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Journal of Chromatography A, 886 (2000) 217–224

JOURNAL OF
CHROMATOGRAPHY A

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Qualitative and quantitative analysis of a thermoset polymer, poly(benzoxazine), by pyrolysis–gas chromatography

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Received 14 February 2000; received in revised form 20 April 2000; accepted 20 April 2000

Abstract

The chemical composition of a poly(benzoxazine) thermoset polymer (a copolymer of bisphenol-A benzoxazine and *tert*-butylphenol benzoxazine) has been studied by pyrolysis–gas chromatography (Py–GC). Major pyrolysates have been identified and the possible degradation pathways have been investigated. A specific pyrolysate was identified for quantitative analysis after carefully proving the linear relationship between the pyrolysate signal intensity and monomer concentration over a wide range of compositions. A method to determine the concentration of the monomer that potentially acts as a cross-linking unit has been developed. In this study, Py–GC was shown to be an excellent analytical technique for the qualitative and quantitative analysis of thermoset polymers. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Polymers; Poly(benzoxazine); Butylphenol; Bisphenol A; Phenols

1. Introduction

Thermoset polymers are commonly referred to as network polymers or cross-linked polymers. When a polymer system is cross-linked, the major portion of the system may be considered as one gigantic molecule. Because of cross-linking, the polymer chain mobility is limited. Thus, thermoset polymers possess excellent dimensional stability as well as thermal stability. There are two major types of cross-linked polymers. The type I polymers are formed by adding cross-linking reagents into existing thermoplastic polymers. One good example of this category is the vulcanization of polybutadiene elastomers [1]. Peroxides, sulfur and sulfur-containing compounds have been commonly used for this purpose. The type

II polymers achieve its cross-link by copolymerization with multifunctional monomers. One of good example in this area is the styrene–divinylbenzene copolymer [2]. The divinylbenzene serves as the cross-linking monomer in the polystyrene backbone.

One of the major families of thermoset polymers is the phenolic polymer. Phenolic polymers always exhibit good thermal stability [3]. Major application areas are focused on flameproof fibers, thermal insulation and protective clothing [4] in the construction, automotive, household and electrical facilities [5]. Phenolic polymers are also widely used as lacquers and varnishes, molding compounds, laminates and adhesives [6].

Poly(benzoxazine) is a newly developed type II cross-linked polymer which is based on the ring opening polymerization of benzoxazine precursors [7]. This family of polymers seems to have better

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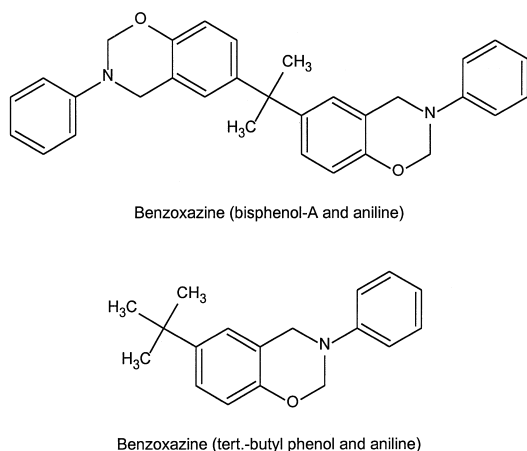


Fig. 1. The benzoxazine precursors' structures.

physical and mechanical properties than traditional phenolic and epoxy resins [8,9]. The benzoxazine moiety can be the reaction product of either bisphenol-A or *tert.*-butylphenol and aniline. The benzoxazine precursors' structures are demonstrated in Fig. 1. The ring opening polymerization will form the polymer as shown in Fig. 2.

Many separation and spectroscopic methods used in chemical characterization of polymers require the sample to be in the liquid form, either polymer in a liquid phase or dissolved in a solvent. However, when a thermoset polymer is cured (cross-linked), it cannot be dissolved without breaking the covalent bonds. Because of this reason, it is difficult to chemically analyze a thermoset polymer by any direct analytical technique.

The typical approach for chemical composition

analysis of a thermoset polymer is achieved by indirect measurement of its physical property and then correlating it back to its chemical composition. The results based on these types of composition analysis are occasionally misleading especially when the system variables are not carefully and appropriately controlled. It is always better if the chemical composition can be directly measured by an analytical technique.

Pyrolysis–gas chromatography (Py–GC) [10] is one of the important techniques used for polymer analysis. Py–GC is a technique 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 detecting with appropriate detection methods. Flame ionization detection (FID) is one of the most commonly 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 composition data [11]. The oligomers or oligomer-related fragments are used to elucidate microstructure information [12].

In this study, the chemical composition of benzoxazine-based thermoset polymers was qualitatively studied by Py–GC–MS. After careful study of the degradation pathways, a specific pyrolysate was chosen for quantitative analysis. In addition to that, the concentration of the cross-link related monomer was correlated to the degree of cross-linking of the polymer. For example, in a completely cured thermoset polymer, the concentration of cross-link

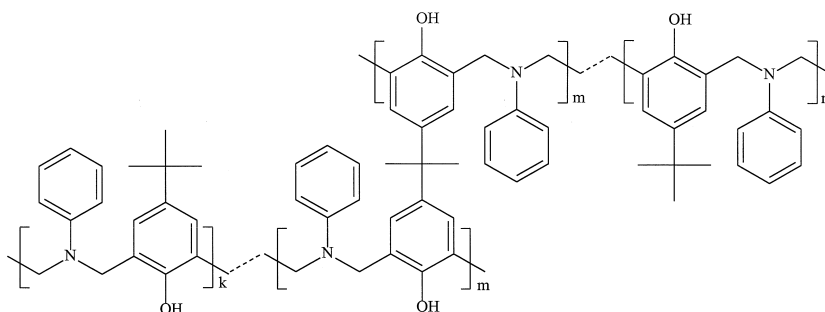


Fig. 2. The polymer formed by the ring opening polymerization of benzoxazine precursors', within the polymer chain, every bisphenol-A unit can serve as a cross-linking point.

monomer is an index to the degree of cross-linking. However, the degree of cross-linking is not easily determined. The concentration of the cross-link monomer can serve as an indication of the potential degree of cross-linking. In this study, Py–GC was shown to be a good analytical technique for the qualitative and quantitative analysis of thermoset polymer systems.

2. Experimental

2.1. Reagent sources

All chemicals and reagents were purchased from Aldrich and used without further purification. The benzoxazines were synthesized based on a literature method [7]. Polymers with different composition were synthesized by heating the mixture of appropriate amounts of bisphenol-A-based benzoxazines and *tert.*-butylphenol-based benzoxazines at 175°C for 2 h.

2.2. Py–GC conditions

Samples of polymer (0.5–1.0 mg, as solid cured resin) were carefully deposited into the middle of a quartz tube. The quartz tube was put into an off-line pyrolysis interface for 5 min at 300°C to evaporate any nonpolymeric material (water, unreacted reagents). After this cleaning procedure, the quartz tube was equilibrated for 5 min 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 700°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 pyrolysis products were split in the 300°C injection port, with 250:1 split ratio, a fast flow program (15 p.s.i./0.2 min, 75 p.s.i./min, to 90 p.s.i./8.8 min), and separated 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) then detected by FID (1 p.s.i.=6894.76 Pa).

2.3. Py–GC–MS conditions

The sample preparation and pyrolysis in the Py–GC–MS experiments was the same as Py–GC experiments. The GC instrument 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, 30:1 split ratio; 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 MS system 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 component identification.

3. Results and discussion

Fig. 3 shows three pyrograms of poly(benzoxazines). The top one is the benzoxazine precursor made with 100% bisphenol-A, the middle one is the benzoxazine precursor made with 2:1 mole ratio of *tert.*-butylphenol and bisphenol-A, the bottom one is the benzoxazine precursor made with *tert.*-butylphenol. All major pyrolysates have been labeled and identified by MS and listed in Table 1.

Based on the pyrolysates of poly(benzoxazine) produced from both bisphenol-A-based benzoxazine, *tert.*-butylphenol-based benzoxazine and the mixture of both, the degradation pathways can be summarized as shown in Fig. 4.

Two major types of compounds were found in the pyrolysates: *N*-methyl substituted anilines and alkyl substituted phenols. Based on the polymer microstructure, if the bisphenol-A can be considered as a combination of two 4-alkyl substituted phenol units, the whole polymer can be described as an alternating arrangement of 4-alkyl substituted phenol units or 4-*tert.*-butylphenol units and aniline which are all connected with methylene bridge. The methylene bridge is attached on the 2 and 6 positions in the

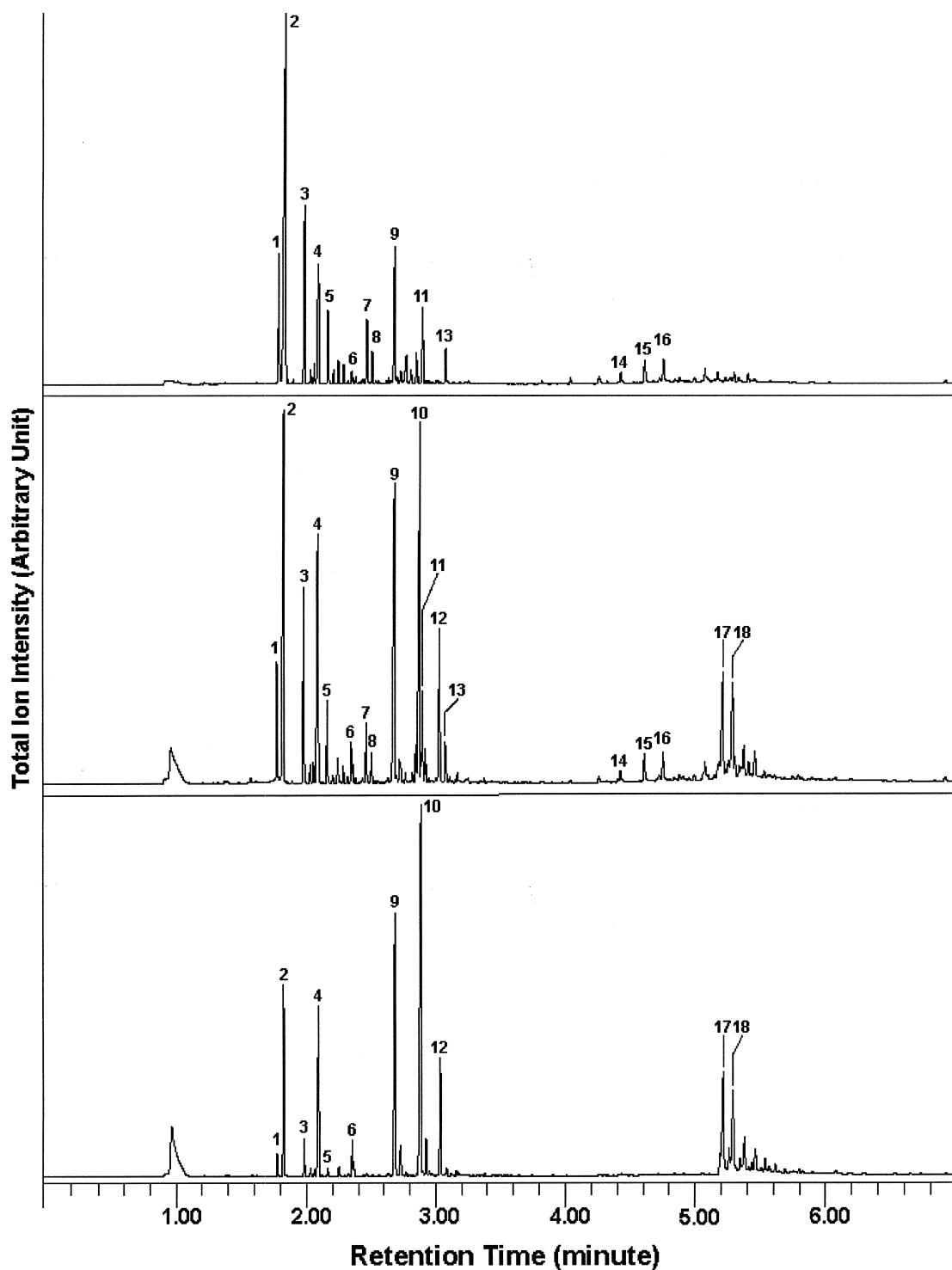


Fig. 3. Three pyrograms of poly(benzoxazines). The top one is the benzoxazine precursor made only with bisphenol-A, the middle one is the benzoxazine cured resin made by 2:1 mole ratio of *tert*-butylphenol and bisphenol-A, the bottom one is the benzoxazine cured resin made with *tert*-butylphenol. All peaks labeled are identified and listed in Table 1.

Table 1
Peak assignment for the pyrograms of poly(benzoxazines) (Fig. 3)

| Peak No. | M_r | Structure |
|----------|-------|--|
| 1 | 94 | Phenol |
| 2 | 93 | Aniline |
| 3 | 108 | 2-Methylphenol |
| 4 | 107 | Methylphenylamine |
| 5 | 122 | 2,6-Dimethylphenol |
| 6 | 121 | Dimethylphenylamine |
| 7 | 136 | 4-(Methylethyl)phenol |
| 8 | 136 | 4-(Ethyl)-2-methylphenol |
| 9 | 150 | <i>p-tert.</i> -Butylphenol |
| 10 | 164 | 4-(<i>tert.</i> -Butyl)-2-methylphenol |
| 11 | 164 | 2,6-Dimethyl-4-(methylethyl)phenol |
| 12 | 178 | 4-(<i>tert.</i> -Butyl)-2,6-dimethylphenol |
| 13 | 162 | 2,6-Dimethyl-4-(1-methylvinyl)phenol |
| 14 | 193 | 10-Methylphenanthridine |
| 15 | 213 | 2-[(Methylphenylamino)methyl]phenol |
| 16 | 213 | 6-Methyl-2-[(phenylamino)methyl]phenol |
| 17 | 269 | 4-(<i>tert.</i> -Butyl)-2-[(methylphenylamino)methyl]phenol |
| 18 | 269 | 4-(<i>tert.</i> -Butyl)-6-methyl[(phenylamino)methyl]phenol |

phenol unit and is connected at the nitrogen in the aniline unit.

Because of the similarity in structure between bisphenol-A and *tert.*-butylphenol, a number of alkyl substituted phenol-related fragments could be produced from both bisphenol-A benzoxazine and *tert.*-butylphenol benzoxazine. From a quantitative analysis point of view, at least one pyrolysate has to be identified as composition dependent. In order to illustrate the relationship between pyrolysate intensities and their precursors, an overlapped three-dimensional plot of pyrograms with different composition was prepared and is shown in Fig. 5. There are several pyrolysates that can potentially be used for qualitative and quantitative analysis because their intensities vary with the composition, as shown in the figure. Three are potentially useful for quantitative analysis: *p-tert.*-butylphenol (peak 9, formula $M_r=150$), 4-(*tert.*-butyl)-2-methylphenol (peak 10, formula $M_r=164$) and 4-(*tert.*-butyl)-2,6-dimethylphenol (peak 12, formula $M_r=178$). They all have large enough intensities so that they can be used to cover a wide range of composition. Further examination of the pyrogram of poly(benzoxazine) with benzoxazines made by 100% bisphenol-A (pyrogram labeled 100/0 in Fig. 5) shows that peaks 10 and 12 do not exist in the pyrolysate. This means that the pyrolysates, 4-(*tert.*-butyl)-2-methylphenol

and 4-(*tert.*-butyl)-2,6-dimethylphenol, are only produced from *tert.*-butylphenol benzoxazine. In terms of qualitative analysis, these two peaks can be used as indicators for the existence of *tert.*-butylphenol monomer in a poly(benzoxazine).

These two pyrolysates, 4-(*tert.*-butyl)-2-methylphenol and 4-(*tert.*-butyl)-2,6-dimethylphenol, can also be used in the quantitative determination of the chemical composition of the copolymer. When discussing the quantitative analysis of this polymer, instead of using mole ratios as the traditional composition unit, an alternate term, equivalent mole, has been used. The definition of this term is mole multiplied by the functionality. This term is intended to reflect the functionality of monomers in the polymer. For example, 1 mole of bisphenol-A is counted as two equivalent moles because bisphenol-A has two equivalent connection units in the polymer. In contrast, 1 mole *tert.*-butylphenol is counted as one equivalent mole because *tert.*-butylphenol A has only one equivalent connection unit in the polymer.

As described previously, the copolymer can be described as an alternating copolymer of 4-alkyl substituted phenol or 4-*tert.*-butylphenol and aniline. Based on this alternating structure, the polymer should have equal “equivalent moles” of aniline and “equivalent moles” of 4-alkyl substituted phenol

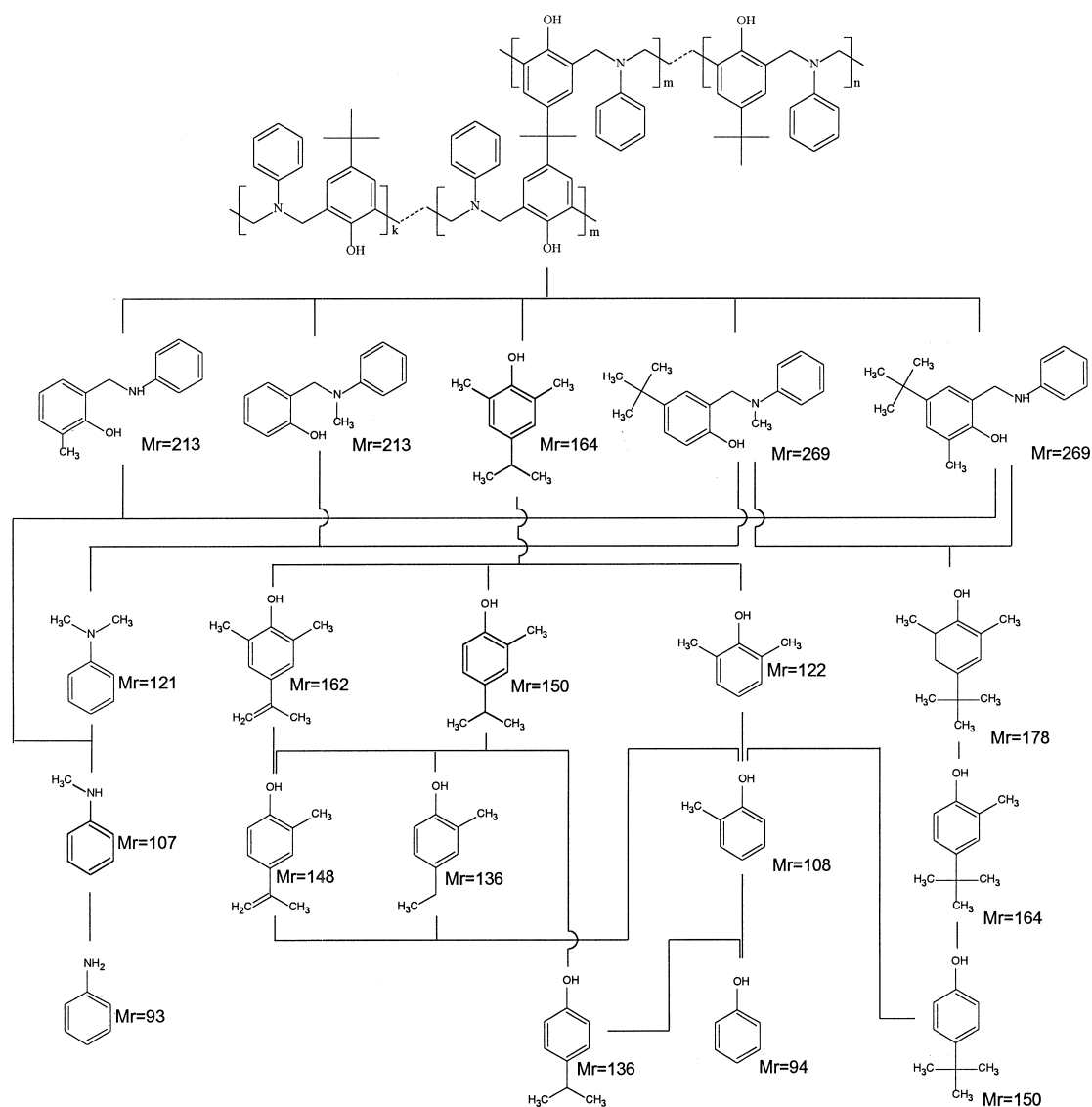


Fig. 4. The degradation pathways of poly(benzoxazine) which were produced from both bisphenol-A-based benzoxazine, *tert*-butylphenol-based benzoxazine and the mixture of both.

plus 4-*tert*-butylphenol. To correlate the pyrolysate peak intensity to the monomer concentration in the polymer, it must be assumed that the pyrolysis efficiency and the GC detection efficiency are the same for both 4-*tert*-butyl-2-methylphenol (peak 10) and aniline (peak 2) for all compositions. A linear relationship has been obtained when plotting the peak intensity ratio of 4-*tert*-butyl-2-

methylphenol (peak 10) divided by that of aniline (peak 2) versus composition.

The advantage of normalizing the key pyrolysate intensity [4-*tert*-butyl-2-methylphenol] relative to aniline intensity is that all data should be independent of the amount of sample pyrolyzed. This means the sample does not have to be accurately weighed but can be within a certain size range, such as

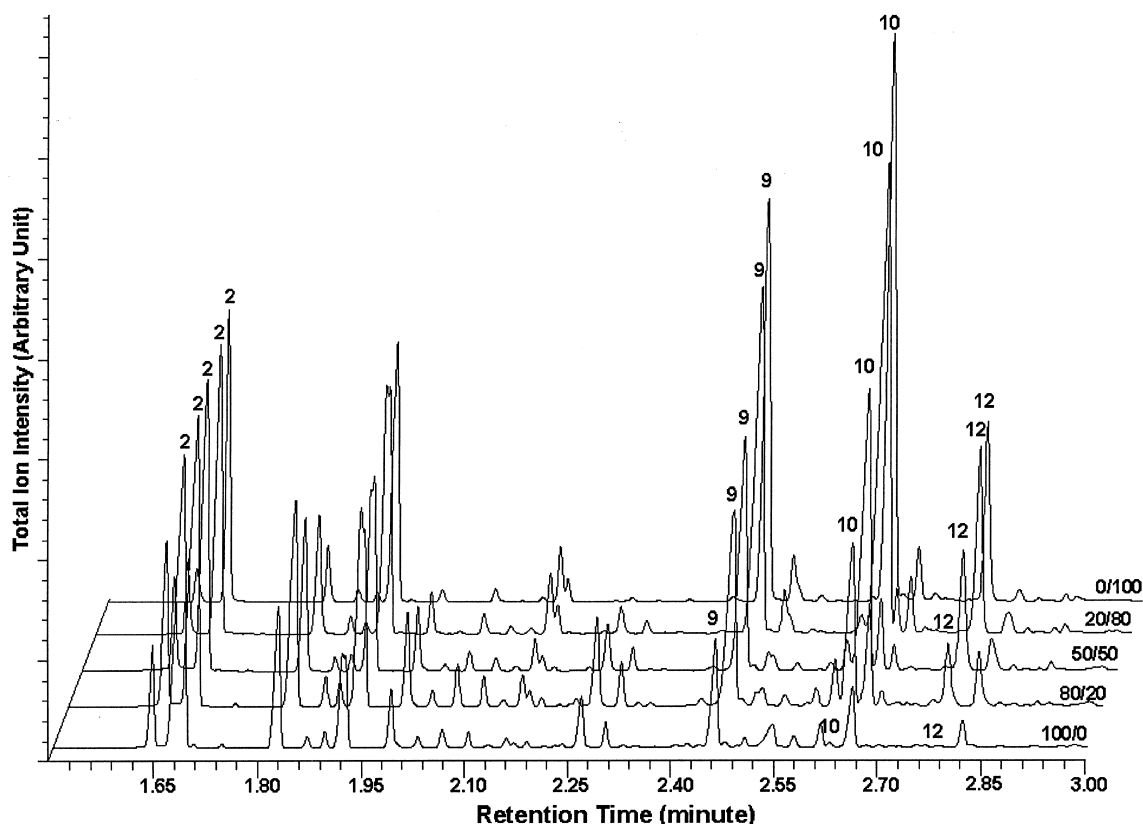


Fig. 5. The pyrograms of poly(benzoxazine) copolymers. The concentration of *tert*-butylphenol benzoxazine and bisphenol-A benzoxazine is labeled at the end of each pyrogram (the unit used is the equivalent mole percent). All peaks labeled are identified and listed in Table 1.

between 0.5 mg and 1.0 mg, where complete pyrolysis is expected.

The degree of cross-linking is an important quantity in most thermoset polymers. The degree of cross-linking will affect almost every physical property. Unfortunately, there is no easy and standard chemical analysis technique that can measure the degree of cross-linking directly. Thus, degree of cross-linking measurements are often based on indirect physical property measurements such as swelling properties [13], dynamic mechanical properties [8], etc.

Py-GC has been used in the degree of cross-linking study for several polymer systems [14,15]. However, Py-GC could not be used to measure the degree of cross-linking in this thermoset polymer, because of the pyrolysis mechanism. The time required for the sample temperature to reach the pyrolysis temperature is in the millisecond range

[10], but the time required for the formation of a chemical bond is in the microsecond range [16]. A partially cured thermoset polymer will become increasingly cured or completely cured in a pyroprobe at that instant just before the pyrolysis mechanism occurs. However, there are other types of pyrolysis instrumentation, such as the micro-oven or Curie point pyrolyzer that may have different ways to introduce the thermal energy. In those instruments the time for the temperature rise for pyrolysis may be fast enough to compete with the time required for the bond formation. Nevertheless, the heat transfer or the thermal conductivity of the polymeric materials will still introduce uncertainty. Furthermore, the dependence of the pyrolysates produced for benzoxazines of varying cross-linking should be studied in order to verify that the degree of cross-linking can be measured. As long as bond formation is much faster than

pyrolysis, information regarding the degree of cross-linking will not be revealed by this technique.

Py–GC can be used to measure the concentration of all monomer units in the copolymer including the one that potentially serves as the cross-linking unit. If the copolymer is completely cured, the degree of cross-linking may approach the concentration of bisphenol-A measured. Even for copolymers that are not completely cured, the degree of cross-linking in a specific set samples might be proportional to bisphenol-A concentration if the cure condition and time is kept the same for the entire set of samples. If the poly(benzoxazine) consists of 100% *tert*-butylphenol based benzoxazine, then, it is a thermoplastic polymer.

4. Conclusions

The chemical composition of a benzoxazine-based thermoset polymer was qualitatively studied by Py–GC–MS. With appropriate choice of pyrolysate, quantitative analysis was accomplished for this polymer. In addition, the concentration of the cross-linking monomer was used to measure the potential degree of cross-linking of the polymer. Actually degree of cross linking could not be measure directly with the technique. The real degree of cross-linking has to be established using both concentration of cross-linking monomer, and conditions and time of cure.

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