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Polymer additive analysis by pyrolysis–gas chromatography II. Flame retardants

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Abstract

Flame retardants are widely used in thermoplastic polymers for household and transportation applications. Flame retardants as well as most of the other additives in the polymer can be qualitatively analyzed by pyrolysis–gas chromatography (Py–GC) simultaneously with the polymer composition. The key to successful analysis of flame retardants not only requires a thorough knowledge of the various types of flame retardants but also necessitates an understanding of the parent polymer and its targeted applications. In this study, several flame retardants in different polymer matrices have been studied to demonstrate the utility of Py–GC for the analysis of flame retardants. The advantages of Py–GC for flame retardants analysis have also been discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Flame retardants; Polymers

1. Introduction

Flame retardants are a class of materials that are compounded into plastics to have certain defined reactions during combustion. These reactions cause the initially flammable substances to ignite with more difficulty and will inhibit the flame propagation compared to the original substrate under laboratory test conditions. The term “flame retardant” associated with certain plastic materials indicates that these plastic materials meet specific requirements when tested in accordance with recognized laboratory flammability test procedures. A plastic material with a flame retardant additive does not mean it will not burn or that it will actually extinguish the fire. In other words, the term “flame retardant” is a relative

term and is not intended to describe the hazards presented by these plastic materials under actual fire conditions.

The main applications for flame-retardant polymers are in the construction, transportation, electrical, and electronics industries. In building construction applications, the polymers are mainly used for insulation, linings for walls and ceilings, floor coverings, partitions, roofing and exterior cladding. In transportation applications, the polymers are used for cars, buses, trains, subways, airplanes and ships in cabin interiors, and seating. In electrical applications, the polymers are used for cabinets for electrical equipment such as television sets, audio equipment, business machines, switch boxes, connectors and plugs. Electronic applications of these polymers are printed circuit boards, integrated circuit packaging, wire and cable insulation.

Compared with other plastic additives, flame

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retardants are generally used at high levels and can significantly impair the performance properties of the parent polymer. The basic rule for the selection of flame retardant is that it meets minimum performance requirements at the least possible raw material and processing costs. Also there should be no concerns for toxicity and environmental safety. Certainly, other factors such as easy compounding, thermal stability, light stability, corrosivity, appearance, permanency, influences of other physical properties are also to be considered.

The major groups of flame-retardant chemicals are the halogenated organics, the halogenated or non-halogenated phosphate esters, the antimony oxides and aluminum trihydrate. Other compounds of commercial importance are magnesium hydroxides, ammonium phosphates, melamine and various borates and molybdates used primarily as smoke suppressants. Besides the pure organic or inorganic flame retardants, sometimes the combination of them gives even better results. Halogen/antimony synergism is the most famous of these. Antimony oxide shows no significant flame retardant property by itself. However, it produces a marked synergistic effect with halogen-containing compounds.

Based on the ways that flame retardants are incorporated with polymers, flame retardants are often classified as being “additive” or “reactive”. The “additive” type of flame retardants is physically mixed with the parent polymer either prior to, during or right after the polymerization. These flame retardants are used especially in thermoplastics. There is no chemical bonding between the flame retardants and parent polymer. If they are compatible with the polymer, they may also behave like plasticizers, otherwise they may be considered fillers. The “reactive” type of flame retardants will react with other monomer units by copolymerization or by grafting. The flame retardant compounds are chemically bonded into the polymer backbone. This prevents them from bleeding and volatilizing out of the polymer. They are used mainly in thermosets in which they can be easily incorporated.

Each class of flame retardants may react differently when burned. However, they are generally thought to function in terms of “physical action” and “chemical action” in one or more of the following ways. The physical action retardants function by

cooling, isolating or diluting. They absorb the heat being generated from combustion, making sustained burning more difficult. They form a non-flammable char or coating to insulate the rest of polymer from heat, exclude oxygen, and slow the rate of diffusion of volatile flammable pyrolysis fragments. They liberate non-flammable products to dilute the concentration of flammable species and render burning of the substrate more difficult. The chemical action may operate by separating flammable material, or interfering with flame chemistry. They enhance decomposition of the substrate, resulting in dripping the substrate away from the flame. They generate volatile species to interfere with exothermic free radical propagating reactions in the flame, reducing burn velocity and narrowing flammability limits of the substance.

Flame retardants normally have very high boiling points, the additive type (most of them are organic compounds) may be analyzed by gas chromatography (GC) or liquid chromatography (LC) methods if these compounds can be successfully separated from the original polymer matrix. However, if the flame retardant is in the polymeric form, most GC methods will not be that effective because of the high boiling point and high molecular mass. Most LC methods also are hampered because of the high molecular mass. In addition, even if there is a LC method that is capable of separating polymeric flame retardants from their original polymeric matrix, detection and identification will still be a rigorous task. There is no universal in-line detection device that can effectively detect and identify these polymeric flame retardants. If the flame retardant is a reactive type, the flame retardant unit is copolymerized into the polymer backbone. Therefore, the separation and detection of it by GC or LC maybe difficult or impossible.

Owing to these separation and detection difficulties, the analytical techniques available to resolve the additive types of polymeric flame retardants as well as the reactive type of flame retardants are greatly limited. Pyrolysis–gas chromatography (Py–GC) [1] is one of the techniques that is suitable not only to attack this problem, but also for general-purpose flame retardant analysis. Py–GC is an important technique used for polymer composition and microstructure analysis that uses thermal energy

(pyrolysis) to break down a polymeric chain to monomers, oligomers, and other fragments, followed by the separation of pyrolysates with GC and detection with appropriate detectors. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS) or mass-selective detection is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data [2]. The oligomers or oligomer-related fragments are used to elucidate microstructure as well as composition information [3].

One of the advantages of the pyrolysis technique is the simple sample preparation. For a solid sample, the only preparation required is to cut the solid into the appropriate size and weigh a sample of suitable (approximately 500 μg) amount. The purpose of this preparation is to fit a sample into the pyroprobe while, at the same time, ensuring complete pyrolysis. This technique is extremely useful in the study of a solid sample or additives in the solid where there is no simple way to separate the additive from the solid. Flame retardants have been studied by pyrolysis for a long time. Most of the studies focused on thermal degradation under certain pyrolysis or fire conditions [4,5]. The pyrolysates produced have been evaluated for the safety of humans and the environment around the fire area [6,7]. Other studies of flame retardants emphasized the flame resistance capability or the mechanism of flame propagation prevention [8,9]. Few reports focused on the analytical identification of the type of flame retardants in the polymers [10–13].

The Py–GC technique is only amenable to the analysis of organic materials. Organic flame retardants such as halogenated organics and the halogenated or non-halogenated phosphate esters can be qualitatively and quantitatively analyzed by Py–GC simultaneously with the polymer composition and microstructure. If the flame retardant is a mixture of organic and inorganic materials such as the halogen/antimony synergistic pair, only the organic portion can be explored. Depending on the cost, each different polymer may have a specific flame retardant package associated with a specific application area to meet a required flammability specification. The key

to the successful analysis of flame retardants in a polymer for a specific application not only requires a comprehensive understanding of commercial flame retardants but also requires knowledge of the parent polymer and its targeted application, as well as the required test to be passed for that specific application. In this study, the flame retardants used in different polymers for different applications have been investigated to demonstrate that Py–GC with MS is a good tool to investigate the flame retardants in the polymer. In addition, atomic emission detection (AED) is very effective in monitoring different halogen-containing and phosphorus-containing pyrolysates after Py–GC. The types of flame retardants used in the polymers were identified by peak pattern recognition through an AED halogen element trace. The advantages and disadvantages of using AED have been discussed in the literature [14]. The discussion in this study will focus on MS where the advantages of using Py–GC in this flame retardant analysis are discussed.

2. Experimental

2.1. Polymers

A personal computer made by a leading retailer has been used for samples to obtain the polymers used in the electronic applications. These include a printed circuit board (motherboard), a circuit board edge connector, an extension board connection socket and a personal computer case. Other samples were directly obtained from commercially available resins. They include a fiber reinforced poly(butylene terephthalate) (PBT) resin, CASTIN-LW9330-FR507, obtained from DuPont, an acrylonitrile–butadiene–styrene terpolymer (ABS) resin SNKKI UB801A, from Sumitomo Naugatuck, a polycarbonate and ABS blend resin (PC–ABS) resin, SNKKI F-101, from Sumitomo Naugatuck, and another PC–ABS resin, Bayblend FR-90, from Bayer. All polymers were used as they were received without any further purification.

2.2. Py–GC conditions

Samples of polymer (approximately 0.5 mg) were

carefully deposited into a quartz tube. The quartz tube was put in a 300°C interface connected to the injection port of a Hewlett-Packard (HP) Model 6890 gas chromatograph equipped with a FID system. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 950°C. The coil was heated to the calibrated temperature at 20°C/ms and held at the set temperature for a 20-s interval. The pyrolysates were split in the 300°C injection port, with 250:1 split ratio. The GC system was set up with a fast flow program, 15 p.s.i. (1 p.s.i.=6894.46 Pa)/0.2 min, 75 p.s.i./min, to 90 p.s.i./8.8 min. The separation was carried out on a fused-silica capillary column (J & W Scientific DB-5, 10 m×0.10 mm I.D., 0.4 µm film) using a fast temperature ramping program (50°C/0.2 min, 100°C/min, to 100°C/0 min; 80°C/min, to 140°C/0 min; 60°C/min, to 200°C/0 min; 50°C/min, to 280°C/0 min; 40°C/min, to 320°C/5.2 min).

2.3. Py-GC-MS conditions

The sample preparation and pyrolysis in the Py-GC-MS experiments were the same as in the Py-GC experiments. The GC system used is a HP model 5890 gas chromatograph. The pyrolysis products were split in the 300°C injection port, with 10 p.s.i. head pressure, and 30:1 split ratio. The pyrolysates were separated on a fused-silica capillary column (J & W Scientific DB-5, 30 m×0.25 mm I.D., 1.0 µm film) using a linear temperature program (40°C/4 min, 10°C/min, to 320°C/18 min); and detected by a HP 5791 mass-selective detector. The GC output region to the mass-selective detector was kept at 300°C. An electron ionization mass spectrum was obtained every second over the mass range of 15 to 650 u. The results of Py-GC-MS are used mainly for pyrolysates identification.

3. Results and discussion

Fig. 1 shows a pyrogram of a printed circuit board (personal computer motherboard). The major pyrolysates detected are phenol, methylphenol, methylethylphenol, bromophenol, dibromophenol and different bromine substituted bisphenol-A indicating that brominated bisphenol-A was used along

with bisphenol-A as part of monomer unit in the polymer. Printed circuit boards are usually made of cross-linked epoxy resin that is a thermoset of bisphenol-A diglycidyl ether. In this printed circuit board application, the brominated bisphenol-A has been added with bisphenol-A as the starting monomers for the epoxy resin in order to achieve the necessary flame retardation test. Brominated bisphenol-A served as a “reactive” flame retardant in this case. Because the flame retardant is chemically bonded into the polymer backbone, there is no issue of volatilization, migration and permanence.

Fig. 2 shows a pyrogram of a green colored edge connector of a printed circuit board. The connector is made of poly(diallylphthalate) with a cycloaliphatic chlorinated flame retardant, Dechlorane Plus (chemical name and structure can be seen in Fig. 2). The pyrolysates produced from the flame retardant elute at the same time with the major pyrolysates from the polymer matrix. This situation makes the identification of the flame retardant a little difficult. However, as the pyrolysates due to the flame retardant contain unique ions that can be extracted/located by the single-ion monitoring (SIM) technique, qualitative identification of the flame retardants is possible. The identification of Dechlorane Plus is based on the two major pyrolysates, 1,2,3,4-tetrachloro-1,3-pentadiene and 1,2,3,4,5-pentachloro-1,3-pentadiene.

Other polymers can also be used to fabricate the personal computer extendable inset card socket. Fig. 3 is a pyrogram of a personal computer insert card socket which is made of PBT. The detection of bromophenol, dibromophenol and tribromophenol indicates that the flame retardant is a brominated phenol type. The possibility of other types of brominated compounds such as brominated diphenyl oxides, brominated polystyrene and brominated bisphenol-A have been ruled out because pentabromobenzene, brominated styrene and brominated bisphenol-A were not detected in the pyrolysates. The possible candidates of brominated phenols include 1,2-bis-(2,4,6-tribromophenoxy)ethylene, bis(pentabromophenoxy)ethane, tribromophenylallyl ether and polydibromophenylene oxide.

Depending on the application, the same polymer matrix may have different flame retardant packages. Fig. 4 is a pyrogram of PBT, CASTIN-LW9330-FR507, used in high-temperature applications. De-

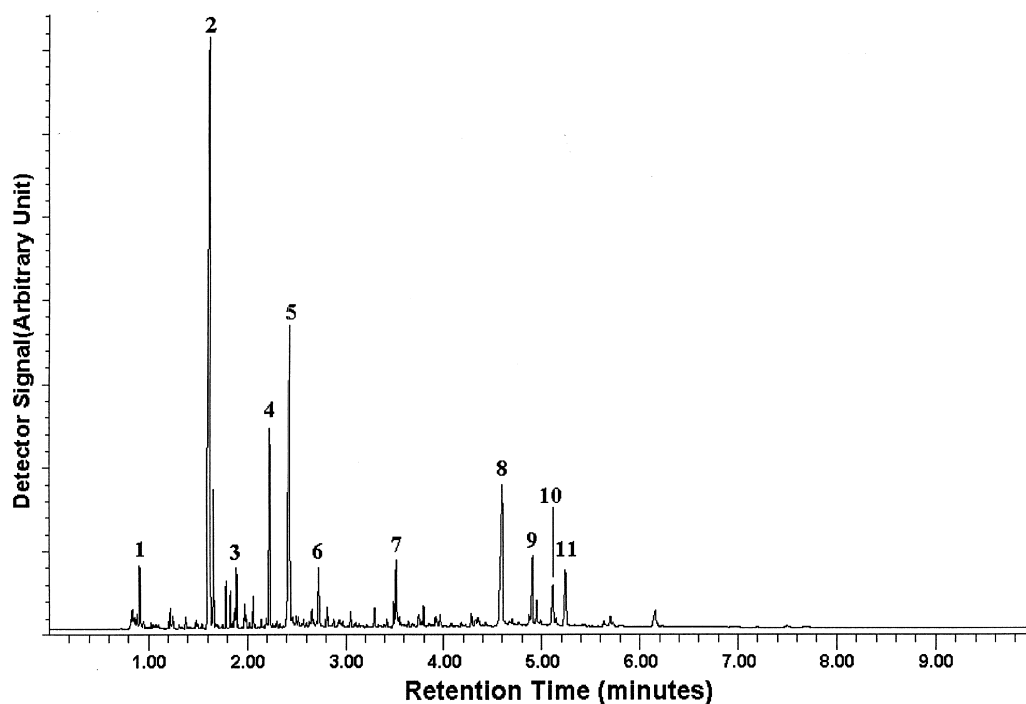


Fig. 1. The pyrogram of a printed circuit board polymer. The tentative identification of major pyrolysates is (1) acetone, (2) phenol, (3) 2-bromophenol, (4) 4-methylethylphenol, (5) 4-methylethenylphenol, (6) 2,6-dibromophenol, (7) 2,6-dibromo-4-methylethenylphenol, (8) bisphenol-A, (9) bromobisphenol-A, (10) dibromobisphenol-A, (11) tribromobisphenol-A.

tection of the specific pyrolysates, bromostyrene, dibromostyrene and tribromostyrene, indicated that the organic portion of the flame retardant used in this polymer is brominated polystyrene. The advantage of having a polymeric compound as an additive type flame retardant is the thermal stability and low volatility in the high-temperature application environment.

Fig. 5 shows a pyrogram of a personal computer chase, the chase is composed of an ABS–poly(vinyl chloride) (PVC) alloy. In this example, the flame retardant is a polymer and it is an additive type. The PVC is widely used as a base polymer in many other applications. However, because the chlorine content is more than 50% (w/w) in this polymer, PVC is also a very good flame retardant. The existence of PVC can be proved by the detection of the extraordinary intensity of benzene, which is the result of PVC dehydrochlorination followed by chain scission. If MS is used, the detection of hydrochloric acid as an early-elution component in GC is further evidence.

Again, ABS is also used in a lot of other applications. PVC is not necessarily the only flame retardant associated with ABS. Fig. 6 shows a pyrogram of ignition-resistant ABS with octabromodiphenyl oxide as the flame retardant. Except for the pyrolysates from ABS, the major pyrolysates from octabromodiphenyl oxide are tetrabromobenzene and pentabromobenzene. These pyrolysates can be found/identified by their specific parent ion/mass pattern because of their isotope combination of multiple bromine atoms.

As mentioned in the Introduction, a flame retardant normally possesses a very high boiling point as well as very high molecular mass. Even though the flame retardant is a polymeric type molecule (with multiple repeating monomer units) or a large single unit molecule, the flame retardant will still break down along with the parent polymer to produce pyrolysates. However, experience shows that the efficiency of pyrolysis of a large single unit molecule is not high. The pyrolysate production is

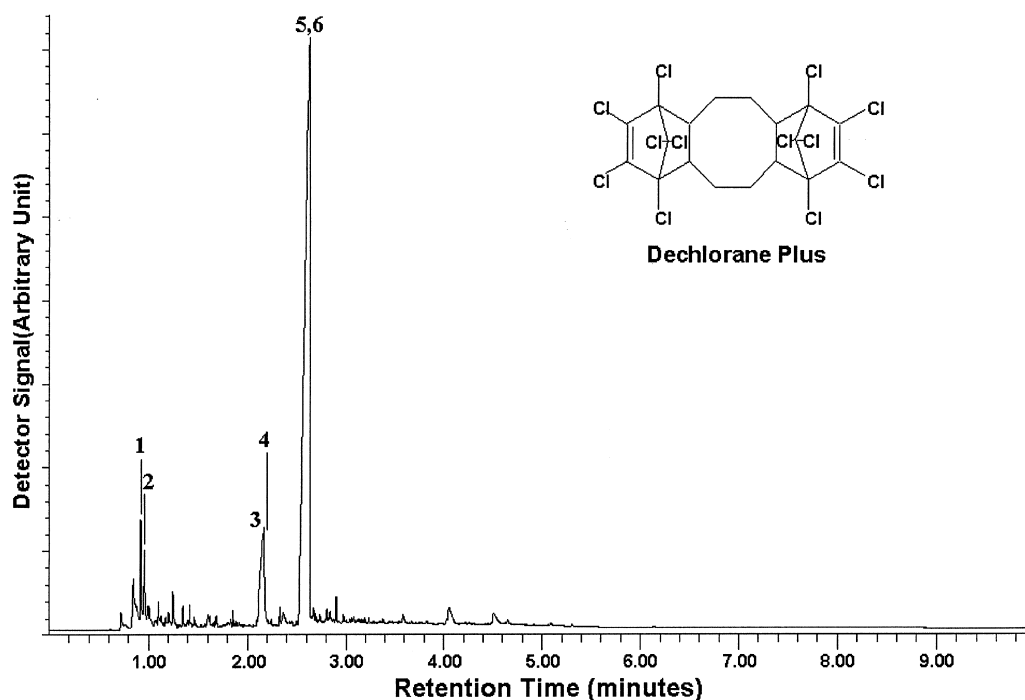


Fig. 2. The pyrogram of a printed circuit board edge connector. The flame retardant used is Dechlorane Plus. The chemical name is 1,2,3,4,7,8,9,10,13,13,14,14-dodecahydro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo[*a,e*] cyclooctene. The tentative identification of major pyrolysates is (1) propylene oxide, (2) 2-propen-1-ol, (3) benzoic acid, (4) 1,2,3,4-tetrachloro-1,3-cyclopentadiene, (5) benzoic anhydride, (6) 1,2,3,4,5-pentachloro-1,3-cyclopentadiene.

not abundant in general. The key to identifying it is to understand what type of pyrolysate is produced as well as what are the likely polymer/flame retardant pairs. Sometimes, the identification instrument used (such as HP 5971 mass-selective detector) may not have enough mass range to show the full mass spectrum such as octabromodiphenyl oxide (molecular mass 820) and decbromodiphenyl oxide (molecular mass 980). The identification of this flame retardant has to rely on the lower-molecular-mass pyrolysates and their retention times under specific Py-GC-MS conditions.

Fig. 7 shows a pyrogram of a polycarbonate-ABS blend (PC-ABS). This engineering thermoplastic has a wide application for business machines and instrument panels of transportation vehicles. The common flame retardant used is a brominated phenol. However, the concerns of using halogenated flame retardant have increased in recent years be-

cause of issues of safety, toxicity as well as environmental impact. For example, does the flame retardant have a low order of toxicity, so that it can be handled safely on a plant scale? Is it biodegradable? Does it bioaccumulate? What affect does it have on the environment? Because of these concerns, in the last few years, there has been a trend for phosphate compounds to gradually replace halogenated flame retardants. Fig. 8 shows a pyrogram of another PC-ABS blend. The flame retardant used in this polymer does not contain any halogen atom, it is a triphenyl phosphate.

Traditionally, the flame retardant can be directly analyzed by Py-GC-MS, especially when the flame retardants contain halogen elements, such as chlorine and/or bromine. Because the chlorine and bromine elements possess characteristic pairs of isotopes with well-known ratios, it is relatively easy to detect chlorine and/or bromine in a component through its

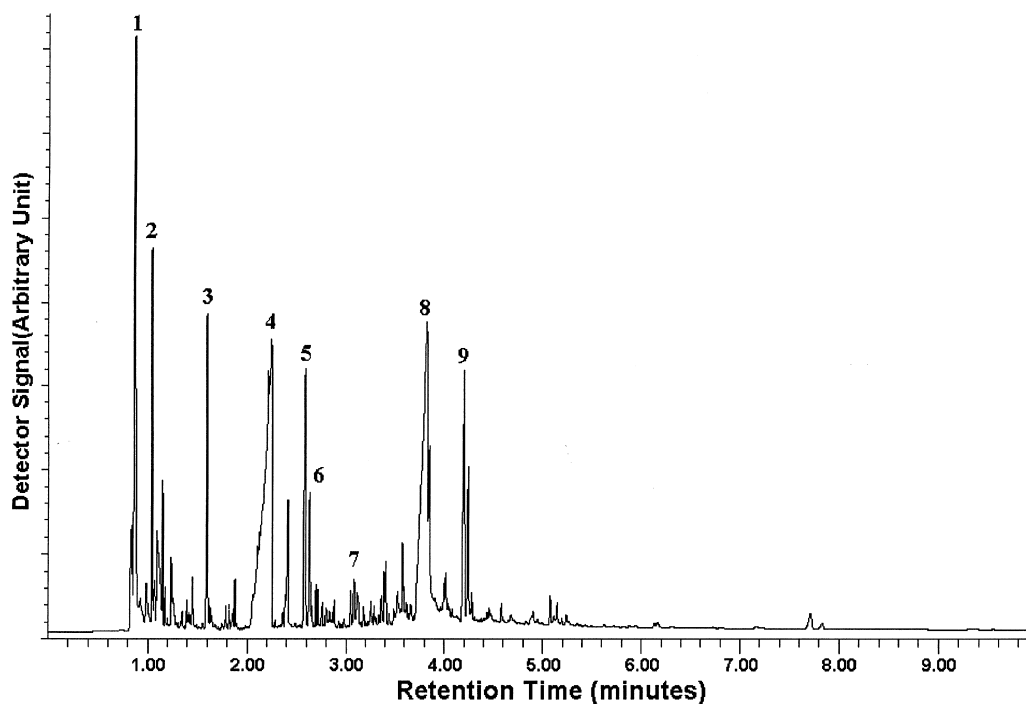


Fig. 3. The pyrogram of a personal computer extension circuit board insertion socket. The polymer is PBT and the flame retardant is a brominated phenol type compound. The tentative identification of major pyrolysates is (1) butadiene, (2) tetrahydrofuran, (3) phenol, (4) benzoic acid, (5) benzoic acid, butyl ester, (6) 2,6-dibromophenol, (7) 2,4,6-tribromophenol, (8) dibenzoic acid, butenyl ester, (9) 1,4-butandiol dibenzoate.

mass spectrum. However, if the flame retardant is a phosphorus-containing compound, the identification through MS will be the same as for all other pyrolysates. There is no quick way to recognize the ion/mass pattern through its mass spectrum. In addition, there may be superimposed and partially overlapped peaks, such that the mass spectrum of one peak may represent the combination of two or more pyrolysates. Because of the large number of pyrolysates produced during the pyrolysis of the polymer matrix with flame retardants, interpretation and identification of all components can be rather time consuming. An understanding of which pyrolysates originally came from the flame retardants may not be straightforward. Sometimes, SIM may be a way to explore certain fragments in the pyrolysates. However, without knowing the identity of the flame retardant, there is no simple way to predict which fragment ion/mass to monitor. Even

though these flame retardants contain halogen elements, there is no good way to know the identity of the aliphatic or aromatic counterpart to which the halogen element is attached.

In this situation, AED may be superior to MS for the detection of specific-element-containing fragments and their relative intensity pattern. Depending on the specific atomic emission lines chosen, AED will detect those components that contain the specific element of interest (such as phosphorus, chlorine, and bromine). The major advantage of using AED is the selectivity of detection. The ability to detect specific-element-containing components while at the same time discriminating any other possible complications is the key point of this effective detection. Unlike MS, AED does not have direct identification capability for those components detected. However, AED can still be used as an identification tool by a retention time index and a peak pattern recognition

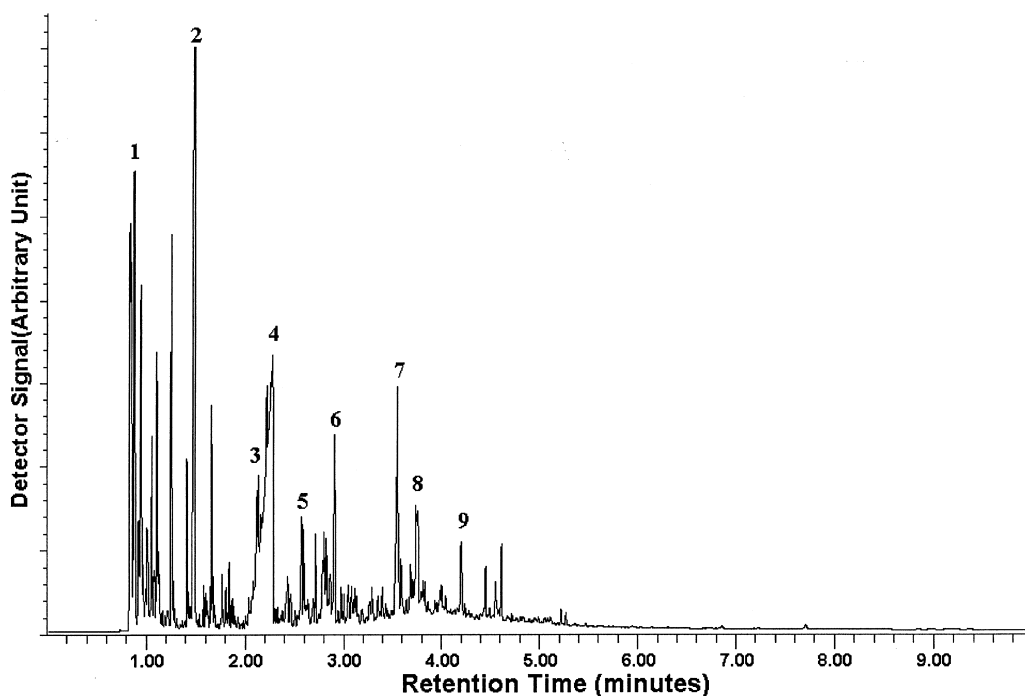


Fig. 4. The pyrogram of a fiber reinforced polymer for high-temperature application. The polymer is PBT, CASTIN-LW9330-FR507, and the flame retardant is a brominated polystyrene. The tentative identification of major pyrolysates is (1) butadiene, (2) styrene, (3) bromostyrene, (4) benzoic acid, (5) benzoic acid, butyl ester, (6) dibromophenol, (7) 2,4,6-tribromophenol, (8) benzoic anhydride, (9) 1,4-butandiol dibenzoate.

approach. A unique element trace pyrogram can be used to identify the specific-element-containing flame retardant. There is little chance that two different flame retardants will have the same set of pyrolysates plus similar relative pyrolysate intensity ratios, which produce the same GC elution pattern.

There are significant secondary reactions that occurring during the pyrolysis of most of the flame retardant-containing polymers. The examples include the butylene fragment from PBT and aliphatic amines from the aliphatic polyamides. These reactive pyrolysates may react with pyrolysates from flame retardants to form new components that are not found in the pyrolysates from either the polymer or the flame retardants. These secondary reaction products may cause some confusion in the peak pattern recognition during the identification of flame retardants. One example can be found in the Py-GC analysis of different aliphatic polyamides (nylon-4,6, nylon-6,6 and nylon-6,9) with brominated poly-

styrene as the flame retardant [14]. An extra component (the secondary product) appears in the nylon-4,6 pyrogram and in the nylon-6,6 and -6,9 pyrograms. This component has been identified (by Py-GC-MS) as 4-bromo-1-butene in the nylon-4,6 case and 6-bromo-1-hexene in the nylon-6,6 and -6,9 cases. On the basis of the repeat unit structure of nylons [nylon-4,6 is poly(tetramethyleneadipamide), nylon-6,6 is poly(hexamethyleneadipamide), and nylon-6,9 is poly(tetramethylenenonanediamide)] and the structure of the extra component produced from the secondary reaction, the reactants must come from the aliphatic amine part of the polyamides and hydrogen bromide (HBr) from the flame retardant. The reaction mechanism can be postulated as the aliphatic amine reacting with HBr to form the aliphatic bromide where the amine group has been replaced by the bromine during the reaction. The second example is when polymer contains decabromodiphenyl oxide or octabromodiphenyl oxide as

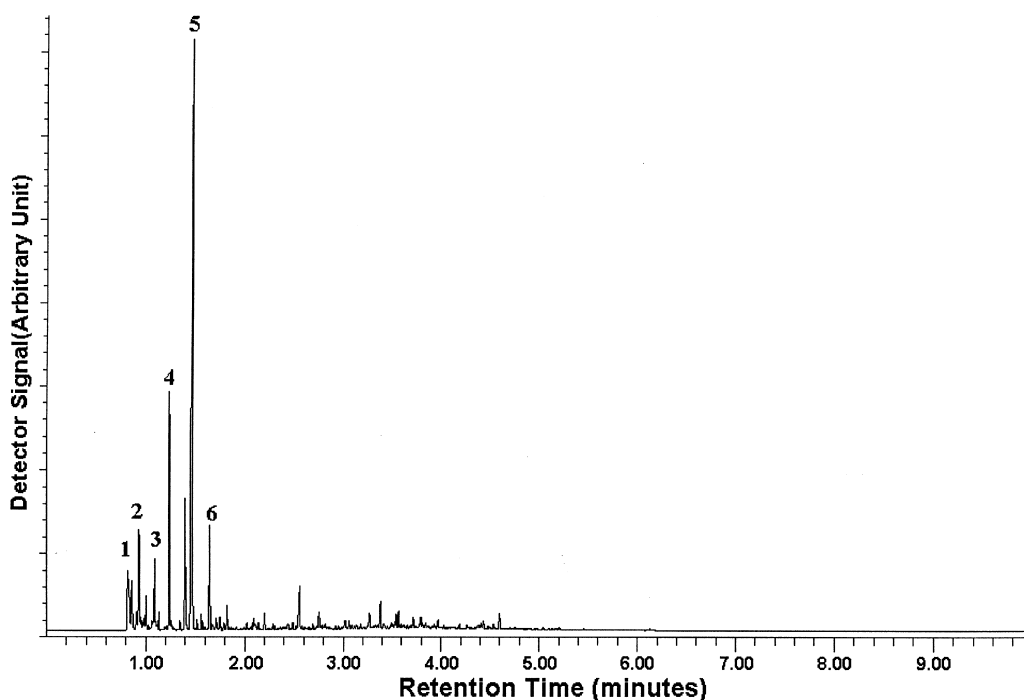


Fig. 5. The pyrogram of a personal computer chase. The polymer is an ABS–PVC alloy. The PVC is used as a flame retardant. The tentative identification of major pyrolysates is (1) butadiene, (2) acrylonitrile, (3) benzene, (4) toluene, (5) styrene, (6) α -methylstyrene.

flame retardant, a small amount of hexabromobenzene is always produced during pyrolysis. Based on the structure of these two flame retardants, there is no chance to produce hexabromobenzene unless there is a secondary reaction causing the partially brominated benzene to be completely brominated. However, if the secondary reaction products and the mechanism of formation can be understood, the extra pyrolysate could be explained upon analyzing for the flame retardant for that polymer family.

4. Conclusions

Organic flame retardants such as halogenated organics and the halogenated or non-halogenated phosphate esters can be qualitatively and quantitatively analyzed by Py–GC simultaneously with the polymer composition and microstructure. If the flame retardant is a mixture of organic and inorganic

materials such as halogen/antimony synergistic pair, only the organic portion can be explored by Py–GC. The key to the successful analysis of flame retardants in a polymer for a specific application not only requires a comprehensive understanding of commercial flame retardants, but also requires knowledge of the parent polymer and its targeted application, as well as the test required for that specific application. In this study, Py–GC with MS has been proved useful for the investigation of flame retardants in polymers. However, AED is very effective in monitoring different halogen-containing and phosphorus-containing pyrolysates after Py–GC. The type of flame retardant used in the polymers can be identified by peak pattern recognition through an AED-specific element trace. The discussion of the advantages and disadvantages of using AED can be found in literature. MS as a general-purpose Py–GC detection methods can effectively detect/identify halogenated flame retardants by the specific isotope ratios of chlorine and bromine.

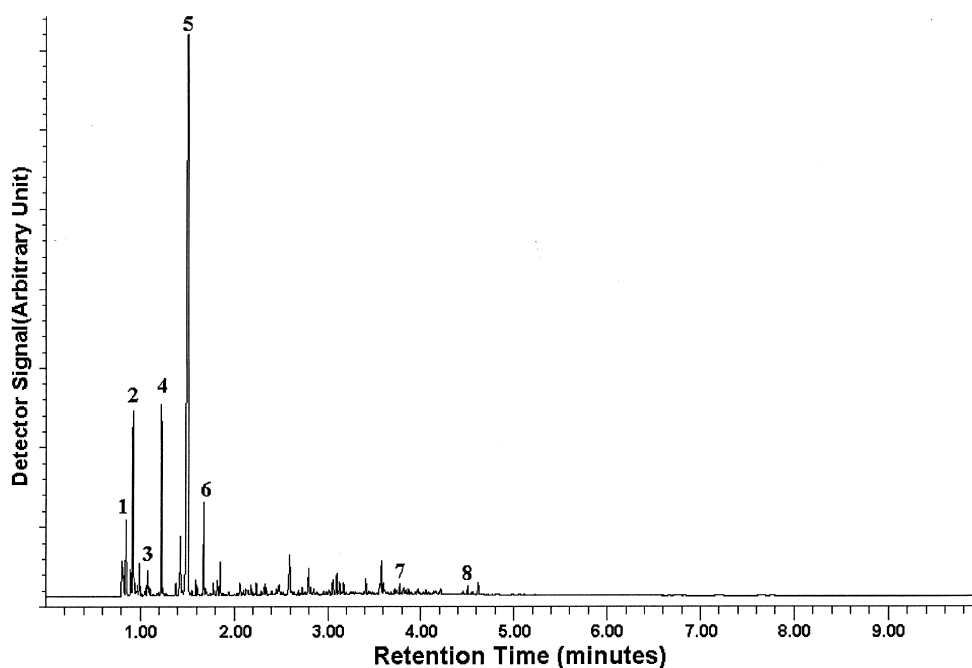


Fig. 6. The pyrogram of an ABS and the flame retardant is an octabromodiphenyl oxide. The tentative identification of major pyrolysates is (1) butadiene, (2) acrylonitrile, (3) benzene, (4) toluene, (5) styrene, (6) α -methylstyrene, (7) tetrabromobenzene, (8) pentabromobenzene.

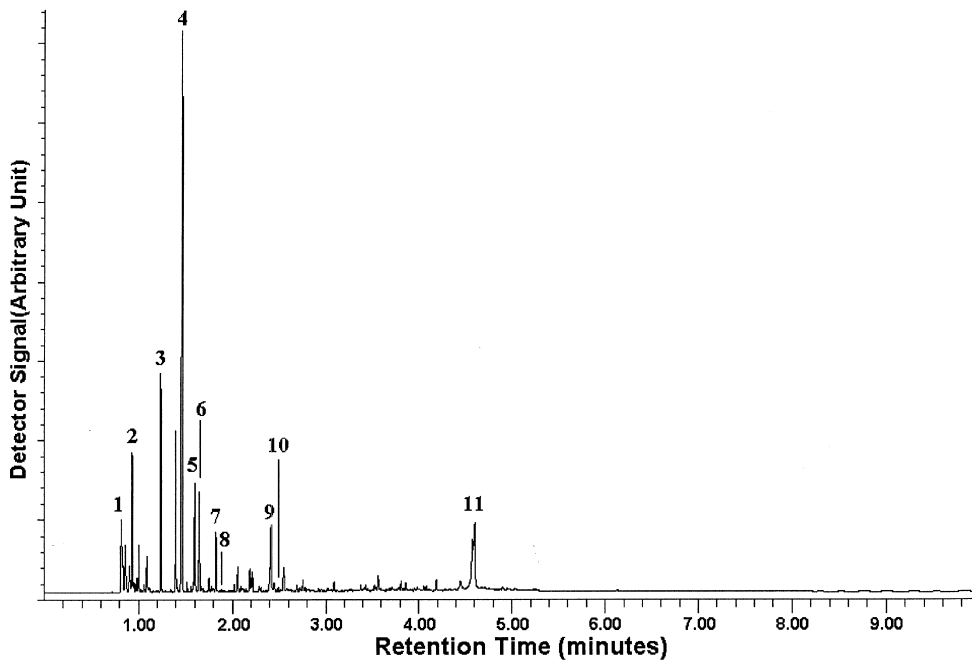


Fig. 7. The pyrogram of a PC-ABS blend and the flame retardant is a brominated phenol. The tentative identification of major pyrolysates is (1) butadiene, (2) acrylonitrile, (3) toluene, (4) styrene, (5) phenol, (6) α -methylstyrene, (7) 4-methylphenol, (8) bromophenol, (9) *tert*-butylphenol, (10) dibromophenol, (11) bisphenol-A.

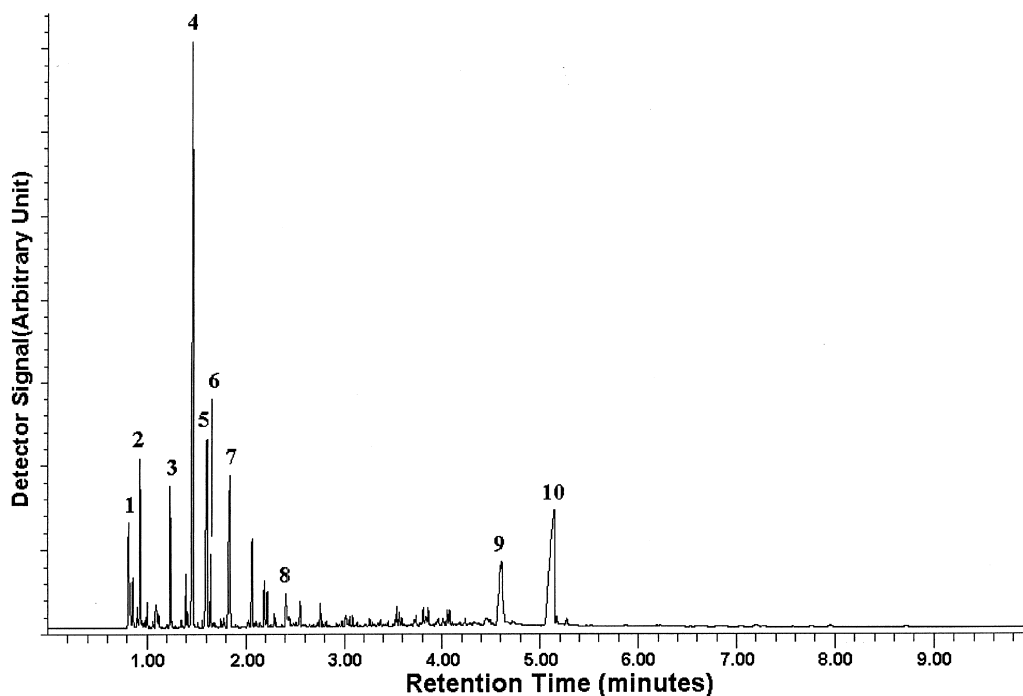


Fig. 8. The pyrogram of a PC–ABS blend and the flame retardant is a brominated phenol. The tentative identification of major pyrolysates is (1) butadiene, (2) acrylonitrile, (3) toluene, (4) styrene, (5) phenol, (6) α -methylstyrene, (7) 4-methylphenol, (8) *tert.*-butylphenol, (9) bisphenol-A, (10) triphenyl phosphate.

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