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Review

Polymer analysis by pyrolysis gas chromatography

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Abstract

Pyrolysis gas chromatography (Py–GC) has been an important technique in the qualitative and quantitative analysis of polymers for more than thirty years. Recent developments in Py–GC technology are mainly focused on pyrolysis operation and applications. In the former category, the focus is on the development of flexible pyrolysis instrumentation, ‘‘pre-’’ and ‘‘post-’’ pyrolysis derivatization and database creation/maintenance. In the application field, the development focused on kinetics of thermal degradation, structure determination and integrate techniques associated with pyrolysis to perform qualitative and quantitative analysis of low level additives in polymers.

Keywords: Pyrolysis; Derivatization, GC; Polymers

Contents

1. Introduction

Pyrolysis is an important technique for the study of synthetic polymers. For more than thirty years development of this technique, the applications of pyrolysis to synthetic polymers focused on qualitative and quantitative composition analysis as well as structure exploration. Because of advances in instrumentation, computer technology, and laboratory sample preparation procedures, several methods associated with pyrolysis and gas chromatography (GC) have been re-visited in order to capture the advantages of this progress.

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Based on the goal of the analysis and the experimental approach, this review has been divided into different sections. All methods discussed are associated with pyrolysis gas chromatography (Py–GC) or pyrolysis-gas chromatography–mass spectrometry (Py–GC–MS). The applications are confined to the area of synthetic polymers. Methods such as the structure determination of copolymers and pre-pyrolysis derivatization are discussed in detail because recent developments differ from the traditional approach. There are also methods where not too much change has occurred, such as the study of the kinetics of thermal degradation as well as qualitative and quantitative analysis. In other ways, some methods associated with pyrolysis have been improved in order to increase sensitivity of detection to meet the requirements of certain applications.

2. Pyrolysis technique

2.1. Instrument configuration

Py–GC–MS remains the most convenient method to qualitatively analyze polymers. The heated filament, Curie-Point, and furnace are three major types of pyrolyzer used in the experiments. The standard configuration is the pyrolyzer mounted on top of the GC injection port. Once the pyrolyzer is attached, the GC is exclusively used for pyrolysis experiments. On the detection side of the GC, in addition to flame ionization detector (FID) and mass selective detection (MSD), there are other GC detection methods such as atomic emission detection (AED), flame photoionization detection (FPD), nitrogen–phosphorus detection (NPD) etc., which have been used. Besides using different types of detector, instrument configuration may be varied or other thermal analysis equipment may be converted to meet specific applications.

Different configurations include utilizing a programmable temperatures vaporization (PTV) injector to conduct the multi-step thermal desorption and programmed Py–GC experiments. Polymers have been studied by using a high-temperature programmable temperatures vaporization (PTV) injector to thermally treat the polymer sample at different temperatures [1]. The GC system is used to separate the complex mixtures of several polymers and additives. The individual chromatograms of the various constituents of the polymeric sample were correlated with those of the final material in order to identify additives (thermal desorption) and degradation products (pyrolysis). The advantage of using the PTV injector for this purpose is that no heated transfer line and switching values are needed. This will eliminate the risk of losses of high-molecular-mass components. Other advantages of the proposed technique are simplicity, versatility and low cost.

Another configuration approach is the creation of a dual inlet (pyrolysis and autosampler) system, sufficiently flexible to use both kinds of injection system. In a conventional Py–GC system, the pyrolyzer was interfaced on top of the GC system which blocks the normal sample injection port. In this study, a different approach has been developed [2]. The pyrolyzer is mounted differently so it can coexist with the traditional sample injection device, namely an autosampler. The advantages of this configuration are that the pyrolyzer attachment does not interfere with sample introduction through the injection port; the GC system can be easily converted to a Py–GC system without mounting or dismounting of the equipment; and when operated as a Py–GC unit, the conventional sample injection port can be used as an auxiliary sample introduction route to greatly enhance the capability of Py–GC data handling in qualitative and quantitative analysis.

The third development in the instrument configuration is the development of a Py–GC system with a movable reaction zone [3]. The device enables the thermal degradation of polymers inside a capillary pre-column and transfer of the reaction zone into a column oven. The pyrolysis procedure described protects the thermally sensitive compounds prior to pyrolysis, prevents the process of irreversible condensation of high-boiling pyrolysis products during the chromatographic process and eliminates extra-column effects on peak broadening.

The use of a thermal extraction unit for a furnace-type pyrolysis interface has been studied for the analysis of polymers [4]. Pyrolysis is achieved by accurate temperature programming of the pyrolysis cell from ambient to very high temperatures. The suitability of the thermal extraction unit for use as a pyrolyzer was evaluated by analyzing several model polymers. The results obtained demonstrated that this unit can be used as a pyrolyzer. The main advantages of the technique are good reproducibility, minimum secondary reactions, capability for quantitative analysis, and minimum sample handling.

2.2. Pyrolysis with derivatization

Derivatization is a well-known technique in chromatographic analysis used to enhance chromatographic separation and/or detection for those compounds not suitable for separation/detection. The same concept has been adapted to Py–GC or Py–GC–MS analysis.

However, the scope of the derivatization reaction should be expanded from the conventional chromatographic analysis point of view to include the pyrolysis process. The derivatization reaction serves not only to enhance the chromatographic separation and/or detection, but also to allow thermal degradation pathway re-selection to improve the pyrolysis process for qualitative and quantitative analysis. In Py–GC, the derivatization reaction does not have to be limited to the ‘‘pre-column’’ and ‘‘post-column’’ situation. The derivatization reaction may be divided into ‘‘pre-pyrolysis’’ and ‘‘post-pyrolysis’’.

In ‘‘post-pyrolysis’’, the derivatization techniques have experienced additional development in pyrolysis analysis of polymers. The major portion of the derivatizations involve the methylation of alcohols and acids. The most popular methylation regents are tetramethyl ammonium hydroxide (TMAH) and trimethyl sulfate (TMS). The purpose of derivatization is to modify the pyrolysates in order to obtain better separation and detection results.

There is another development in derivatization which can be called ‘‘pre-pyrolysis’’ derivatization. The purpose of this type of derivatization is to convert the functional group in the polymer to obtain a favorable thermal degradation pathway during pyrolysis. The term favorable pathway means a major monomer or monomer related fragment is produced to allow for easier qualitative and quantitative analysis. The major difference between the ‘‘pre-pyrolysis’’ derivatization and ‘‘post-pyrolysis’’ derivatization is the polymer backbone must be stable enough to resist the attack from the derivatization reagent in ‘‘pre-pyrolysis’’ derivatization. Pyrolysis is merely the mechanism to decompose the polymer to fragments.

2.2.1. Pre-pyrolysis derivatization

In ‘‘pre-pyrolysis’’ derivatization, the main considerations of this modification or derivatization are four-fold: (1) Ease and convenience. The derivatization reaction takes place without rigorous conditions such as heating the sample to high temperature or reacting in high pressure. (2) Reduced interference from surrounding materials. Most derivatization reagents for primary amines are hydrogen sensitive, which means these reagents cannot be used in aqueous solutions or with chemicals with alcohol or acid functional groups. (3) The final product must degrade with a favorable thermal degradation pathway. The derivatization reaction will produce a stable functional group. Under thermal degradation, this derivatized polymer will depolymerize with either an unzipping pathway or a major fragment-producing pathway. (4) The major monomer or fragment produced either by the unzipping reaction or by monomer-related chain cleavage should be suitable for GC separation and detection. For example, the monomer or fragment should be a nonpolar compound when using a nonpolar capillary separation column. The elution time of the fragment should not be so fast as to lose the resolution from other pyrolysates in the separation. At the same time, the elution time should not be too long, which would waste analysis time.

A thermal degradation pathway re-selection study of polymethacrylic acid through derivatization [5] has demonstrated the value of pre-pyrolysis derivatization in qualitative and quantitative Py–GC analysis. The pyrolysis of polymethacrylic acid will produce a number of pyrolysates which reflect the unzipping degradation as well as the random chain session and recombination. If the polymer has been derivatized by TMAH to convert the acid functional group to methyl ester, the thermal degradation of poly(methyl methacrylate) only produces one major fragment which is the methyl methacrylate monomer. In the study, several copolymers containing low level of methacrylic acid have been successfully identified by this ‘‘pre-pyrolysis’’ derivatization technique.

2.2.2. Post-pyrolysis derivatization

The ‘‘post-pyrolysis’’ derivatization technique in the Py–GC study of polymers has been developed for a long time. For example, the pyrolysates can be derivatized ‘‘simultaneously,’’ ‘‘in-situ,’’ or ‘‘on-column’’ to reduce the difficulties of polar pyrolysates being separated in a nonpolar capillary column [6]. In another example, unsaturated aliphatic alkenes can be derivatized by hydrogenation to simplify the number of fragments and increase the possibility of structural exploration [7]. In general, these techniques modify the pyrolysates produced by the pyrolysis process. Post-pyrolysis derivatization implies that during the course of pyrolysis, there is no intention of altering the thermal degradation pathway through derivatization.

In-situ hydrolysis/methylation pyrolysis gas chromatography for the characterization of polyaramids has been studied [8]. Some parameters which influenced in-situ methylation by TMAH during pyrolysis were explored. Both pyrolysis temperature and excess TMAH (pH effect) influenced the methylation of carboxy-, aromatic, amino-, and hydroxyl-functional groups. The solvent of TMAH, i.e., methanol or water, significantly affected the methylation for the polyaramids but hardly influenced other model compounds studied. The explanation given assumed a transesterification mechanism rather than hydrolysis/methylation. However, *n*-methylation prior to the decomposition of polyaramids may not be excluded.

A study of characterization of copolymer type polycarbonates by reactive Py–GC in the presence of TMAH has been reported [9]. In this study, Py–GC in the presence of TMAH was successfully applied to the determination of chemical composition and end group content of two kinds of polycarbonate (PC) copolymers, thermally and light stabilized PCs. The Py–GC with post-derivatization of these PC copolymers enabled almost quantitative detection of the constituents of the polymer sample as their methyl ethers on the resulting pyrograms. On the basis of these peak intensities, the compositions as well as the number-average molecular masses were accurately estimated without using any reference polymer.

The reagent used in the post-pyrolysis does not have to be limited to organic alkali, there are other types of reagent that have been used for this purpose. The sequence distribution study of polyacetals by post-pyrolysis Py–GC in the presence of cobalt sulfate is an example [10]. In this study, post-pyrolysis of copolymer polyacetals in the presence of cobalt sulfate incorporated with Py–GC was applied to the study of sequence distribution. The ethylene oxide content and the distribution of ethylene oxide sequences up to seven monomer units in the polymer chain were evaluated on the basis of peak intensities of cyclic ethers in the pyrogram. These values were in good agreement with those obtained by hydrolysis.

Another polymer composition study through derivatization is the study of alternating olefin–carbon monoxide copolymers and their derivatives by Py–GC–MS [11]. Alternating copolymers of carbon monoxide and olefins (ethylene, styrene and norbornadiene) and their modified polymers with primary amines, P_2S_5 and P_2O_5 were prepared. These polymers were then pyrolyzed at 550°C for 10 s in a Py–GC–MS system. In each pyrolysis, hydrocarbons arising from the corresponding olefin comonomer were detected as the volatile products. Py–GC–MS confirmed that these 1,4- arrangements of the ketonic groups in the alternating copolymers were converted into pyrrole, thiophene, or furan-containing chains with primary amines, P_2S_5 or P_2O_5, respectively. The oxygen-containing groups, which remained intact during the modification with P_2S_5, were detected in small amounts in the pyrolysates.

2.3. Database and library

Chromatography databases such as for GC and liquid chromatography (LC), based on the retention time have been available for many years [12–14]. Because chromatography techniques focus on separation, the peaks in a chromatogram are representative of the number of components in that mixture and relative elution/retention order of that specific mixture under that experimental condition. The elution/retention time of peaks can be affected by many factors. These factors include type of mobile phase, type of stationary phase, thickness of stationary phase, mobile phase flow-rate and elution temperature.

Because the retention time is highly dependent on experimental conditions, it may not be suitable as a searchable parameter in a database. To solve this problem, there have been different types of retention indices developed [15–17]. The most commonly accepted indices is the Kovats retention indices. More recently, the concept of retention indices has been further developed in the chromatography field (especially in GC) to accommodate various experimental conditions [18,19]. Even with retention indices, there are still difficulties when comparing chromatograms obtained from different types of stationary and mobile phases. This is one of the major reasons why there is no universal chromatography database widely available. However, there are small chromatography databases for specific groups of compounds for specific purposes [20,21].

As mentioned above, chromatography focuses on the separation of the mixture. The mobile phase, stationary phase and experimental conditions are optimized to obtain the best separation. These parameters should not be standardized to obtain a consistent retention time. The reference chromatogram in the database should be used mainly to determine the separation phases and experimental conditions, the elution/separation order, the components in the mixture, and the relative abundance of components. If these are the most important parameters in the chromatography database, the database design should concentrate on how to find the desired reference chromatograms and the information about those components with minimum effort.

The creation and maintenance of a Py–GC database of polymers has been described previously. However, these databases are in book [22] form as a collection of chromatograms (pyrograms) or in an electronic [23] or hard copy format [24]. The depth of information included is limited. The search capability is restricted to a polymer index in the database or library. The users have to carry the electronic files or book to have the database available. In order to create and maintain a chromatography database in the electronic form, there are issues which have to be addressed. The issues include inputting data from different sources, maintaining (add, delete, and modify the entries) the database, access/distribution management, compatibility with other similar databases, potential to integrate with other databases, access from different computer platforms, and the cost of software.

A hyper text markup language (HTML) based database for chromatographic database creation and maintenance has been developed [25]. In this development, a Py–GC database has been used as an example to demonstrate the structure and the architecture of a chromatographic database. The database program, the users and database interface, as well as the distribution issues of a database have been discussed.

3. Applications

Analysis of synthetic polymers is one of the major areas for the application of pyrolysis technology. From another perspective, pyrolysis technology is frequently used to characterize synthetic polymers. Pyrolysis retains its important role in composition identification as well as in thermal degradation kinetic studies. The major advantage of pyrolysis compared with other technologies is the simple sample preparation. In addition to composition identification, pyrolysis was able to explore the copolymer structure with statistical theory applied. Pyrolysis can also study the stereoregularity of the homopolymers through tetramers or higher oligomers.

3.1. Kinetics of thermal degradation

Pyrolysis experiments have continued to play an important role in the evaluation of the thermal stability, thermal degradation mechanisms, as well as kinetic measurements of degradation of polymeric materials. Different types of polymers (thermoplastic and thermoset) are continuously being pyrolyzed to investigate their thermal behavior and degradation mechanism under different temperature conditions.

In thermoplastic polymers, sulfur containing polymers such as poly(*p*-phenylene ether-sulfone) (PES) resin and a polysulfone resin (PSR) were studied by Py–GC with FID, FPD and MSD [26]. This study was to evaluate the kinetics of SO_2 formation from PES and PSR by sequential pyrolysis. A similar study of the thermal degradation of four polythiophenes has also been reported [27]. The different chemical environment of the thiophenic ring influenced the rate of formation of H_2S and the yield of sulfur.

The thermal degradation mechanism of polyisobutylene was studied by Py–GC [28]. This study focused on the detailed mechanistic information which was related to pyrolysis product yields (closely dependent on sample thickness). A Py–GC method for quantitative analysis of 2,6-di-*tert.*-butyl-4-methylphenol (butylated-hydroxytoluene, BHT) antioxidant in samples of solvent-formulated liquid adhesive and in cured polychloroprene adhesive films has been developed using internal standards [29]. A Curie-point Py–GC has been applied to analyze the volume effects of stereoisomers of 2,4-diphenylpentane (a styrene dimer) and other styrene oligomers [30].

Py–GC has been used in kinetic measurements of polystyrenes (PSs) and poly(methyl methacrylate) (PMMA) to deduce their thermal degradation mechanisms [31]. A thermocouple feedback-controlled resistive filament pyrolyzer was used to study the kinetics and rates of degradation. Py–GC–MS analysis of glass fiber/vinylester thermal degradation products has been reported [32]. The result demonstrates that thermal degradation begins with a polystyrene chain depolymerization. It continues with the breaking of vinyl ester prepolymer chains at higher temperatures. The presence of glass fiber in the vinyl ester matrix decreased the number of crosslinking points and the thermal degradation occurred more readily in the prepolymer chain end.

In thermoset polymers, Py–GC was applied to study the thermal behavior of some epoxy-acrylic polymers based on phenol and para-alkyl substituted phenols in the temperature range of 80–600°C [33]. A method has been developed to determine the novolac resin thermal decomposition products by Py–GC–MS [34]. Quantitative analysis of the pyrolysis products can serve as a model for the foundry industry to predict the amount of volatile organic compounds (VOCs) produced before actually carrying out the casting process.

3.2. Structure determination

There are two major developments in the structure determination for the polymers by Py–GC. The first is the structure (the number-average sequence length) determination for copolymers through trimmers. The second is the structure (stereoregularity) determination for homopolymers through tetramers or high oligomers. The copolymer structure or the monomer arrangement in the polymer chain can be determined by the triad intensities that have been studied previously, especially using a ^{13}C-nuclear magnetic resonance (NMR) technique. This concept has been adapted to the Py–GC study of the copolymer structures.

The number-average sequence length of a monomer A in an A–B copolymer chain can be defined as n_A, where n_A equals the total number of A monomers in the polymer chain divided by the total number of blocks of monomer A. The formula can be expressed as:

$$n_{\mathrm{A}} = \frac{\text{Total number of A}}{\text{Total blocks of A}} \tag{1}$$

This definition and the formula associated with it has been used for polymer chain characterization for a long time [35]. The total number of A monomers can be expressed with the triad terms as AAA+(AAB+BAA)+BAB. The total number of blocks can be expressed with a triad term as (1/2)(AAB+BAA)+BAB. If the total number of monomers A and the total number of blocks of A can be expressed as these triad terms, the number-average sequence formula can be obtained based on the triad terms as follows:

$$n_{\mathrm{A}} = \frac{n_{\mathrm{AAA}} + n_{\mathrm{AAB+BAA}} + n_{\mathrm{BAB}}}{\frac{1}{2} n_{\mathrm{AAB+BAA}} + n_{\mathrm{BAB}}} \tag{2}$$

$$n_{\mathrm{B}} = \frac{n_{\mathrm{BBB}} + n_{\mathrm{ABB+BBA}} + n_{\mathrm{ABA}}}{\frac{1}{2} n_{\mathrm{ABB+BBA}} + n_{\mathrm{ABA}}} \tag{3}$$

Based on the definition of the number-average sequence length, it is not difficult to derive the next two formulas for the composition. The mole percentage can be calculated from the number-average sequence length. Because in a copolymer chain, the total number of block A is either equal to total number of block of B or different by one. Then, the total number of blocks (either A or B) will be canceled in both numerator and denominator, the mole percent of A will be equal to the total number of A divided by the total number of monomers in the copolymer which is exactly the definition of mole percent. The composition formula in terms of the number-average sequence length can be expressed as follows:

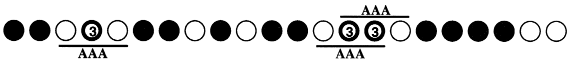
$$\text{Mol\% of A} = \frac{n_\text{A}}{n_\text{A} + n_\text{B}} \tag{4}$$

$$\text{Mol\% of B} = \frac{n_\text{B}}{n_\text{A} + n_\text{B}} \tag{5}$$

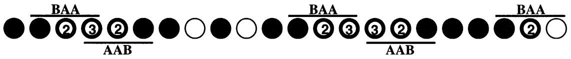
In order to prove that the expression of the number-average sequence length formula by triad terms is that simple, an arbitrarily created small copolymer chain for easier demonstration and explanation has been included as:

●●○○○●●○●○●●○○○○●●●●○○

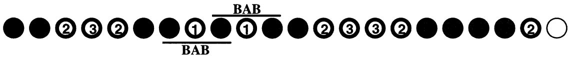
where monomer A is represented by white balls and monomer B is represented by black balls. Since we are looking for the triad term, the triad term will be selected according to the center monomer in the triad. If the center monomer is monomer A, that triad term will be counted during the monomer A counting process. For the term AAA, there are three possibilities of producing AAA term.



In order to make sure that no monomer unit is being counted more than one time, every monomer A unit counted will get marked with a black circle and a number (AAA = 3). For the triad of two As, there are AAB, BAA, and ABA. In ABA case, because the center monomer unit is not an A monomer unit, it is not counted in the monomer A counting process. There are five possibilities to produce AAB and BAA triad terms. Again, those five center A monomer units have been marked with a black circle and a number (two As = 2).



Finally, consider the triad with only one A. There is only one term BAB to be considered during A monomer counting process. There are two possibilities to produce BAB. Again, mark those center A monomer units with black circle and a number (one A = 1).



Re-examining the polymer chain, all A monomer units have been accounted for through these triad counting exercises except one at the edge. The one at the edge will be an error built into this formula, it will be demonstrated later that the amount of error present will be the result of this edge monomer unit not being counted. The next step is counting the total number of blocks. For every A block, they are either surrounded with two A monomer units with a label of 2 at both edges of the block or covered by an A monomer unit with a label of 1 with only one A in the block. So, the total number blocks of A monomer can be expressed by (1/2)(AAB + BAA) + BAB.

To summarize the counting processes, put all numbers into the formula. The number-average sequence length of A as the polymer chain is displayed is equal to 2.22. Compared with the number-average sequence length by counting monomer one by one, the number-average sequence length value is equal to 2.20. This value was obtained because the total number of A monomer units is equal to 11 (3 + 1 + 1 + 4 + 2). The total block of monomer A in the polymer chain is equal to 5. Comparing the number 2.22 and 2.20, there is a 1% error. This 1% error is from the edge monomer which not counted when utilizing the center monomer counting expression through triad counting. In a polymer chain with 22 monomers, the formula expression of number-average sequence length through triad distribution has a 1% error from the real value. If the polymer chain is longer, such as 100–1000 monomer units, the error will be much smaller and should be able to be ignored. This example proves that the number-average sequence length calculation formula is a real expression of the monomer distribution in the copolymers. There is no distribution assumption used. This formula is a direct mathematical expression of the number-average sequence length of a copolymer chain. In practice, there is no way to count polymer chain structure by counting monomer units, the number-average sequence length will be the representation of the polymer chain structure. The same approach can be used on monomer B units. Based on the number-average sequence length formula, there are other distribution related terms which can be derived from that formula to emphasize the different types of distribution.

There are several ways to produce a polymeric system containing monomer A and monomer B. This polymeric system can be produced in the simplest way by blending polymer A and polymer B. In a much more complex way, such as monomer A and monomer B copolymerized. If it is a copolymer, it can be in an alternate form or a homogeneous random form. Furthermore, with today's catalyst technology, a copolymer with monomer A and B can be produced with many different types of A–B distribution. The monomer arrangement in the polymer chain during a copolymerization reaction does not have to purely rely on their reactivity ratio or the monomer reaction kinetics. One can obtain a designed/desired copolymer structure with a special monomer arrangement sequence by utilizing special catalyst with regard to the monomer reactivity. Certainly, if the copolymer is produced by homogeneous copolymerization, the polymerization kinetic will depend on the monomer reactivity. Which may fall into Bernoullian's model or Markov's zero-order, first-order, or second-order model. No matter how the polymer structure is arranged, the polymer chain is an alternate or a blend. The number-average sequence length calculated from triad intensity will work as well. The number-average sequence length formula will always precisely reflect the structure.

What is the relationship between triad intensity and the pyrolysis trimer peaks area? Because the pyrolysis process is application of thermal energy to break down the polymer chain into different size fragments, the peak area obtained is a combination result of pyrolysis efficiency and detector efficiency after the GC separation. A parameter K can be used as a coefficient to express the relation between the pyrolysis peak area to the triad distribution. This K value reflects that combination of factors of pyrolysis efficiency and GC detection efficiency. This K value can be obtained by calibrating through copolymers with known composition. The homogeneous copolymer of known composition standards is preferred because they produce all trimer peaks allowing good calibration.

In order to utilize the number-average sequence formula to explore the structure, all the trimer peaks in the pyrogram must be identified. Theoretically, there are eight different trimer peaks in a copolymer system. A styrene–butyl acrylate copolymer system can be used as an example. Those eight trimers can be expressed as SSS, SSBa, BaSS, SBaS, BaSBa, BaBaS, SBaBa, BaBaBa (where S = styrene, Ba = butyl acrylate). In order to identify those eight trimer components, the first step is to run a GC–MS experiment. Based on the parent ion mass of these components, the SSS, BaBaBa, (SSBa, BaSS, SBaS), and (BaBaS, SBaBa, BaSBa) can be identified. The second step is to run an alternating copolymer, the only two peaks in the trimer area should be SBaS and BaSBa. The separation and identification of the rest of other peaks is not required by the number-average sequence length formula. If the GC–MS system is not available, or if the alternating copolymer is not available, there are still other ways to identify the trimer peaks, such as to compare with homopolymer. It is easy enough to match with retention times to find out which one is SSS and which one is BaBaBa. Furthermore, the rest of trimers can be compared with similar types of copolymer in the literature, by observing the fragments of the mass spectrum.

Therefore, what is the step-by-step procedure to analyze composition and structure by this number-average sequence calculation method? The procedures are as follows: (1) Run a Py–GC–MS experiment to qualitatively identify the monomers and trimers. (2) Pyrolyze one or two similar copolymers with known composition to find out the K values. (In previous experience, five out of six K values are the same.) (3) Use the same set of K values to calculate the unknown composition and structure.

The study of the styrene and butyl acrylate copolymer system [36] has demonstrated that the statistical distribution of triad can be correlated to the trimers obtained from Py–GC. If all eight trimers can be well resolved in the pyrogram and peak area can be obtained, the number-average sequence length as well as composition can be calculated from these trimer peak intensities.

In many other polymer cases, because of the stability of the trimer component, they do not always have all trimer peaks in the pyrogram. An example is the styrene and methyl methacrylate copolymer system [37]. The dimers and trimer of methyl methacrylate do not normally exist in the pyrogram for almost all pyrolysis conditions. Structure information still can be obtained by utilizing the monomer peak intensity to generate the composition along with the information obtained from other trimers.

The trimers produced from pyrolysis of polymers do not always exist as a component with three monomer units bonded together. Sometimes, the trimer may go through a decomposition to lose certain easy to lose fragments to form more stable compounds. An example is the vinyl chloride and vinylidene chloride copolymer system [38]. The pyrolysis products of trimers went through a dehydrohalogenation to form benzene, chlorobenzene, dichlorobenzene, and trichlorobenzene. With the knowledge of monomer reactivities and polymerization kinetics, the assumption can be made for the distribution of various trimers to the same final detected components. The copolymer structure as well as composition can be elucidated.

Polymeric structure determination does not have to be limited by the copolymer system. Other polymers which are produced by other methods may be treated as a copolymer system consisting of two different types of monomers. The chlorinated polyethylene system is such an example [39]. A chlorinated polyethylene system can be considered as a copolymer system of vinyl chloride and 1,2-dichloro ethylene. By examining the appropriate fragments which correspond to the trimer combination of vinyl chloride and 1,2-dichloro ethylene, one can utilize the statistical formula to calculate the number-average sequence length and composition. One can also explore the chlorine content as well as the arrangement of chlorine atoms in the polyethylene chain.

The polymer structure study heavily depends on the production of trimers during pyrolysis. Certain types of monomer do not form stable fragments after pyrolysis. An example is maleic anhydride. In order to study the structure and composition of styrene and maleic anhydride copolymer, [40] a derivatized method was developed. The anhydride functional group was derivatized with methylamine to form a cyclic-imide functional group, allowing the structure and composition to be studied.

In the structure (stereoregularity) determination method, the first example is the stereoregularity study of PS [41]. Py–GC–MS was able to detect and identify diastereoisomers such as tetramers and pentamers. The minimum requirement for a diastereoisomer is the inclusion of more than two asymmetric carbons in the molecule. This means that tetramers are the smallest possible candidates. In order to allow quantitative interpretation of data, the Py–GC method was calibrated by a set of standards with known tacticity (by NMR).

The second example is the determination of the tacticity of various stereoregular PMMA [42]. The experiment was achieved by separating the associated diastereometric tetramers. In this study, stereoisomers at slightly shorter retention times were also detected. Using the combination of two diastereoisomers, in addition to other stereoisomers, the ratio of different tacticity can be calculated. Again, these values are in a very good agreement with NMR data.

There is a review about structural characterization of polymeric materials by Py–GC–MS [43]. This review started with the history and scope of analytical pyrolysis, and then the instrumental and methodological aspects of Py–GC–MS. Some applications to the structural characterization of various polymeric materials are discussed in detail. These include the studies of sequence distribution of polyacetals by reactive pyrolysis in the presence of a catalyst, stereoregularity of PS and PMMA, and terminal groups of various PSs, PMMAs and PCs.

3.3. Qualitative and quantitative analysis

Composition (qualitative and quantitative) analysis is based on the relative intensity of monomers or monomer related pyrolysates which were produced from pyrolysis. This type of analysis has been developed for a long time. Recent development focused on the enhanced detection for low level chemical species in the polymers. The low level co-monomer or other additives which were hard to separate from the polymers may be identified by direct pyrolysis. In order to effectively detect those chemical species, other techniques along with pyrolysis are required. The other techniques mainly for separation and re-concentration purpose, such as separation, trapping, extraction, as well as derivatization have been developed around pyrolysis to improve the capability of low level chemical species detection.

Pyrolysis with a trapping scheme has been developed in order to determine low level acrylic acid and methacrylic acid in emulsion polymer [44]. The advantages of the trapping set-up are the flexibility of trapping solvent selection, sample accumulation, and the option of choosing the separation technique after the trapping. Low levels of acrylic acid and methacrylic acid were qualitatively detected in an emulsion polymer by this method. A similar technique has been applied to determine the acrylamide monomer in the emulsion polymer [45]. The trapped pyrolysate mixture was separated and identified by GC–MS. Because many other low level fragments elute at the same time, a single ion monitoring technique must be used to clearly catch the peak. It has been demonstrated in this study that the trapping technique is effective to detect low levels monomers of the acrylamide and methacrylamide in emulsion polymers.

The detection of low level monomers not only can be approached by this trapping technique, but also can be achieved by derivatization. The qualitative study of fumaric acid and itaconic acid in emulsion polymers [46] is an example. The fumaric acid and itaconic acid were derivatized by methylamine to form a cyclic-imide type functional group. The derivatized products were able to produce a stable pyrolysate which can be detected at relatively low concentrations.

Most additives are molecules used in the polymers which can be analyzed by extraction from polymers followed by gas or liquid chromatography methods. When an additive is in the polymeric form, an extraction followed by a GC/LC method will not work. A Py–GC method has been developed to explore low level polyacrylamide in polyvinyl alcohol [47]. Because of the large number of pyrolysates produced from the cellulose matrix, AED must be used to selectively detect the nitrogen containing fragments from pyrolysis of polyacrylamide.

There is a study of composition analysis of multicomponent acrylic resins by Py–GC [48]. In this study, Py–GC was used to analyze the composition of ethyl acrylate–butyl methacrylate copolymers and ethyl acrylate–styrene–ethyl methacrylate terpolymers. The characteristic peaks of the pyrolysis products, up to the pentamers, were almost completely separated on the pyrogram. The quantification of end groups in anionically polymerized PMMA by Py–GC has been studied [49]. The molecular mass distribution was determined. The characteristic fragments reflecting the end groups on the pyrogram of the PMMA were identified by comparison with those of a radically polymerized PMMA together with the mass spectra of the characteristic peaks on the resulting pyrograms. Py–GC–MS has been used to investigate the degree of cure of polyimide systems [50]. Pyrolysis products characteristic of both initial components and the cured polymer were identified. Changes in the pattern of pyrolysis products could be related to the progress of polymerization.

4. Conclusions

In recent years, several different configurations of instrumentation have been developed in order to accomplish pyrolysis by several similar types of thermal analysis equipment. In addition to the conventional qualitative and quantitative analysis, which is based on the relative intensity of monomers or monomer related fragments, structure analysis has been re-visited/developed and has become a new territory for Py–GC. Structure analysis includes the exploration of monomer arrangement in the copolymer system, such as the number-average sequence length and various stereoregular distribution in homopolymers. The development of derivatization techniques continues to grow in order to match the demand of different types of applications. In addition to the traditional post-pyrolysis derivatization, pre-pyrolysis derivatization has been developed in order to effectively re-select degradation pathways to achieve the purpose of analysis.

References

[1] M.H.P.M. van Lieshout, H.-G. Janssen, C.A. Cramers, M.J.J. Hetem, H.J.P. Schalk, J. High Resolut. Chromatogr. 19 (1996) 193.

[2] F.C.-Y. Wang, J. Chromatogr. A 753 (1997) 201.
[3] J. Hetper, M. Sobera, J. Chromatogr. A 776 (1997) 337.
[4] S.G. Roussis, J.W.R. Fedora, Rapid Commun. Mass Spectrom. 10 (1996) 82.
[5] F.C.-Y. Wang, Anal. Chem. 70 (1998) 3642.
[6] J.M.J. Challinor, Anal. Appl. Pyrolysis 16 (1989) 323.
[7] H. Ohtani, S. Tsuge, T. Usami, Macromolecules 17 (1984) 2557.
[8] A. Venema, R.C.A. Boom-van Geest, J. Microcol. Sep. 7 (1995) 337.
[9] Y. Ishida, S. Kawaguchi, Y. Ito, S. Tsuge, H. Ohtani, J. Anal. Appl. Pyrolysis 40–41 (1997) 321.
[10] Y. Ishida, H. Ohtani, K. Abe, S. Tsuge, K. Yamamoto, K. Katoh, Macromolecules 28 (1995) 6528.
[11] J. Kiji, T. Okano, T. Chiyoda, F. Bertini, G. Audisio, J. Anal. Appl. Pyrolysis 40–41 (1997) 331.
[12] M. Mulholland, K. McKinnon, P.R. Haddad, J. Chromatogr. A 739 (1996) 25.
[13] N.E. Skelly, S.W. Barr, A.P. Zelinko, J. Chromatogr. A 535 (1990) 199.
[14] M.K. Andari, H. Behbehani, H. Qabazard, Fuel Sci. Technol. Int. 14 (1996) 897.
[15] E. Kovats, Helv. Chim. Acta 41 (1958) 1915.
[16] G. Janssens, Anal. Chim. Acta 95 (1977) 153.
[17] R.B. Watts, R.G.O. Kekwick, J. Chromatogr. 88 (1974) 165.
[18] Y. Sun, R. Zhang, Q. Wang, B. Xu, J. Chromatogr. A 657 (1993) 1.
[19] G. Tarjan, S. Nyiredy, M. Gyoer, E.R. Lombosi, T.S. Lombosi, J. Chromatogr. A 472 (1989) 1.
[20] J.B. Reeves, G.C. Galletti, Org. Mass Spectrom. 28 (1993) 647.
[21] M.A. Poirier, A.E. George, Fuel 61 (1982) 182.
[22] C.G. Smith, J. Anal. Appl. Pyrolysis 15 (1989) 209.
[23] M.J. Matheson, T.P. Wampler, L. Johnson, L. Atherly, L. Smucker, Am. Lab. 5 (1997) 24C.
[24] S. Tsuge, H. Ohtani, Pyrolysis Gas Chromatography of High Polymers Fundamentals and Data Compilation, Techno-System, Tokyo, 1989, 371 pp.
[25] F.C.-Y. Wang, Anal. Chem. 69 (1997) 667A.
[26] P. Almen, I. Ericsson, Polym. Degrad. Stab. 50 (1995) 223.
[27] P. Selsbo, E. Ericsson, Polym. Degrad. Stab. 51 (1996) 83.
[28] M.R. Grimbley, R.S. Lehrle, Polym. Degrad. Stab. 48 (1995) 441.
[29] R.A. Franich, H.W. Kroese, G. Lane, Analyst (Cambridge, UK) 120 (1995) 1927.
[30] M. Wada, S. Fujishige, S. Uchino, N.J. Ohguri, Anal. Appl. Pyrolysis 33 (1995) 149.
[31] D.M. Bate, R.S. Lehrle, Polym. Degrad. Stab. 53 (1996) 39.
[32] N. Regnier, B. Mortaigne, Polym. Degrad. Stab. 49 (1995) 419.
[33] C.N. Cascaval, D. Rosu, I. Agherghinei, Polym. Degrad. Stab. 52 (1996) 253.
[34] C.A. Lytle, W. Bertsch, M.J. McKinley, Anal. Appl. Pyrolysis 45 (1998) 121.
[35] J.C. Randall, Polymer Sequence Determination, Academic Press, New York, 1977, p. 41.
[36] F.C.-Y. Wang, B.B. Gerhart, P.B. Smith, Anal. Chem. 67 (1995) 3536.
[37] F.C.-Y. Wang, P.B. Smith, Anal. Chem. 68 (1996) 3033.
[38] F.C.-Y. Wang, P.B. Smith, Anal. Chem. 68 (1996) 425.
[39] F.C.-Y. Wang, P.B. Smith, Anal. Chem. 69 (1997) 618.
[40] F.C.-Y. Wang, J. Chromatogr. A 765 (1997) 279.
[41] T. Nonobe, H. Ohtani, T. Usami, T. Mori, H. Fukumori, Y. Hirata, S. Tsuge, J. Anal. Appl. Pyrolysis 33 (1995) 121.
[42] T. Nonobe, S. Tsuge, H. Ohtani, T. Kitayama, K. Hatada, Macromolecules 30 (1997) 4891.
[43] S. Tsuge, H. Ohtani, Polym. Degrad. Stab. 58 (1997) 109.
[44] F.C.-Y. Wang, B.B. Gerhart, C.G. Smith, Anal. Chem. 67 (1995) 3681.
[45] F.C.-Y. Wang, B.B. Gerhart, Anal. Chem. 68 (1996) 3917.
[46] F.C.-Y. Wang, B.B. Gerhart, Anal. Chem. 68 (1996) 2477.
[47] F.C.-Y. Wang, J. Chromatogr. A 786 (1997) 107.
[48] S. Mao, H. Ohtani, S. Tsuge, J. Anal. Appl. Pyrolysis 33 (1995) 181.
[49] H. Ohtani, Y. Takehana, S. Tsuge, Macromolecules 30 (1997) 2542.
[50] R.C. Galipo, W.J. Egan, J.F. Aust, M.L. Myrick, S.L. Morgan, J. Anal. Appl. Pyrolysis 45 (1998) 23.