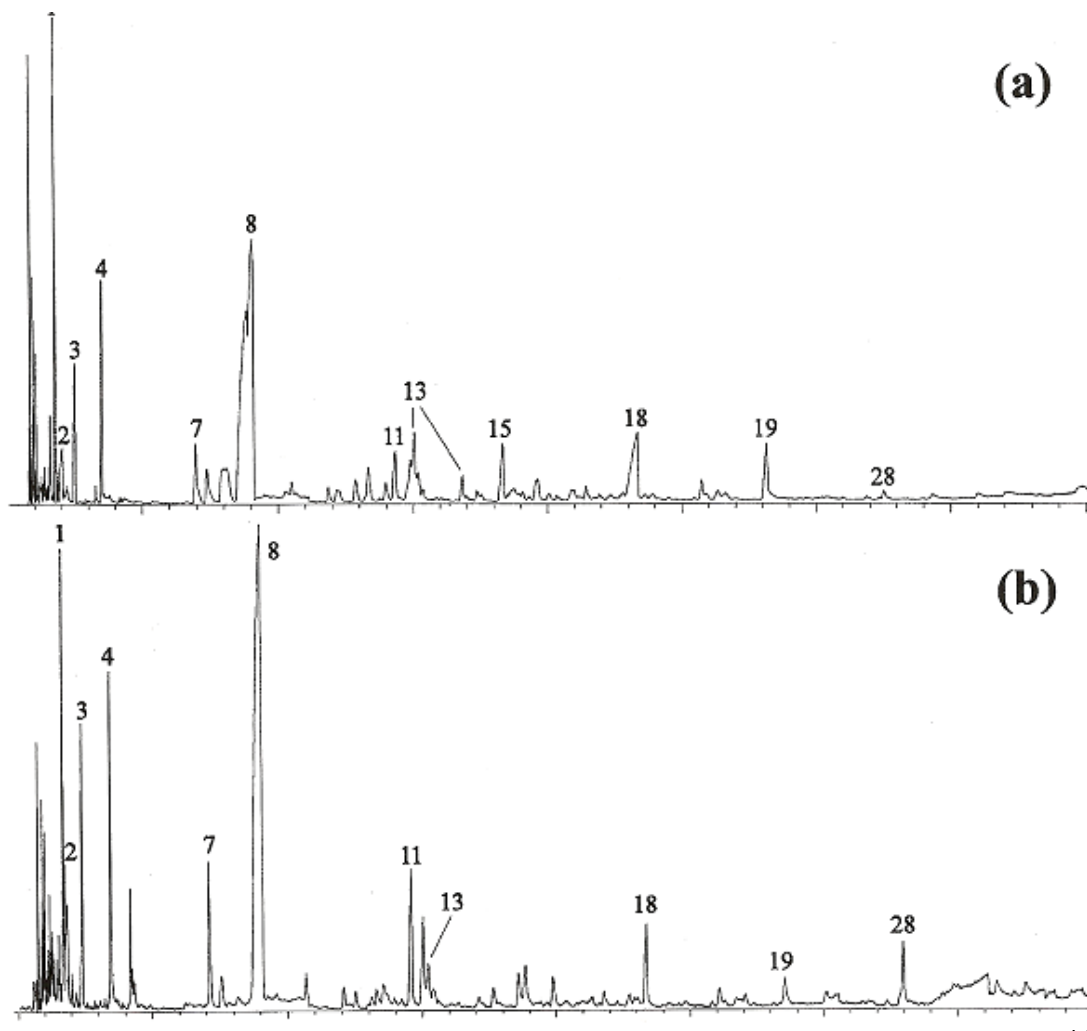


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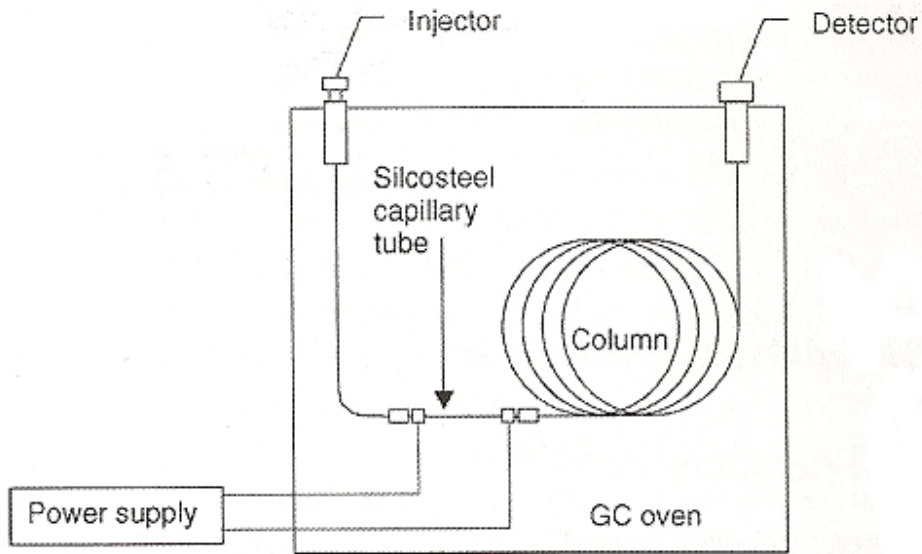
Figure 2



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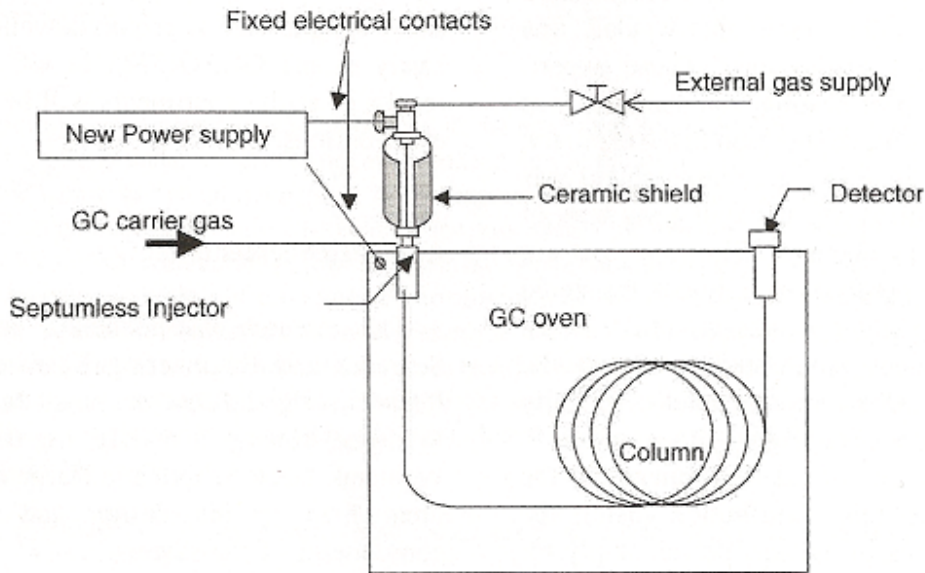
Figure 3



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Figure 4

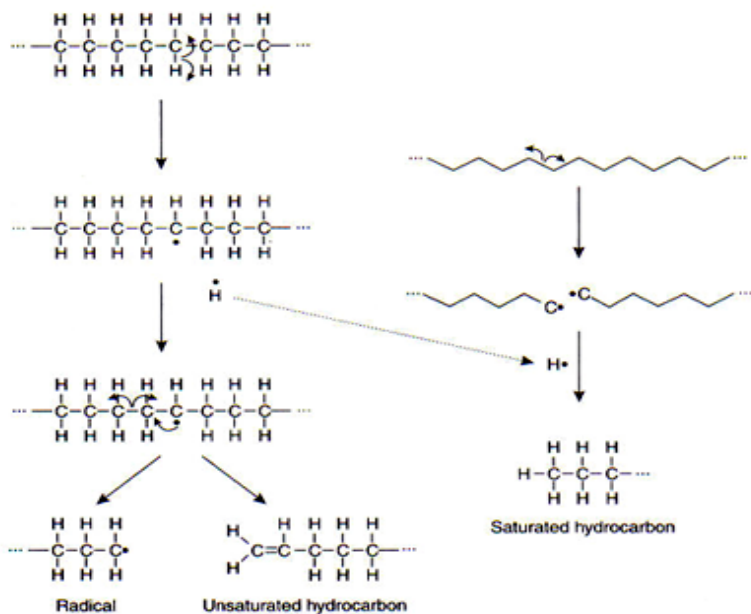


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Figure 5

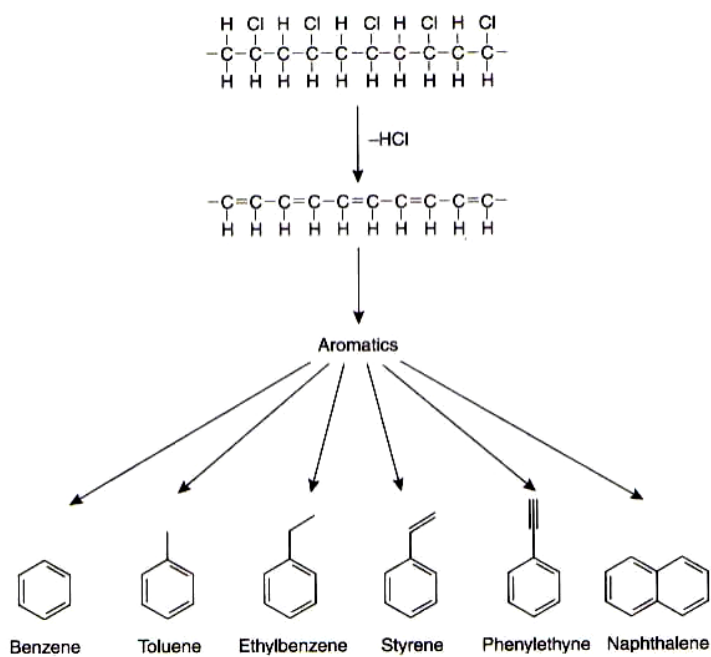
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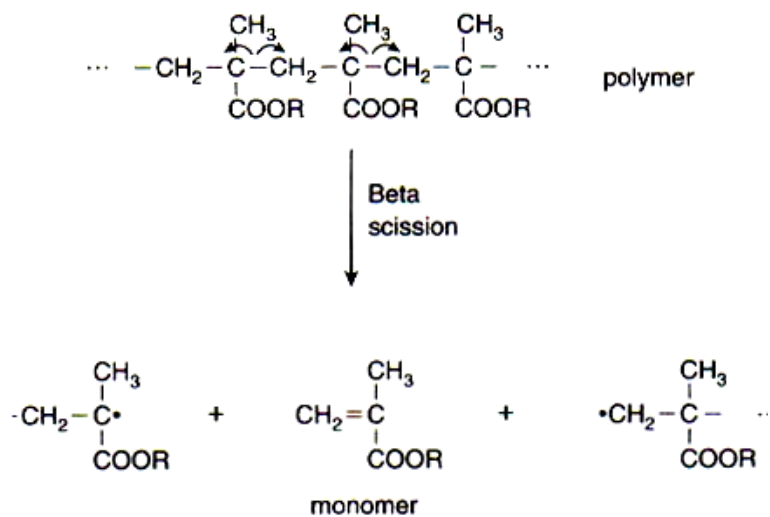
Figure 6



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