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Thermal decomposition processes in aromatic amine-based polybenzoxazines investigated by TGA and GC–MS

Kasinee Hemvichian, Hatsuo Ishida*

Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, OH 44106-7202, USA

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Abstract

Three different aromatic amine-based polybenzoxazines are subjected to thermal decomposition in a thermogravimetric analyzer. The degradation products, which are volatile compounds evaporating out of the furnace as gases, are trapped and analyzed further by a gas chromatograph which is coupled with a mass selective detector (GC–MS). All the degradation products are separated by GC and come out at different retention times, as seen in the total ion chromatogram. All the compound's mass are selectively identified by MS. The chromatograms are divided into two regions; the low column temperature region containing low molecular weight and highly volatile compounds, and the high column temperature region containing higher molecular weight and less volatile compounds. The evolved gas analysis performed by GC–MS allows us to identify the molecular weight and also the structure of the volatiles. This information is then used to illustrate the processes occurring during the thermal decomposition of aromatic amine-based polybenzoxazines. © 2002 Published by Elsevier Science Ltd.

Keywords: Polybenzoxazine; Thermal degradation; GC–MS

1. Introduction

The thermal decomposition processes in polybenzoxazines have been investigated in our laboratory and reported in the previous studies [1–4]. One of the useful techniques used for the study was a thermogravimetric analyzer interfaced with a Fourier transform infrared spectrometer (TGA–FTIR) [1]. The polymers were subjected to thermal degradation in the TGA instrument. The degradation products, which are volatile compounds, evaporated from the TGA furnace as gases. The evolved gases traveled through the transfer line to the infrared gas cell, which is equipped with a deuterated triglycine sulfide (DTGS) detector. The evolved gases can be detected and monitored continuously in real time. The advantage of this technique is that it is possible to identify the type of compounds that come out at different times and temperatures, according to the IR fingerprints. However, it is difficult to specifically identify the actual structure of each compound. A complementary technique is the evolved gas analysis (EGA) performed by using a gas chromatograph coupled with a mass selective detector (GC–MS).

GC–MS offers a number of advantages for the decomposition study. GC–MS is the technique that allows us to detect simultaneously the presence of decomposition products qualitatively and quantitatively [5]. The number of peaks seen in the total ion chromatogram (TIC) represents the number of compounds detected by GC–MS. The relative intensity of each peak corresponds to the relative concentration of each compound to one another. The identification of each decomposition product can also be confirmed by either using model compounds and/or comparing the spectrum with those in the GC–MS library. However, the GC–MS configuration used in our experimental set-up lacks the capability to provide the information about the time at which the degradation products evolved. Therefore, the combination of the results from TGA–FTIR and GC–MS analysis provides a better understanding of the thermal decomposition mechanisms, considering the advantages associated with each type of analysis.

The thermal decomposition study of polymers can be difficult since the polymers can release a large number of degradation products during pyrolysis. Model compounds can be utilized to simplify the difficulties associated with the polymeric systems. The studies have been conducted recently on aliphatic amine-based polybenzoxazine model

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* Corresponding author. Tel.: +1-216-368-4285; fax: +1-216-368-4164.
E-mail address: hxi3@po.cwru.edu (H. Ishida).

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dimers and oligomers [6,7]. In these studies, the thermal decomposition was simplified by using a series of benzoxazine dimers and oligomers as model compounds for polybenzoxazines. Using a series of dimers and oligomers as model compounds not only allows us to study the decomposition processes fundamentally and systematically, but also makes the study less complicated. The results from these studied were then used to assist the interpretation of the degradation study of aliphatic amine-based polybenzoxazines [8]. However, these are not the only polymers of our interest. In fact, polybenzoxazines synthesized from aromatic amines (especially aniline) have been studied extensively in many areas of interest [9–15]. The aliphatic and aromatic amine-based polybenzoxazines have shown different properties and are expected to have different thermal decomposition mechanisms as well. The study on the degradation of aromatic amine-based polybenzoxazine model dimers [16] have indeed shown some different results from that of the aliphatic amine-based ones. The objective of this work, therefore, is to complement the thermal decomposition study of aliphatic amine-based polybenzoxazines, by investigating the degradation of aromatic amine-based polybenzoxazines.

2. Experimental

2.1. Materials

Phenol (Aldrich, 99%), 4,4′-*iso*-propylidenediphenol (Bisphenol A) (Aristech Chemical Co., Polycarbonate grade), *para*-formaldehyde (Fluka Chemicals, 95%), aniline (Aldrich, 99%), and 3,5-xylidene (Aldrich, 98%) were used without further purification to synthesize three different benzoxazine monomers as shown in Table 1. The monomers were prepared by a solventless synthesis method [17] and purified according to the previous study [18]. After the synthesis and purification, the benzoxazine monomers were then cured by a step profile as follows: 140 °C (30 min), 160 °C (30 min), 170 °C (45 min), 180 °C (45 min), 190 °C (75 min), 200 °C (90 min). The monomers underwent thermal ring-opening polymerization reactions, without any added initiators or catalysts, to give thermosetting polybenzoxazines. Approximately 40 mg of the polymers were taken and subjected to thermal degradation in a thermogravimetric analyzer.

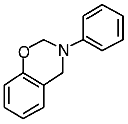
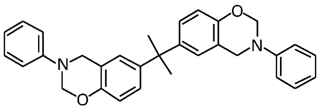
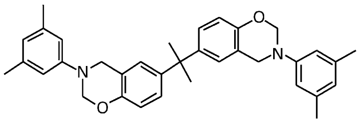
2.2. Thermogravimetric analysis (TGA)

A TGA from TA Instruments, High Res TGA 2950, was used for thermogravimetric analysis. All thermal degradation experiments were done under nitrogen purge, with a flow rate of 90 ml/min. A heating rate of 10 °C/min from ambient temperature to 820 °C was used for all experiments. EGA was carried out by passing the gases evolved from the EGA furnace through HPLC grade chloroform. The gases dissolved and were trapped in the chloroform. The solution was manually injected into a gas chromatograph coupled with a mass spectrometer (GC–MS).

2.3. Gas chromatography-mass spectrometry

The GC–MS used was a Hewlett-Packard 6890 Gas Chromatograph coupled with the 5973 Mass Selective Detector. Separation of the degradation products in the evolved gases was obtained by using a non-bonded capillary column coated with 5% phenyl–methyl polysiloxane (30.0 m × 250 μm × 0.25 μm). The injection port of the GC was set at 250 °C. The GC column was programmed from 70 °C (1 min) with a heating rate of 5 °C/min to 250 °C (20 min). Note that the different retention times for the same compounds reported here, compared with those reported in our previous works [3,4], are a result of different heating rate. The slower heating rate is supposed to provide better separation of compounds with very similar volatility. The energy of 70 eV was used for electron ionization. Helium

Table 1
The structure of benzoxazine monomers, weight loss data and char yield (determined at 800 °C) from the thermal decomposition in nitrogen

Monomer	Abbreviation	Char yield (%)	5% Weight loss (°C)	10% Weight loss (°C)
	**Ph–a**	35	326	353
	**BA–a**	30	312	337
	**BA–35x**	28	339	348

was used as a carrier gas for all the GC–MS experiments. When the solvent comes off the GC column and hits the MS detector, the concentration of the solvent can be so high that it is destructive to the instrument. To prevent this from happening, the detector is programmed to be turned off during the time when the solvent hits the detector. As a consequence, the detection of compounds coming off at the same time as the solvent is impaired. The maximum molecular weight that can be detected by this GC–MS instrument is approximately 600 Da. Nevertheless, only more volatile compounds can go through GC column and be detected. The assignments are confirmed by either consulting the Refs. [19–21], using the model compounds commercially available or synthesized in our laboratory, or searching the NIST MS library software, Nbs75k.

3. Results and discussion

Three different aromatic amine-based polymers were selected to represent different types of polybenzoxazines in this study. The first one is phenol–aniline-based (**Ph–a**) polybenzoxazine. The abbreviation used for the monomer will also be used to designate the polymer derived from the monomer when there is no danger of confusion. **Ph–a** represents a monofunctional benzoxazine monomer. Monofunctional benzoxazines have not received as much attention as difunctional benzoxazines. This could be due to the fact that an earlier report [22] indicated that monofunctional benzoxazine monomers having a substituent at either *ortho* or *para* position could not yield molecular weight more than 1600. Nevertheless, in this case, phenol does not have any blocking groups at both the *ortho* and *para* positions. Both positions are thus subjected to C-aminoalkylation reaction happening during ring-opening polymerization of benzoxazines [3,4]. As a result, benzoxazine monomer based on phenol and aniline can be thermally polymerized to become thermosetting polybenzoxazine. The second polybenzoxazine used in this study is based on bisphenol A and aniline, **BA–a**. **BA–a** is one of the very first polybenzoxazines synthesized in our laboratory and has been studied extensively ever since, in almost every area of our interests. Thereby, **BA–a** was used here to represent the standard difunctional polybenzoxazines. Bisphenol A and 3,5-xylidene-based polybenzoxazine, **BA–35x**, is the third polymer used in this study. **BA–35x**, representing a new generation of polybenzoxazines, has been developed recently in our laboratory [3,4]. The study demonstrated that electron-donating alkyl substituents at both *meta* positions help in activating the sites on the pendant aromatic rings toward electrophilic aromatic substitution. This regioselectivity results in a lowered exotherm peak during curing, increasing amounts of methylene linkages, enhanced glass transition temperatures, and the delayed onset of thermal degradation, all compared with those of **BA–a**.

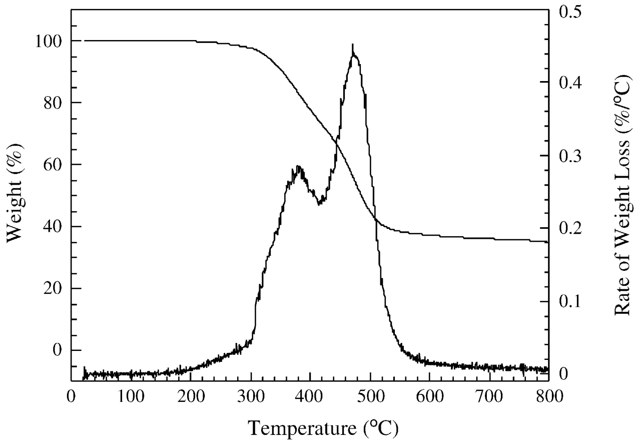


Fig. 1. TGA thermogram and its derivative from the degradation of **Ph–a** polybenzoxazine in nitrogen.

3.1. Thermal decomposition pattern

The TGA thermograms and their derivative thermograms from **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen are shown in Figs. 1–3, respectively. The char yield determined at 800 °C and weight loss data for each polymer are also collected and presented in Table 1. For **Ph–a**, the derivative of weight loss showed a two-stage process. The first process started before 300 °C and reached its maximum rate of 0.29%/°C at 382 °C. The second weight loss process developed later and showed a higher maximum rate of 0.45%/°C at 472 °C. The amount of char left at 800 °C is 35%. For **BA–a**, the polymer began to lose weight at 260 °C. Then a three-stage weight loss process was observed, centered approximately at 310, 390, and 470 °C, with the one in the middle having the highest maximum rate of weight loss of 0.44%/°C. The char residue of 30% was found at 800 °C. **BA–35x** is the only one in these three polymers that started to degrade after 300 °C. The polymer started losing weight rapidly after the onset of degradation, and reached the maximum rate of weight loss of 0.59%/°C at 350 °C. At 415 °C, the second process reached its maximum

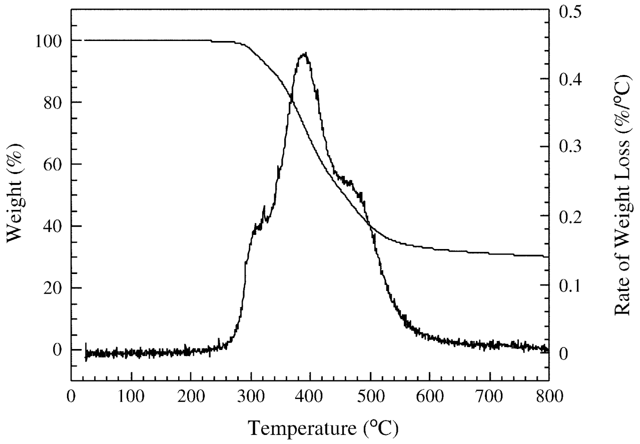


Fig. 2. TGA thermogram and its derivative from the degradation of **BA–a** polybenzoxazine in nitrogen.

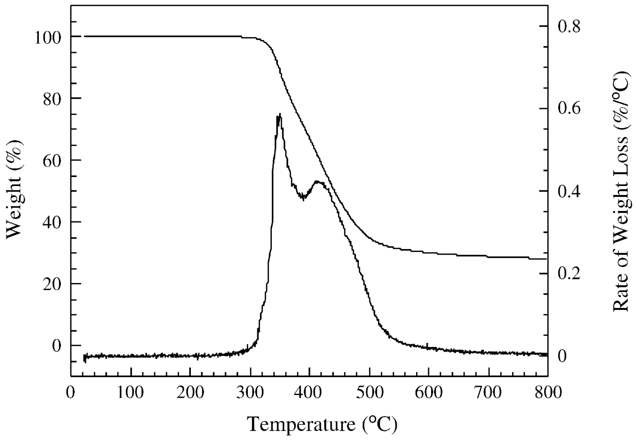


Fig. 3. TGA thermogram and its derivative from the degradation of **BA–35x** polybenzoxazine in nitrogen.

rate of 0.43%/°C. Despite the delayed onset of degradation, **BA–35x** has the lowest char yield of 28% among these three polymers, probably due to the loss of the methyl groups. Note that the correlation between the decomposition mechanisms and the peaks in the derivative thermograms can be found from the previous studies [1,2].

The results from TGA have shown that the char yield of **Ph–a** is higher than those of **BA–a** and **BA–35x**. In addition, the temperatures at 5 and 10% weight loss of **Ph–a** are higher than those of **BA–a**. Wang [23] mentioned that the reason for this phenomena is due to the absence of *iso*-propylidene linkage in **Ph–a**. The study on a bisphenol-A-based polybenzoxazine exposed to ultraviolet radiation has revealed that the *iso*-propylidene linkage was the reactive site of cleavage and oxidation [24]. In addition, **Ph–a** is also different from the **BA–a** and **BA–35x** polybenzoxazines in terms of substituents. **BA–a** and **BA–35x** have only one unblocked *ortho* position (to the hydroxyl group) that is subjected to electrophilic aromatic substitution happening during ring-opening polymerization. On the other hand, **Ph–a** has two unblocked positions, one at the *ortho* and another at *para* position. The study on polybenzoxazine model dimers [6] has demonstrated that the absence or presence of the substituents has profound effects on the thermal decomposition patterns and the char formation of the dimers. Therefore, the absence of *iso*-propylidene moiety along with the absence of substituents at both *ortho* and *para* positions are likely to be the cause for the thermal stability behavior of **Ph–a**. For **BA–35x**, the polymer did not show the first of the three-stage weight loss process (before 300 °C) found in **BA–a**. As mentioned earlier, the use of arylamines with methyl-substituted *meta* positions helps in activating the sites on the pendant aromatic rings toward electrophilic aromatic substitution. This, thereby, has brought about the additional arylamine Mannich bridges and methylene bridges, i.e. the presence of additional cross-linked structures. As for the char yield, the fact that the char yield of **BA–35x** is almost the same as that of **BA–a** is expected, since **BA–35x** has similar chemical functionalities to **BA–a**, without any additional reactive functional groups. Increased char yield due to the higher cross-linking density in **BA–35x** than **BA–a** is offset by the evaporating methyl groups, resulting in a very similar char yield.

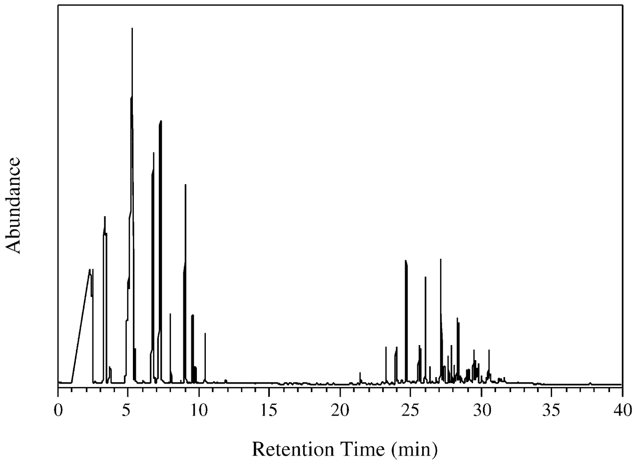


Fig. 4. TIC of evolved gases from the degradation of **Ph–a** polybenzoxazine in nitrogen.

3.2. Structure of the decomposition products

The TIC of evolved gases, detected by GC–MS, from the thermal degradation of the **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen are shown in Figs. 4–6, respectively. The chromatograms can be divided into two regions. The low column temperature region with retention times shorter than 20 min contains low molecular weight, highly volatile compounds. The high column temperature region with retention times higher than 20 min contains high molecular weight, less volatile compounds. The thermal decomposition products are either a direct result of the degradation of the polymers or the recombination or degradation of compounds formed during pyrolysis. All

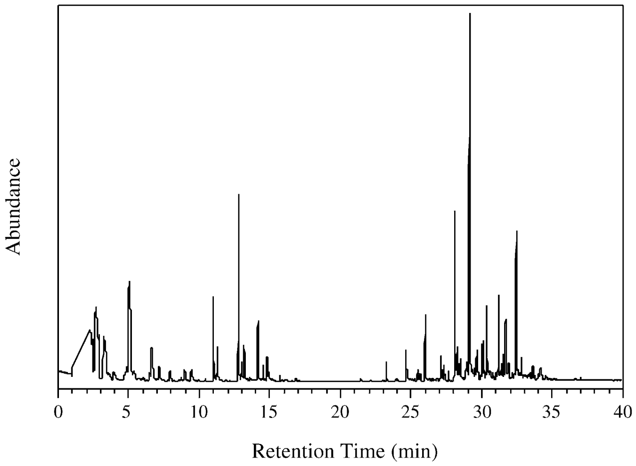


Fig. 5. TIC of evolved gases from the degradation of **BA–a** polybenzoxazine in nitrogen.

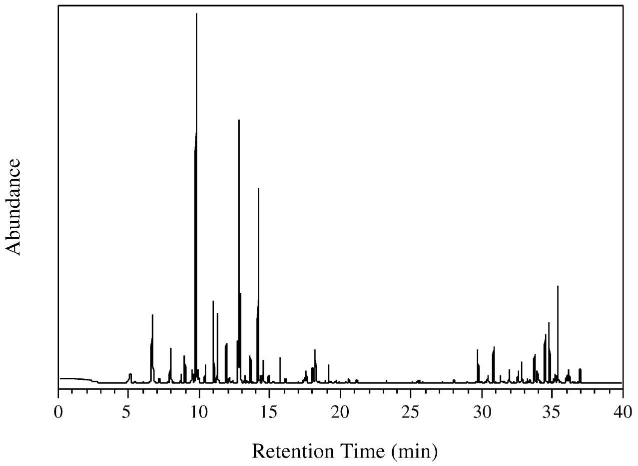
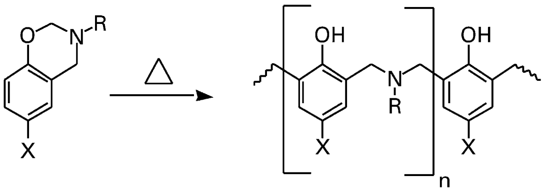


Fig. 6. TIC of evolved gases from the degradation of **BA–35x** polybenzoxazine in nitrogen.

the products were identified by MS and grouped into eight categories as follows: benzene derivatives, amines, phenolic compounds, 2,3-benzofuran derivatives, *iso*-quinoline derivatives, biphenyl compounds, Mannich base compounds, and phenanthridine derivatives, as shown in Tables 2–9, respectively. The percentage of each degradation products was calculated automatically from the integration of area under peak. A percentage report provides information on the relative sizes of the integrated peaks in a chromatogram, i.e. percentage contribution to total area of all peaks.



Scheme 1.

3.2.1. Benzene derivatives

The percentage of compounds which are benzene derivatives detected by GC–MS of each polymer is shown in Table 2. This category contains compounds such as, toluene, dimethylbenzene, trimethylbenzene, etc. As we can see from Table 2, *m*-xylene and 1,3,5-trimethylbenzene are the first two compounds with the highest intensities for all three polymers. For **BA–a** and **BA–35x** polymers, these two degradation products can come directly from the degradation of the polymers, since the ring-opening polymerization illustrated in Scheme 1 will lead to the

Table 2
Percentage of benzene derivatives in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

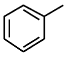
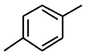
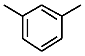
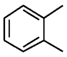
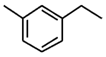
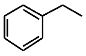
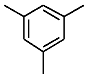
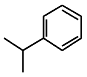
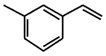
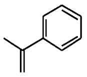
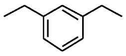
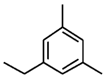
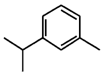
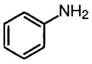
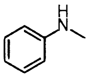
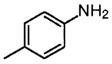
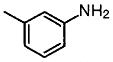
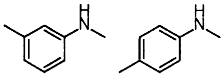
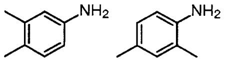
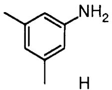
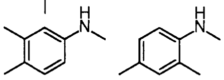
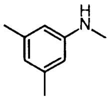
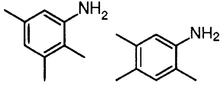
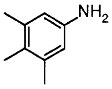
Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
2.44	92		1	<1	<1
3.40	106		2	<1	<1
3.48	106		8	5	2
3.72	106				<1
4.73	120		<1	<1	<1
4.92	106		<1	<1	<1
5.03	120		5	10	3
5.38	120				<1
5.46	118		<1		
5.50	118			<1	<1
6.00	134				<1
6.82	134			<1	1
7.47	134				<1

Table 3
Percentage of amines in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
5.08	93		5	10	3
7.04	107		<1		
7.20	107		9[a]	1	<1
7.31	107		2		<1
9.35 and 9.40	121		<1	<1	<1
9.47 and 10.34	121		1	<1	<1
9.70	121				25
12.34 and 12.76	135		<1	<1	2
12.89	135				4
13.00 and 13.21	135				<1
13.61	135				<1

[a] Integration includes percentage of *p*-cresol, due to highly overlapped peaks.

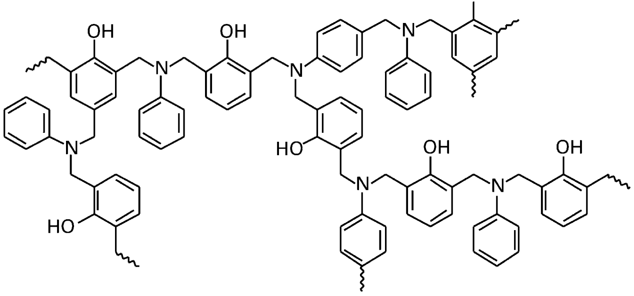
formation of 2,4,6-tri-substituted phenolic structure. This obviously explains the presence of *m*-xylene and 1,3,5-trimethylbenzene in the degradation products. For the **Ph–a** polybenzoxazine, the presence of *m*-xylene and 1,3,5-trimethylbenzene structures is detected despite the absence of the 1,3,5-trimethylbenzene type structure in the monomer. As previously mentioned for **Ph–a**, not only the free *ortho* position but also the free *para* position is subjected to the C-aminoalkylation reaction during the ring-opening polymerization. Therefore, the 2,4,6-tri-substituted phenolic structure is also expected to be present in the network structure of the **Ph–a** polybenzoxazine as shown in Scheme 2.

3.2.2. Amines

Table 3 shows the percentage of amines detected by GC–MS of the evolved gases of three polymers. As can be seen from Table 3, the majority of amines as degradation products for each polymer is the original amine in the monomer structure. That is aniline appears as one of the major degradation products for both **Ph–a** and **BA–a**, whereas 3,5-xylidene does for **BA–35x**. In addition to the presence of original amines used, substituted amines are also detected in the decomposition products. The reason and explanation for the presence of these compounds are well described in detail in our previous work [3,4] and, therefore, would not be repeated here.

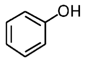
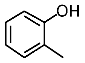
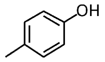
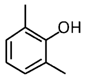
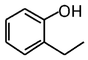
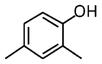
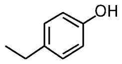
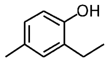
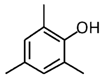
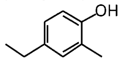
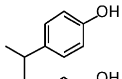
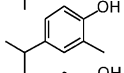
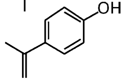
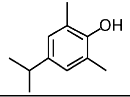
3.2.3. Phenolic compounds

All the phenolic compounds found from EGA are presented in Table 4. The majority of the phenolic compounds found from EGA of the **Ph–a** polymer are phenol, and mono- and di-methylphenol. *p-iso*-propyl phenols are seen only in the **BA–a** and **BA–35x** polymers. Phenolic compounds are the direct result of polybenzoxazine degradation. The studies on the decomposition of the



Scheme 2.

Table 4
Percentage of phenolic compounds in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
5.28	94		21		<1
6.75	108		10	3	6
7.27	108		9[a]		
7.92	122		<1	<1	2
8.72	122		<1	<1	<1
9.04	122		6	<1	2
9.42	122			<1	<1
9.93	136		<1	<1	<1
10.45	136		<1	<1	<1
10.99	136			3	4
11.29	136			1	3
12.78	150			7	2
13.00	134			<1	11
14.15	164			1	8

[a] Integration includes percentage of *p*-toluidine, due to highly overlapped peaks.

polybenzoxazine model dimers and oligomers have also reported phenolic compounds as one of the degradation products [6,7,16]. Nevertheless, there is a remarkable difference between the aliphatic amine-based polybenzoxazine model dimers and aromatic amine-based polybenzoxazines in terms of the detection of phenolic compounds. The molecular ions appearing in the mass spectra of the dimers and oligomers also contain bisphenol compounds [6,7,16], whereas those of the polymers [8] do not. This implies that the degradation of aliphatic and aromatic amine-based polybenzoxazines does not involve recombination of phenolic radicals.

3.2.4. 2,3-Benzofuran derivatives

The structure of 2,3-benzofuran derivatives as well as their percentage are tabulated in Table 5. It is proposed here that the 2,3-hydrofuran derivatives are formed when ethyl phenol and its derivatives degrade further by reaction such as dehydrogenation. The percentage for these compounds are relatively low compared with the other class of compounds.

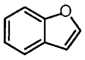
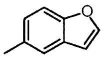
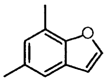
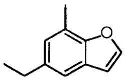
3.2.5. Iso-quinoline derivatives

Table 6 lists the structure and percentage of *iso*-quinoline derivatives detected by the GC–MS. Like 2,3-benzofuran derivatives, the *iso*-quinoline derivatives are present in the decomposition products with very low intensity. The formation of *iso*-quinoline and its derivatives is proposed to be a result of further degradation of another class of degradation products, phenanthridine and its derivatives. The proposed mechanisms for the formation of phenanthridine derivatives will be discussed later.

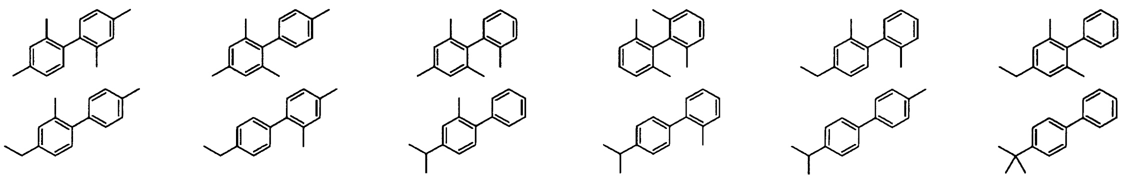
3.2.6. Biphenyl compounds

The percentage and structures of all biphenyl compounds are listed in Table 7 which includes a series of molecular ions in the mass spectra at *m/z* 182, 196, 210, 224, 238, 252, 266, 280, and 294. The mass spectra obtained complied with

Table 5
Percentage of 2,3-benzofuran derivatives in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
6.41	118		< 1	< 1	< 1
7.80, 8.05 and 9.08	132	 and isomers	< 1	< 1	< 1
9.93, 10.33 and 10.56	146	 and isomers	< 1	< 1	< 1
11.97 and 12.79	160	 and an isomer		< 1	< 1

the electronic impact fragmentation mechanisms of biphenyl compounds. The difference of mass *m*/*e* of 14 amu between each biphenyl compounds indicates the addition of one more methyl group. The compounds were grouped by molecular weight without separating the various isomers detected, since a group of a specific molecular weight can have so many isomers as proven by the detection of each group at many different retention times. Examples of the possible isomers are shown below for biphenyl compounds with *m*/*e* 210.



Biphenyl structures are absent in the network structures of polybenzoxazines. Therefore, biphenyl compounds must be formed from the recombination or degradation of compounds formed during pyrolysis. The polybenzoxazine model dimers and oligomers also showed the presence of biphenyl compounds as one of the degradation products [6,7,16]. The study found that the phenyl radicals are formed when phenols lost the hydroxyl groups. These radicals coupled with each other and resulted in the formation of the biphenyl compounds. In this study, the radicals formed, when benzene derivatives, amines, and phenolic compounds lost the substituents, can couple with each other and hence form biphenyl compounds. For example, as shown in Scheme 3, phenolic compounds can lose hydroxyl groups and two of the radicals formed can combine with each other, resulting in the formation of a biphenyl compound. Biphenyl compounds are likely to undergo successive dehydrogenation, cross-linking, and aromatization, which can ultimately lead to the formation of char, as described in Scheme 4.

Table 6
Percentage of *iso*-quinoline derivatives in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

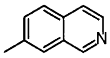
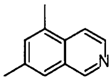
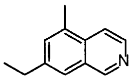
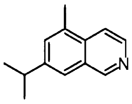
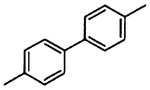
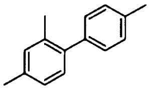
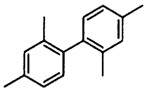
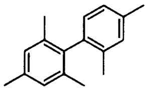
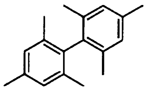
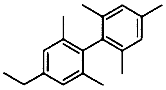
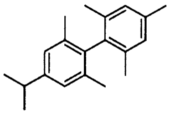
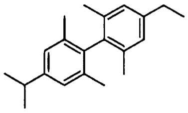
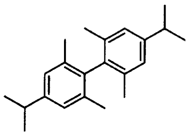
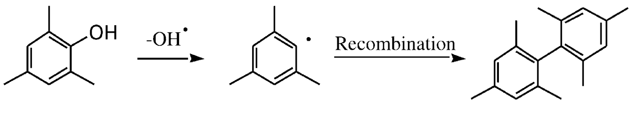
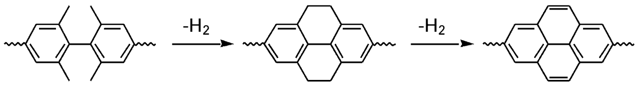
Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
14.43 and 14.51	143	 and an isomer	< 1	< 1	< 1
14.90, 16.04, 16.16 and 16.85	157	 and isomers	< 1	< 1	< 1
17.56, 19.07, 19.14, and 19.46	171	 and isomers		< 1	2
20.83 and 21.13	185	 and an isomer		< 1	< 1

Table 7
Percentage of biphenyl compounds in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
21.42	182		<1		
23.24, 23.62, 23.94, and 24.05	196	 and isomers	2	<1	<1
22.60, 22.96, 24.68, 25.07, 25.23, 25.46, 25.57, 25.63 25.68, 26.16, 26.35, and 26.69	210	 and isomers	5	<1	<1
25.12, 25.24, 25.38, 25.88, 26.84, 27.11, 27.20, 27.42, 27.67, 27.79, 27.88, and 28.26	224	 and isomers	1	4	<1
27.28, 28.06, 28.48, 28.75, 28.81, 28.96, 29.45, 29.65, and 29.75	238	 and isomers	3	4	2
29.05, 29.63, 29.94, 30.44, 30.58, and 31.01	252	 and isomers	<1	<1	2
30.32, 30.65, 31.04, 31.30, 31.45, 31.62, 31.81, 32.15, 32.31, 32.41, 32.89, and 33.08	266	 and isomers		<1	1
31.46, 31.97, 32.27, 33.25, 33.41, 33.99, 34.03, and 34.23	280	 and isomers			<1
33.58, 34.86, and 34.94	294	 and isomers		<1	<1



Scheme 3.

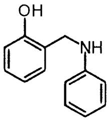
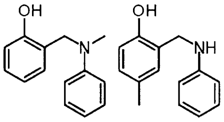
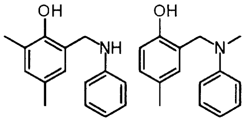
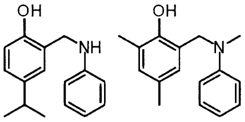
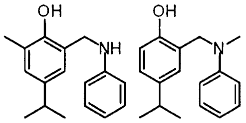
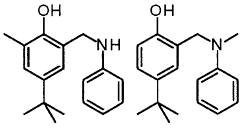


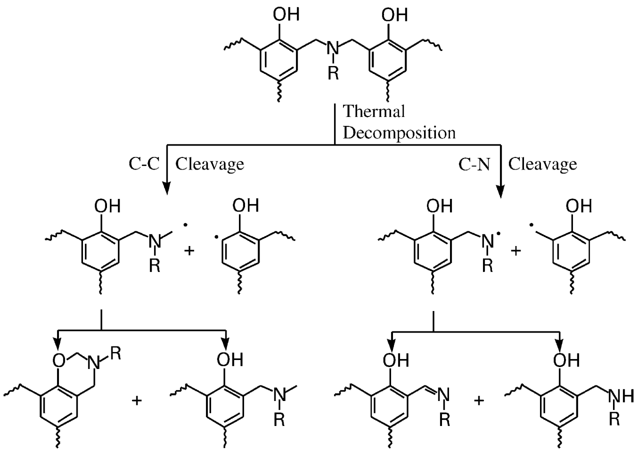
Scheme 4.

3.2.7. Mannich base compounds

Table 8 shows all the Mannich base compounds detected by EGA. These compounds are obviously direct results of the polymer degradation. The previous studies [6,7,16] have shown that there are two fragmentation processes occurring simultaneously during the degradation of benzoxazines, the cleavages of C–C and C–N bonds as depicted in Scheme 5. The first one leads to deaminomethylation, while the latter results in deamination. However, one of these two processes can predominate over the other, depending on the chemical nature of the R group, the substituent at the nitrogen atom. Both steric hindrance and basicity play an important role on the cleavage of Mannich bases [25]. The previous study [6] on the aliphatic amine-based polybenzoxazine model dimers has revealed that the size of the amines indeed has a profound effect on the type of cleavage. The benzoxazine dimers with small amines tend to undergo the C–C cleavage and form monomer, confirming the occurrence of reverse Mannich reaction, while the dimers with large amines tend to favor the C–N cleavage which subsequently causes the formation of Schiff bases. This observation was explained in detail in our study on the decomposition of methylamine-based polybenzoxazines [8], in which the benzoxazine

Table 8
Percentage of Mannich base compounds in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
28.09	199		<1	7	
29.10, 30.02, and 30.34	213	 and isomers	<1	15	
29.31,30.27, 30.60, 31.25, and 31.76	227	 and isomers	<1		
31.68, 32.49, and 32.73	241	 and isomers		3	<1
32.44, and 33.60	255			7	
32.53, and 33.69	269			<1	

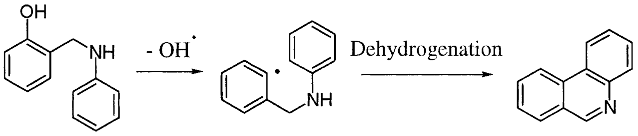


Scheme 5.

monomers were detected as some of the degradation products. The opposite situation exists with aniline-based polybenzoxazines giving off Mannich bases as one of the major pyrolysis products, without any trace of benzoxazine monomers.

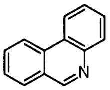
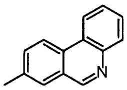
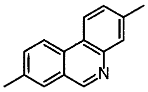
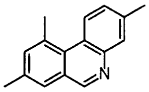
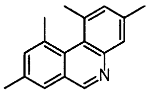
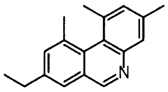
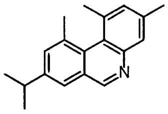
3.2.8. Phenanthridine derivatives

The structure of phenanthridine and its derivatives are presented in Table 9. These compounds are obviously not present in the network structure of polybenzoxazines. The proposed mechanisms for the formation of phenanthridine derivatives are illustrated in Scheme 6. The phenanthridine derivatives are produced from the degradation of Mannich base compounds. When a Mannich base lost a hydroxyl group, the radical formed can undergo successive dehydrogenation and eventually form a phenanthridine. For **Ph–a**, the polymer gave off phenanthridine and its methyl-substituted derivatives. For **BA–a** and **BA–35x**, the polymers also yielded ethyl- and *iso*-propyl-substituted derivatives of phenanthridine. Like biphenyl compounds, phenanthridine structure is likely to undergo cross-linking, dehydrogenation and aromatization which finally leads to the formation of highly condensed aromatic molecules, i.e. char formation.



Scheme 6.

Table 9
Percentage of phenanthridine derivatives in gases evolved from the degradation of **Ph–a**, **BA–a**, and **BA–35x** polybenzoxazines in nitrogen

Retention time (min)	Molecular weight	Structure	**Ph–a** (%)	**BA–a** (%)	**BA–35x** (%)
24.68	179		3	1	
26.05 and 27.14	193	 and isomers	6	4	<1
27.37, 28.29 28.41, 29.16 and 29.44	207	 and isomers	4	3	
29.56, 30.52, and 31.38	221	 and isomers	1	4	<1
31.18, 31.37, 31.53,31.62, 32.81, 33.73, and 33.92	235	 and isomers	<1	4	1
31.87, 32.06 33.37, 34.42 34.77, 35.16 and 35.23	249	 and isomers		<1	5
35.37, 36.08, and 36.17	263	 and isomers			4

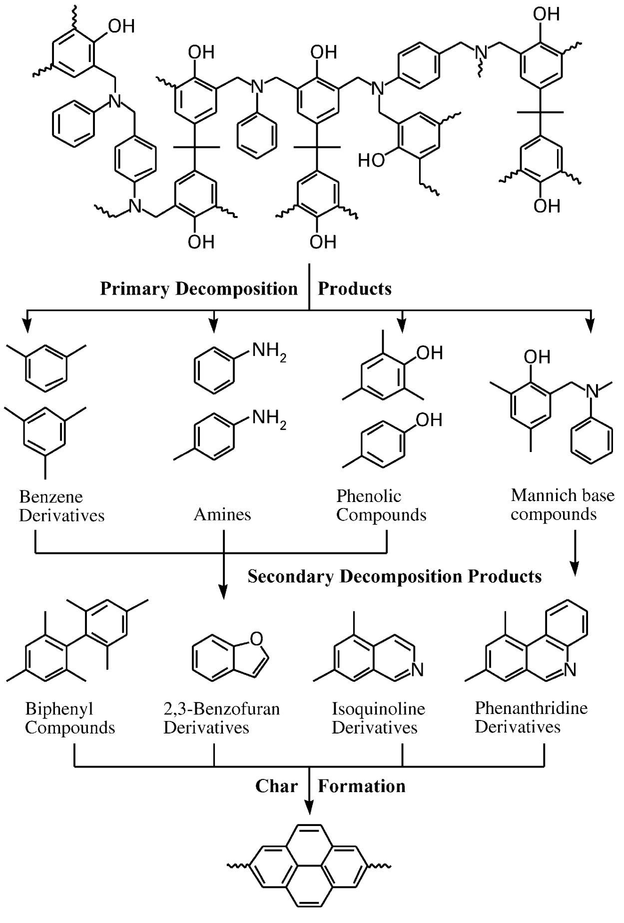
3.3. Thermal decomposition processes inferred from the decomposition products

The thermal decomposition processes in aromatic amine-based polybenzoxazines are inferred from the structure of the decomposition products and summarized in Scheme 7. The degradation products from three different aromatic amine-based polybenzoxazines were grouped into eight different types of compounds. These eight families of compounds can be grouped further into two categories. The first category represents the primary decomposition products such as benzene derivatives, amines, phenolic compounds and Mannich base compounds. These compounds are obtained directly from the degradation of the polymer itself. The mechanism involves chain scissions, such as the C–C, C–O and C–N cleavages, of the network structure of the polymer. The proposed network structure of **BA–a** polybenzoxazine is illustrated in Scheme 7, in which structures of compounds from the primary degradation products are shown as well. The structure of these degradation products is obviously a part of the network structure of the polymer.

The second category contains secondary decomposition products which are 2,3-benzofuran derivatives, *iso*-quinoline derivatives, biphenyl compounds and phenanthridine derivatives. Unlike compounds in the first category, these four secondary decomposition products are not present in the polymer network structure. They can be separated further into two groups. The first group, 2,3-benzofuran derivatives and biphenyl compounds, is derived from the recombination of radicals formed during the degradation of primary decomposition products like benzene derivatives, amines, and phenolic compounds. The second group, *iso*-quinoline and phenanthridine derivatives, originates from the degradation of Mannich base. Presence of these four secondary products is very critical for char formation. They are capable of undergoing successive dehydrogenation, cross-linking, and aromatization, all of which will finally lead to formation of highly cross-linked molecules, i.e. the formation of char.

4. Conclusions

The thermal decomposition processes of three different aromatic amine-based polybenzoxazine polymers are investigated using TGA and GC–MS. The EGA performed by GC–MS has detected eight different categories of compounds as degradation products. The degradation products are either from a direct result of polymer



Scheme 7.

degradation or from the recombination or degradation of compounds formed during the thermal decomposition. Benzene derivatives, amines, phenolic compounds, and Mannich base compounds come directly from the decomposition of polybenzoxazines. 2,3-Benzofuran is derived from the further degradation of phenolic compounds. On the other hand, biphenyl compounds are obtained from the recombination between two phenyl radicals formed after the loss of substituents from benzene derivatives, amines and phenolic compounds. *Iso*-quinoline and phenanthridine derivatives are formed when Mannich base compounds lose the hydroxyl group and undergo successive dehydrogenation. The presence of 2,3-benzofuran derivatives, *iso*-quinoline derivatives, biphenyl compounds and phenanthridine derivatives is critical and responsible for the char formation of aromatic amine-based polybenzoxazine.

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