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Structural effects of phenols on the thermal and thermo-oxidative degradation of polybenzoxazines

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Abstract

The thermal behavior of a series of polybenzoxazines based on aniline and various phenols is examined under both inert and oxidative environments. Under an inert environment, the various phenols substantially affect the char yield of polybenzoxazines without altering the mechanism of Mannich base cleavage. Under an oxidative environment, the various phenols have a significant influence on the degradation behavior of polybenzoxazines below 600°C. The mechanism of the Mannich base cleavage under oxidative degradation has been proposed.

Keywords: Phenols; Polybenzoxazines; Structure

1. Introduction

As a new class of polymeric resin, polybenzoxazines have shown various unique properties. Like epoxies and polyimides, the flexible chemistry of benzoxazines has allowed structural tailoring. Benzoxazine monomers are synthesized from a phenol, primary amine, and aldehyde. Various phenols and primary amines have been used to synthesize polybenzoxazines. For example, polybenzoxazines with mechanical properties comparable to epoxy [1] and polyimide [2] were obtained with the combination of certain phenols and amines. Benzoxazine monomers were found to undergo volumetric expansion upon polymerization and it was found that the extent of volumetric change is affected by various primary amines [3]. Recently, polybenzoxazines with char yields as high as 80% have been reported with a specific phenol and amine [4]. The ability to tailor the structure of a resin necessitates the understanding of structure-property relationship. This paper will explore the effect of phenolic structure on the thermal stability of polybenzoxazines.

Unlike mechanical properties, the structural effect on thermal stability is not easily predictable. For example, it was found that an increase in the number of aromatic rings increases the thermal stability of certain polymers [5]. However, it was also found that polyimides with dianhydrides that have one aromatic ring are thermally more stable than those consisting of two aromatic rings [6]. The thermal stability of polyimides with various dianhydrides and diamines has been studied extensively [7]. The structural effect of various dianhydrides and diamines of the kind, R-aromatic-X-aromatic-R, where R is the amine functional or anhydride function group and X can be C=O, $C(CH_3)_2$, S, SO_2, O and CH_2, has been studied. Similarly, various phenols of the structure, R-aromatic-X-aromatic-R, where R is the phenolic functional group, can be used to determine the structural effect on the thermal stability of polybenzoxazines.

The thermal degradation mechanisms of a series of polybenzoxazines based on bisphenol-A and various primary aliphatic amines have been proposed [8]. The char yield of this series of polybenzoxazines was minimally affected by the various aliphatic amines. The thermal cleavage mechanism of the Mannich base, which is the structure deemed characteristic of polybenzoxazines, has been proposed. Unlike the Mannich base, the phenolic moiety of polybenzoxazine is not unique to polybenzoxazine alone. Nevertheless, the effect of bi-phenols on char yield is significant and essential for understanding the mechanism of char formation. For example, the polybenzoxazine based on bisphenol-A and aniline has a char yield of 32% [9], while that based on 4,4′-dihydroxybenzophenone and aniline has a char yield of 67% [2]. Although the char yields of polybenzoxazines based on various phenols have been reported, there has not been any detailed molecular

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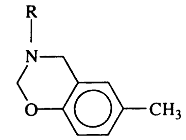
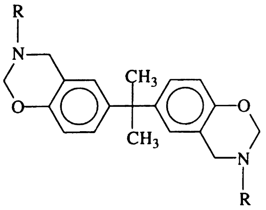
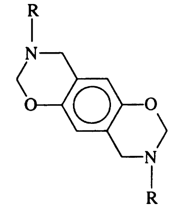
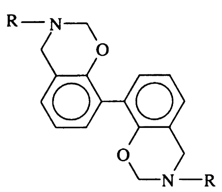
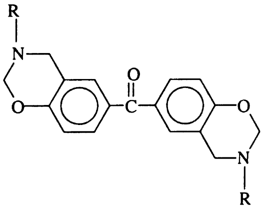
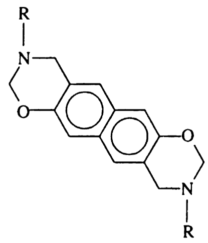
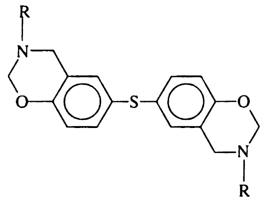
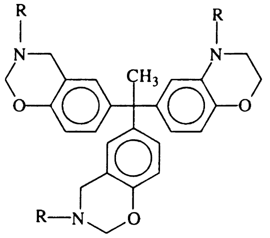
Table 1
Structures of benzoxazine monomers and the char yield under nitrogen degradation. The curing condition of each benzoxazine is shown in parentheses

Benzoxazine monomer[a]	Abbreviation	Char yield[b]
	PC-a (140°C–4 h, 5 wt% phenol was added as initiator)	20%
	BA-a (150°C–1 h, 175°C–2 h, 190°C–2 h)	32%
	HQ-a (150°C–1 h, 180°C–2 h, 200°C–2 h)	44%
	22P-a (180°C–2 h, 200°C–2 h)	52%
	44O-a (180°C–2 h, 210°C–2 h)	61%
	15N-a (autoclaved 240–1 h, 315°C–2 h)	71%
	TP-a (150°C–1 h, 180°C–2 h, 200°C– 2 h)	57%
	TrisP-a (150°C–1 h, 180°C–2 h, 200°C–2 h)	47%

[a] R represents phenyl ring.

[b] Determined at 800°C.

understanding of the effect of various phenols on the thermal stability of polybenzoxazines.

It was reported that, for conventional phenolic resins, both the thermal degradation under nitrogen and the thermo-oxidation under air are oxidative in nature [10]. Although polybenzoxazines have a phenolic-like structure, the above may or may not apply for polybenzoxazines. The thermally induced oxidative degradation of polybenzoxazines will be investigated in this paper.

2. Experimental

Benzoxazine monomers were synthesized using aniline, paraformaldehyde and the following phenols: *p*-cresol, bisphenol-A, hydroquinone, 2,2′-biphenol, 4,4′-dihydroxybenzophenone, 4,4′-thiobiphenol, 1,5-napththol, and 1,1,1-tris(*p*-hydroxyphenyl)ethane. The synthesis was carried out

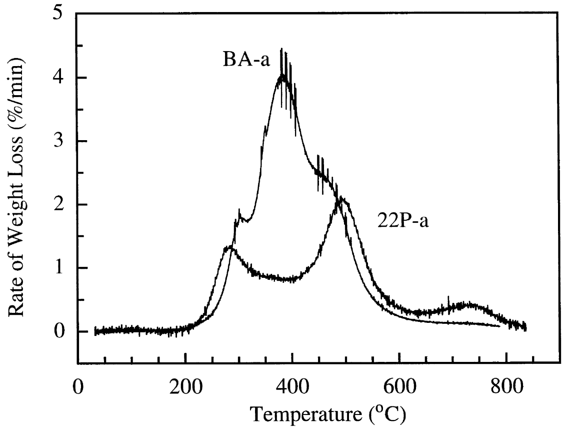


Fig. 1. Derivatives of residual weight for BA-a and 22P-a. The derivatives were obtained from TGA thermograms of degradation under nitrogen.

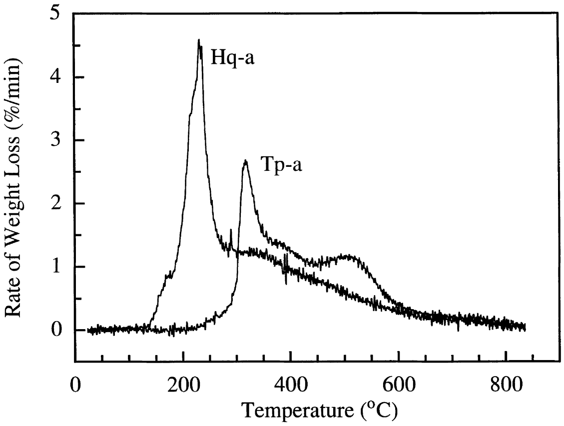


Fig. 2. Derivatives of residual weight for HQ-a and TP-a under nitrogen degradation.

in a solventless system [9] and purified according to the previous paper [11]. Benzoxazines based on 2,2′-biphenol and 4,4′-dihydroxybenzophenone were synthesized in 1,4-dioxane. Detailed synthesis procedures have been reported [11]. All chemicals were purchased from Aldrich Chemical Co., and used as received. All the benzoxazines were polymerized without added initiator or catalyst. For simplicity, abbreviation will be used throughout this paper. The structures and the abbreviations are shown in Table 1. Those abbreviations used to designate monomers are also used for the corresponding polymers since only the polymers are analyzed in this paper. The curing conditions are also shown in Table 1.

A TA Instruments 2950 thermogravimetric analyzer (TGA) was used for the TGA experiments. Thermal degradation experiments were carried out under nitrogen purge, while thermo-oxidative degradation experiments were carried out under dry air flow. Both types of experiments were performed with a flow rate of 90 ml/min. A heating rate of 10°C/min from room temperature to 850°C was used, unless otherwise mentioned. The TGA is interfaced with a Fourier transform infrared (FTIR) spectrometer using a Bio-Rad/TGA interface, which is equipped with a deuterated tryglycine sulfide (DTGS) detector. The gas cell and the transfer line were set at a temperature of 300°C. The spectral resolution of the spectrometer was set at 8 cm^{-1} which resulted in a time resolution of 1 s.

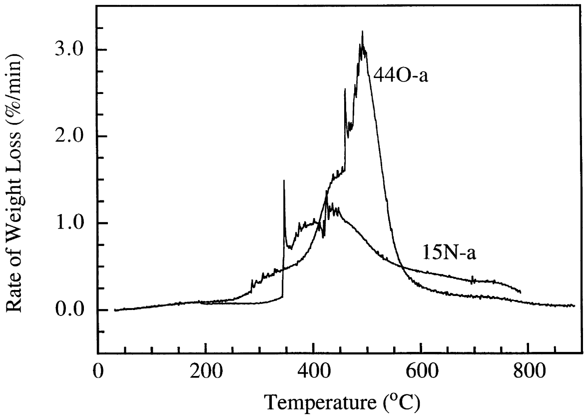


Fig. 3. Derivatives of residual weight for 44O-a and 15N-a. The sharp spikes in the curves are due to noise.

A Hewlett-Packard 6890 gas chromatography-5973 mass selective detector (GC-MS) were used for mass identification of the evolved components. Ultra pure helium is used as the carrier gas for GC, which is a non-bonded capillary column (30 m × 0.25 μm i.d.) coated with 5% phenylmethyl siloxane. Evolved gases from TGA experiments were collected into HPLC-grade chloroform and immediately injected into the GC-MS. The injection port of GC was set at 250°C, while the GC column was programmed from 70°C to 280°C at a heating rate of 8°C/min. The MS operates at an ionization energy of 70 eV. The mass spectra obtained were searched through a NIST MS Library, Nbs75k, for compound identification.

3. Results and discussion

3.1. Thermal degradation under nitrogen

The char yields of polybenzoxazines at 800°C under nitrogen are presented in Table 1, along with the monomer structures and abbreviations of the benzoxazine monomers. As can be seen, the thermal stability of polybezoxazine is greatly affected by the various phenols. Among the bifunctional phenols studied, the trend of stability (based on the char yield at 800°C) is as follows: bisphenol-A < hydroquinone < 2,2′-biphenol < 4,4′-thiobiphenol < 4,4′-dihydroxbenzophenone < 1,5-naphthol. It has been reported that bisphenol-A is the least stable linkage among the structures studied in polypyromellitimides [12]. It is also the case in polybenzoxazines. However, the trend of thermal stability has no generality, namely, this trend does not apply to other polymers. A similar study yields a different trend for the structural effects on thermal degradation of polyimides [6].

The TGA thermograms of these polybenzoxazines have been reported in previous studies [2,4], and therefore will not be presented in this paper. In this paper, the derivatives of the TGA thermograms are presented, since there has not been any analysis performed on the derivative curves. As can be seen, the derivative of weight loss is distinctly different for each polybenzoxazine. It is also obvious that multiple weight loss events occur during the heating from room temperature to 850°C.

The weight loss rate of BA-a is shown in Fig. 1. It can be seen that the derivative curve is trimodal with a maximum rate of 4.0%/min at 388°C. The derivative curve of 22P-a (Fig. 1) shows more than three weight loss events, centered around 290°C, 500°C and 725°C. It is also noted that the derivative curve of 22P-a (Fig. 1) is better separated compared with that of BA-a. This difference allows the distinction on the sequence of the degradation process.

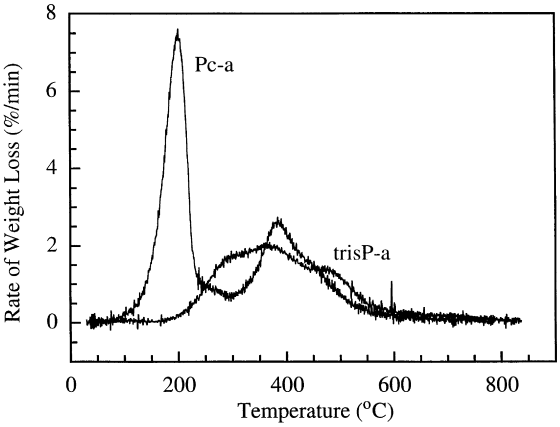


Fig. 4. Derivatives of weight loss for PC-a and trisP-a under nitrogen degradation.

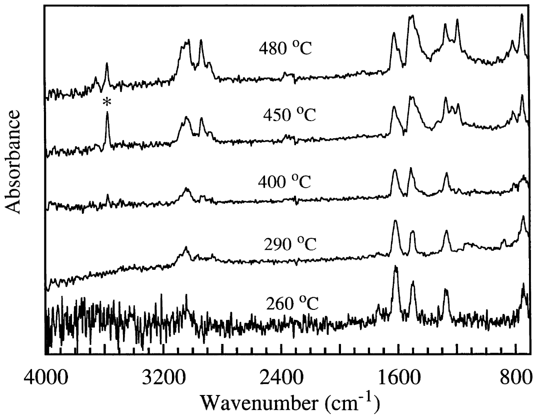


Fig. 6. FTIR spectra of the evolved gases from the degradation of 22P-a under nitrogen environment. Asterisk at 3650 cm^{-1} is the free OH band.

For instance, the overlapped curve in BA-a indicates that the degradation of the phenolic linkage occurs simultaneously with the degradation of the Mannich base but the onset of each type of degradation is different. On the other hand, in 22P-a, the degradation of the phenolic linkage occurs after the degradation of the Mannich base has completed. The well-separated peaks ease the assignment of each peak. The first derivative peak is assigned to the amine evaporation, while the second major derivative peak is assigned to the degradation of the phenolic moiety. This is supported by the FTIR and GC-MS analyses, as will be seen later. In BA-a, the assignment of the bisphenol-A degradation is also supported by the literature report that the cleavage of the isopropylidine group of bisphenol-A occurs at approximately 380°C [13]. In contrast to BA-a, the second major derivative peak of 22P-a has a maximum at approximately 500°C, showing the higher thermal stability of the 2,2′-biphenol linkage.

Derivative curves of TP-a and HQ-a (Fig. 2) are similar. Both curves show a sharp weight loss followed by a broad tail. The degradation occurs at a slower rate over a wider temperature range. In comparison with BA-a and 22P-a, these broad tails indicate that the hydroquinone and 4,4′-thiobiphenol linkages degrade over a wider temperature range. A broad range of degradation is advantageous from a flammability point of view. The initial degradation of HQ-a occurs at a lower temperature and at a higher rate compared with that of TP-a. This explains the lower char yield of HQ-a despite the similarity in the degradation of the phenolic portion.

44O-a and 15N-a (Fig. 3) are considered high char yield polymers [14]. The derivatives of weight loss for these polybenzoxazines are complex compared with the other polybenzoxazines. The onset of weight loss for 44O-a occurs at approximately 260°C, although the weight loss at this temperature is very small. The initial derivative peak seen in BA-a, 22P-a, HQ-a, and TP-a is absent in both 44O-a and 15N-a. Instead, there is a small and broad peak that extends from approximately 260°C to 400°C. This peak is assigned to the amine evaporation as will be seen later. These derivative patterns indicate that the degradation of the Mannich base is retarded in 44O-a and 15N-a. An inspection of the degradation products further shows that the mechanism of

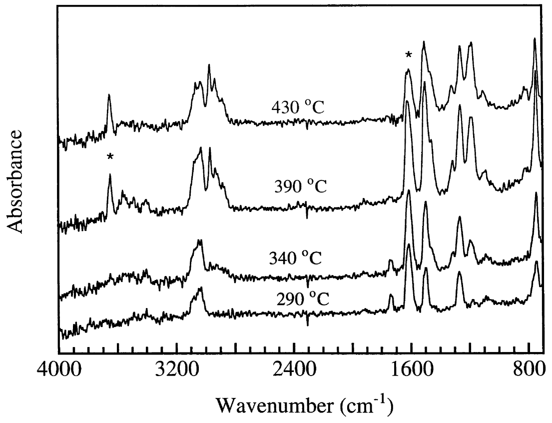


Fig. 5. FTIR spectra of the evolved gases from the degradation of BA-a under nitrogen environment. The asterisk at 3650 cm^{-1} is the free OH band and the asterisk at 1620 cm^{-1} is a hydrogen bonded Schiff base band.

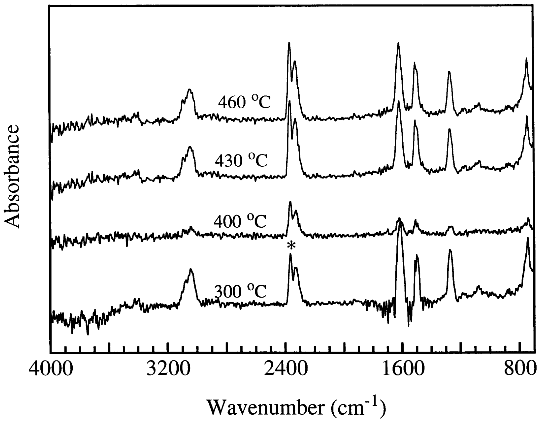


Fig. 7. FTIR spectra of the evolved gases from the degradation of 15N-a under nitrogen environment. Asterisk shows the bands due to CO_2.

Table 2
GC-MS results for thermal-degradation below 400°C, under nitrogen

Retention time (min)	BA-a	22P-a	15N-a	44O-a
5.23	Aniline	Aniline	Aniline	Aniline
6.80	*N*-methylaniline	*N*-methylaniline	–	–

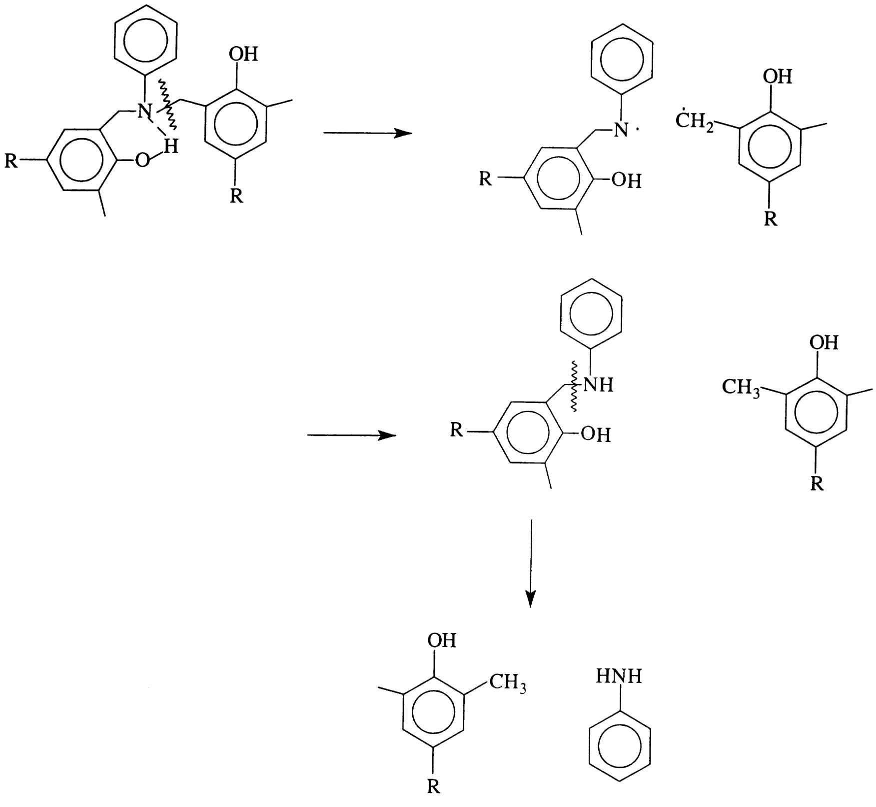
degradation remains to be the same even if the rate of decomposition is different. 15N-a has the highest char yield and the lowest rate of weight loss among all the polybenzoxazines studied in this paper. The maximum rate of weight loss occurs at around 433°C at a rate of 1.1%/min, which is significantly lower than the weight loss rates of BA-a, 22P-a and 44O-a.

A comparison is made among PC-a (monofunctional), BA-a (bifunctional) and trisP-a (trifunctional). The derivative curves for PC-a and trisP-a are shown in Fig. 4. Char yield is found to increase with functionality of the phenols. Monofunctional polybenzoxazine is a linear low molecular weight polymer [15], while the bifunctional polybenzoxazines behave like a crosslinked thermoset [11]. Consequently, it is unclear at this point whether the char yield improvement is a result of an increase in aromatic rings per chemical repeat unit or simply a result of an increase in crosslink density.

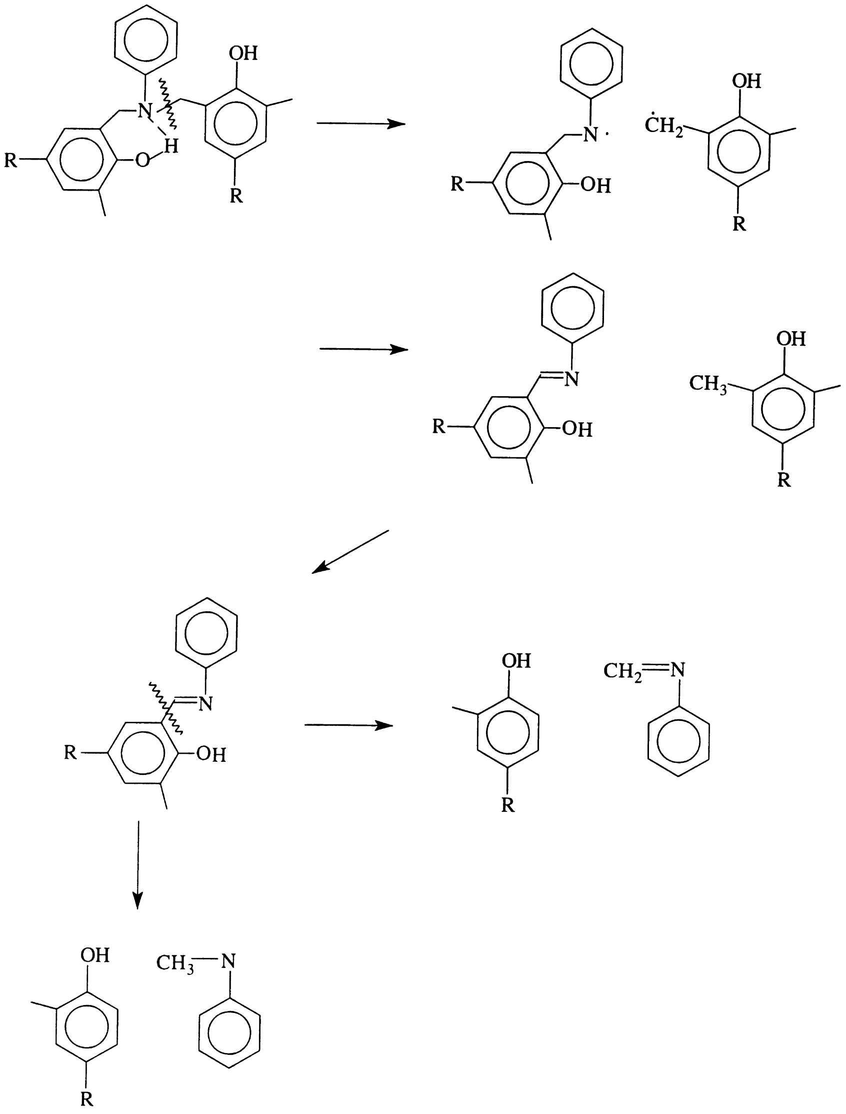
The derivative curve for PC-a shows two well-separated peaks centered around 200°C and 400°C. About 40% of weight loss occurred in the first event. Again, this peak is assigned to the amine evaporation. The monofunctional polybenzoxazine consists of linear oligomers, which tend to decrease the thermal stability. Since the phenolic moiety is small, as soon as bond cleavage and fragmentation occur, the fragmented species are easily evaporated. Going from monofunctional to bifunctional and trifunctional polybenzoxazine, the derivative of weight loss becomes broader and more overlapped. this may be an indication of the increased complexity of the polymer structures. The structural complexity is also reflected in the maximum rate of weight loss at 7.8%/min, 4.0%/min, and 2.0%/min for PC-a, BA-a and trisP-a, respectively.

3.2. FTIR analysis of the evolved gases under nitrogen environment

The FTIR spectra of the evolved gases of BA-a are shown in Fig. 5. A comparison of the first spectrum with the vapor phase FTIR spectrum of aniline shows that aniline is a major degradation component initially. The evaporation of amine, as reported in the previous study [8], is a consequence of the



Scheme 1.

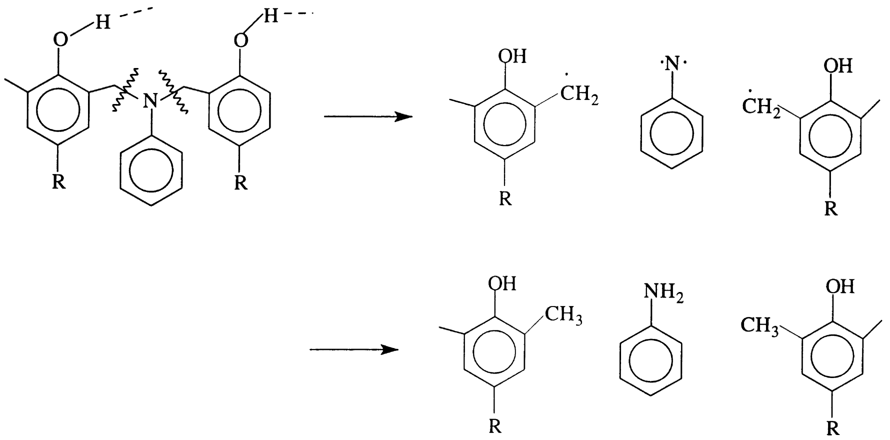


Scheme 1. (*continued*)

Mannich base cleavage. The band at 1735 cm^{-1} indicates the presence of C=O, of which the concentration became almost undetectable at 390°C. It was proposed in a previous study that Schiff base and secondary amide are defect structures or terminal groups in polybenzoxaxines based on bisphenol-A and aliphatic amines [8]. Although not shown here, the FTIR spectrum of BA-a has a band at 1680 cm^{-1} that is due to secondary amide. It is hypothesized that the carbonyl species detected in the evolved gas spectra of BA-a is a result of thermal cleavage of the secondary amide. However, further study is needed to confirm the nature of secondary amide in polybenzoxazines.

At 390°C, a prominent band at 3650 cm^{-1} is detected from BA-a. This band is due to the free OH group of phenol. This is accompanied by a band at 1180 cm^{-1}, which is due to the C–O bond of phenol or substituted phenols. This temperature corresponds to the temperature of the maximum rate of weight loss in the TGA thermogram of BA-a. Consequently, the maximum derivative peak at 388°C in the TGA thermogram is assigned to the phenolic cleavage. At 430°C, an additional band at 1634 cm^{-1} is detected. This band is assigned to Schiff base. Schiff base is also detected as a degradation product in the series of bisphenol-A-aliphatic amine-based polybenzoxazines [8].

The evolved gas FTIR spectra of 22P-a are shown in Fig. 6. The spectra also show a signature of aniline initially. At 290°C, there are also signatures of aliphatic species between 2960 cm^{-1} and 2800 cm^{-1}. The aliphatic signature most likely originates from the methyl group of *n*-methylaniline. As GC/MS analysis shows, *n*-methylaniline is detected from degrading 22P-a initially. At 400°C, the free OH band at approximately 3600 cm^{-1} is detected, which signals the onset of degradation and evaporation of the phenolic moiety. This band becomes more intense at 450°C. The onset of OH detection at 400°C coincides with the onset point of the second derivative peak in the TGA thermogram



Scheme 2.

of 22P-a. This result allows the assignment of the major derivative peak centered at 500°C in the TGA thermogram of 22P-a to the phenol degradation. A major difference in the spectra of BA-a and 22P-a is also found in the region of 1269 cm^{-1} to 1188 cm^{-1}, which is attributed to the different types of phenolic species.

Fig. 7 shows the FTIR spectra of the evolved gases from the degrading 15N-a. A high concentration of CO_2 is detected even in the early stage of degradation. The observation of CO_2 evolution is unique to 15N-a. No other polybenzoxazines show CO_2 evolution at this temperature under inert environment. The evolution of CO_2 will hinder the burning of the polymer in the case of fire. These spectra also show a signature of aniline. However, no phenolic component is detected from these spectra. Under nitrogen environment, the evolution of CO_2 is likely a consequence of the OH cleavage. Since naphthol is a fused benzene ring, the aromatic portion of the polymer is not easily cleaved. This is in contrast to all the other phenolic backbones where the phenolic components evaporate before the OH cleavage occurs.

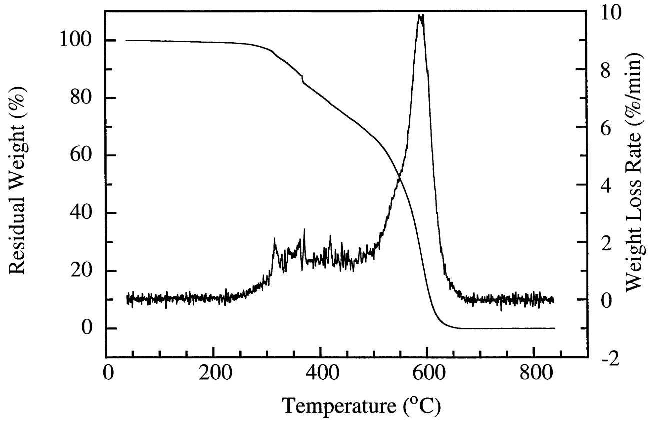


Fig. 8. TGA thermograms of BA-a under oxidative environment.

3.3. GC-MS analysis

The results from GC-MS analysis of the initial degradation products are shown in Table 2. This initial degradation stage was determined such that it corresponds to the first derivative peak in the TGA thermogram. Evolved gases were collected up to the temperature of the first derivative maximum. For example, in BA-a, the gases were collected up to 325°C. Both primary and secondary amines are detected from this series of polybenzoxazines. These results are in agreement with the degradation mechanism proposed in the previous study [4], namely the release of various amines as a consequence of Mannich base cleavage. It is important to point out that the initial degradation products are almost identical in all of these polybenzoxazines. This indicates that the mechanism of Mannich base cleavage is not greatly affected by the various phenols.

The different rates of weight loss demonstrated by these polybenzoxazines could be a result of the different glass transition temperature (T_g). For example, the T_g of BA-a is reported to be 180°C [16], while that of 44O-a is 340°C [14]. The onset of degradation for BA-a is approximately 220°C. At this temperature, BA-a is in the rubbery state and molecules are mobile. As soon as bond cleavage and fragmentation occur, the mobility of the molecules will aid the evaporation of the fragmented molecules. On the other hand, the onset of weight loss for 44O-a is approximately 260°C. At this temperature 44O-a is still in its glassy state, bond cleavage and fragmentation could still occur but the evaporation of the fragmented species will be retarded due to the limited mobility. Thus, the rate of weight loss during the initial degradation is different among these polybenzoxazines.

Table 3 further shows that various phenols are detected at higher temperatures. The percentage of the relative concentration of the degradation products shown in Table 3 was obtained from the relative areas of the GC chromatograms. The types of phenol released are clearly dependent on the structure of the phenolic linkage. It is interesting but not

Table 3
GC-MS results for degradation up to 800°C under nitrogen. The numerical percentage is the relative concentration of the compound

Retention time (min)	BA-a	HQ-a	22P-a	15N-a	44O-a
2.54	Toluene, 0.5%	Toluene, 1%	–	–	Toluene, 7%
3.60	*p*-Xylene, 0.4%	–	*p*-Xylene, 1%	–	*p*-Xylene, 4%
5.14	Phenol, 3%	Phenol, 0.2%	Phenol, 1%	–	Phenol, 20%
5.24	Aniline, 27%	Aniline, 45%	Aniline, 70%	Aniline, 70%	Aniline, 35%
6.52	–	–	2-Methylphenol, 2%	–	2-Methylphenol, 11%
6.83	*N*-methylaniline, 1%	*N*-methylaniline, 1%	*N*-methylaniline, 5%		–
6.88	3-Methylphenol, 0.6%	–	–	–	4-Methylphenol, 3%
6.95	*p*-Aminotoluene, 2%	*p*-Aminotoluene, 1%	*p*-Aminotoluene, 13%	*p*-Aminotoluene, 10%	*p*-Aminotoluene, 12%
7.53	2,6-Dimethylphenol, 1%	–	–	–	2,6-Dimethylphenol, 1%
8.25	2,4-Dimethylphenol, 0.5%	–	–	–	–
10.89	2-Methyl-5-(1-methylethyl)phenol, 0.4%	–	–	–	–
12.82	–	–	–	2,7-Dimethyl-naphthalene, 0.8%	–

surprising to note that no phenol is detected from the degrading 15N-a. This result is in agreement with the FTIR analysis.

An important observation from Table 3 is that *p*-aminotoluene is detected in all of these polybenzoxazines. This could mean that the benzene ring that is attached to the nitrogen is reactive at the para position during the polymerization. In the degradation study reported on the aliphatic amine-based polybenzoxazines, *p*-aminotoluene was not a degradation product. Therefore, this feature is a characteristic of aniline-based polybenzoxazines. The *para*- and *ortho*-positions of the benzene ring are potentially reactive, although at a lower rate in comparison with the benzene ring of the phenols. If the benzene attached to the nitrogen was reacted during the polymerization, this will reduce the amount of dangling groups in polybenzoxazines. The thermal stability of a polymer could be improved if there are less dangling groups. This is supported by the observation that *p*-aminotoluene is detected at the higher temperature of degradation.

From the above results, it is generalized that the first weight loss event in the TGA thermogram of polybenzoxazines is assigned to the amine evaporation. In addition, the rate of weight loss is lowered by the more thermally stable phenols. The second major weight loss is assigned to the phenol degradation and is clearly dependent on the phenolic structure.

The degradation mechanisms for the aniline-based polybenzoxazines are presented in Scheme 1 and Scheme 2. It is noted here that in all the proposed degradation schemes, hydrogen atoms are available via radical abstractions. The discussion on the degradation mechanism will focus on the Mannich base. Scheme 1 is proposed when the nitrogen of the Mannich base is hydrogen bonded. As reported in a previous study [17], this hydrogen bonding results in a stable six-membered ring. There are two possible degradation routes from this scheme. In the first, aniline is produced. In the second, a stable conjugated Schiff base is produced. This type of conjugation is not seen in the aliphatic amine-based polybenzoxazines. In the series of aliphatic amine-based polybenzoxazines, ammonia was detected as part of the degradation products [8]. However, ammonia is not detected in the aniline-based polybenzoxazines.

Since the bond dissociation energy of a C–C bond is lower than that of C=N, a more likely cleavage site of this conjugated Schiff base is the C–C bond. There are two possible degradation routes from the cleavage of this C–C bond (see Scheme 1). Schiff base is detected only from BA-a, while *n*-methylaniline is detected in all the aniline-based polybenzoxazines. Thus, the degradation route that leads to *n*-methylaniline may be favored. It is worth mentioning that Schiff base is detected in the evolved gases spectra of BA-a at 430°C. This temperature is significantly higher than the temperature at which Schiff bases were detected from the degradation of the aliphatic amine-based polybenzoxazines.

Degradation Scheme 2 is proposed when the nitrogen of the Mannich base is not hydrogen bonded. Since the dissociation energy of a C–N bond is lower than that of a C-aromatic bond [18], both C–N bonds in the Mannich base have equal probability of cleavage. Both degradation Scheme 1 and Scheme 2 produce aniline. The GC-MS analysis shows that aniline is the dominating product from the degradation of these polybenzoxazines. Since all the amine analogs produced from these degradation schemes are in fact detected to various extents, both degradation Scheme 1 and Scheme 2 may be occurring competitively during the thermal degradation of polybenzoxazines.

3.4. Thermal oxidation of polybenzoxazines

TGA thermograms of BA-a, 22P-a, 44O-a and 15N-a under oxidative degradation are shown in Fig. 8, Fig. 9, Fig. 10, Fig. 11, respectively. All of the polybenzoxazines studied here completely degraded under air between 650°C and 700°C. However, a further inspection of the TGA thermograms shows that the thermal oxidation behavior is different among these polybenzoxazines between 250°C

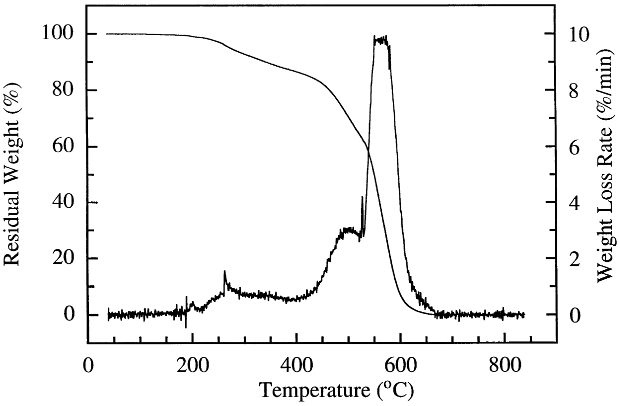


Fig. 9. TGA thermograms of 22P-a under oxidative environment.

and 600°C. Table 4 shows the residual weight of these polybenzoxazines at various stages of the thermal oxidation process. Based on the residual weight, the trend of stability of these phenolic linkages up to 500°C is in accordance with the degradation under nitrogen.

The derivative curve of BA-a shows a small and broad peak between 250°C and 500°C followed by a major peak at approximately 600°C. 22P-a shows three major weight loss events between 200°C and 600°C, while 44O-a shows two well-separated weight loss events centered at approximately 500°C and 620°C. The maximum weight loss in 44O-a is slightly higher than those of BA-a and 22P-a. It is also important to point out that, in almost all of these polybenzoxazines, the derivative curves show a strong peak at approximately 600°C and the weight loss rate of this peak is the same. This implies that the decomposition at this temperature has the same origin in all these polybenzoxazines. It is believed that during the heating to this temperature the polymer has charred, and that the degradation of the char occurs at approximately 600°C.

In order to substantiate the above hypothesis, a char material from the degradation under nitrogen environment was further degraded under air. The TGA thermogram of this char is shown in Fig. 12 for BA-a, 22P-a and 44O-a. The char of BA-a and 22P-a has a major weight loss at approximately 600°C. However, the char of 44O-a has a major weight loss higher than those of BA-a and 22P-a. This trend is in approximate agreement with the weight loss curves of these polymers between 600°C and 700°C under oxidative environment. This is shown in the insert in Fig. 12.

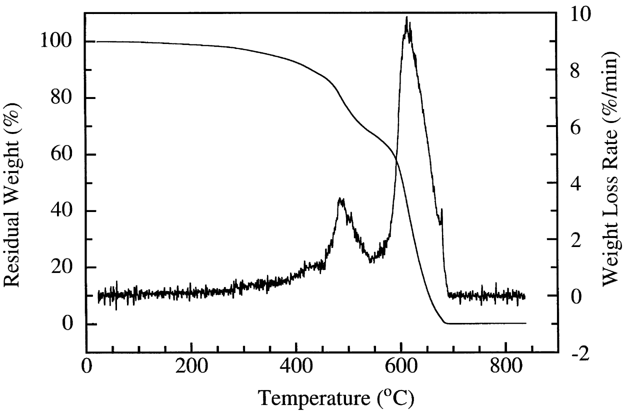


Fig. 10. TGA thermograms of 44O-a under oxidative environment.

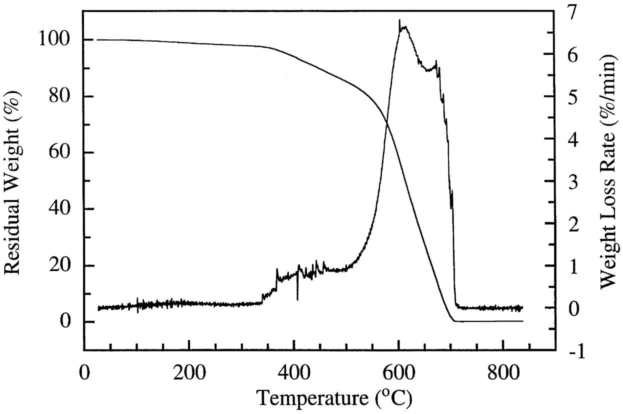


Fig. 11. TGA thermograms of 15N-a under oxidative environment.

The initial weight loss rates of these polybenzoxazines under oxidative environment is found to be lower than those under a nitrogen environment. However, it should be cautioned that weight gain due to oxidation process is possible. This weight gain could compensate for the weight loss process resulting in an appearance of low weight loss rate.

3.5. FTIR analysis of the evolved gases under oxidative degradation

FTIR spectra of the evolved gases under air are shown in Fig. 13 for BA-a. A major difference between thermal degradation and thermal oxidation is the high concentration of CO_2 from thermal oxidation. In BA-a, for example, CO_2 is detected at approximately 400°C. At approximately 600°C, CO_2 is almost exclusively the decomposition product. It is reminded here that this temperature corresponds to the temperature of char decomposition as seen in the TGA thermogram. Therefore, the char decomposes into CO_2 and possibly water. In 15N-a, the FTIR spectra of the evolved gases are overshadowed by the high concentration of CO_2. This is shown in Fig. 14.

Table 4
Residual weight of representative polybenzoxazines at various stages during the thermal oxidation under dry air environment

	400°C	500°C	600°C
BA-a	78%	54%	17%
22P-a	87%	72%	8%
44O-a	93%	77%	54%
15N-a	95%	87%	59%

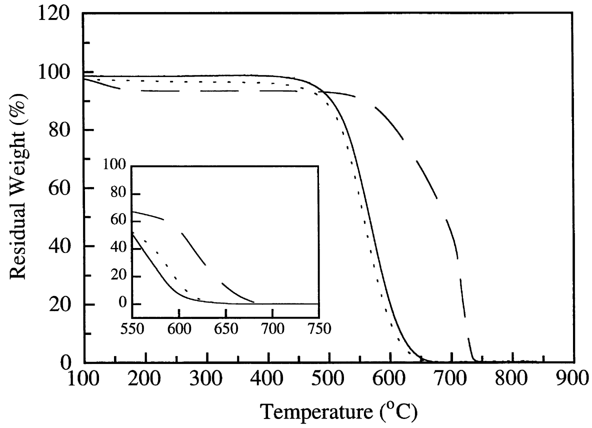


Fig. 12. TGA thermograms of the polybenzoxazine chars under oxidative environment. Char was obtained by degrading the polybenzoxazines under nitrogen environment. BA-a (· · ·), 22P-a (———), and 44O-a (- - -).

3.6. GC-MS analysis

The GC-MS results will be discussed separately for BA-a, 22P-a and 44O-a, so that correlation between the TGA derivative curves and the GC-MS results can be presented. The GC-MS results of the thermal oxidation products of these polybenzoxazines are shown in Table 5 and Table 6.

Previously, the temperature at which the initial degradation products were collected was determined from the TGA derivative curve. However, the TGA derivative curve of BA-a shows a broad peak between 250 and 500°C, and there is no distinction of an individual peak. Table 5 shows that various amines and phenols are detected up to 500°C. Therefore, in BA-a, the cleavage of both Mannich base and phenolic moiety occurs simultaneously. Although to a lesser extent, the overlapping of Mannich base cleavage and phenolic linkage degradation is also seen for the thermal degradation under an inert environment. Table 6 further shows that there are no additional degradation components detected for BA-a beyond 500°C. It should be reminded here that the major degradation product beyond 500°C is CO_2 as discussed in the FTIR analysis.

The thermal degradation of 22P-a under a nitrogen environment shows well-separated weight loss events. This behavior of 22P-a is also evident under oxidative degradation, as the TGA derivative curve of 22P-a shows three well-separated major weight loss events. Table 5 shows that only aniline is detected as the degradation product up to 400°C. This allows the assignment of the first weight loss event to amine evaporation. Beyond 400°C, additional amines and phenol are detected as shown in Table 6. Since the FTIR analysis has assigned the major peak at 600°C to char decomposition, the degradation products shown in Table 6 could be assigned to the second weight loss event in the TGA derivative curve. This peak extends from 400°C to approximately 520°C. During this period, both oxidative cleavage of the Mannich base and the phenolic linkage occur simultaneously. An interesting observation from this result is the detection of isocyanato-benzene at temperatures higher than 400°C, albeit a small amount. Isocyanato-benzene is also detected in BA-a for degradation up to 500°C. Combining these two observations, the isocyanato-benzene is released at temperatures beyond 400°C. The release of isocyanato-benzene is a consequence of oxidation of the Mannich base as will be seen later.

Since the derivative curve of 44O-a shows two well-separated peaks, the first collection of the degradation products was carried out at 550°C, which is the end of the first derivative peak. There is a broad shoulder that extends from approximately 250°C to the onset of the first derivative peak at 450°C. From the earlier discussion, this small shoulder could be assigned to amine evaporation. As shown in Table 5, various amines and phenols are detected for the first weight loss event. These degradation products are identical to those collected up to 800°C as seen in Table 6.

The degradation products for 15N-a under oxidative environment is also shown in Table 6. It is important to

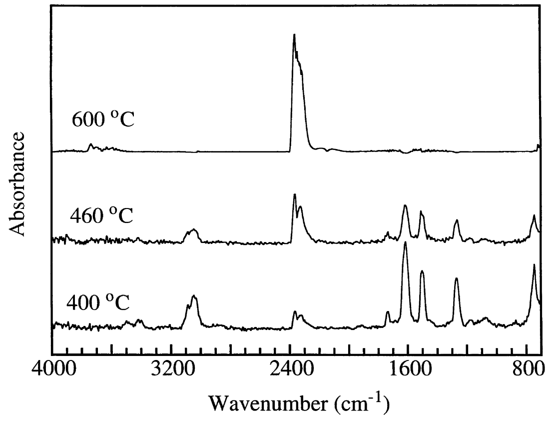


Fig. 13. FTIR spectra of the evolved gases from the thermal oxidation of BA-a.

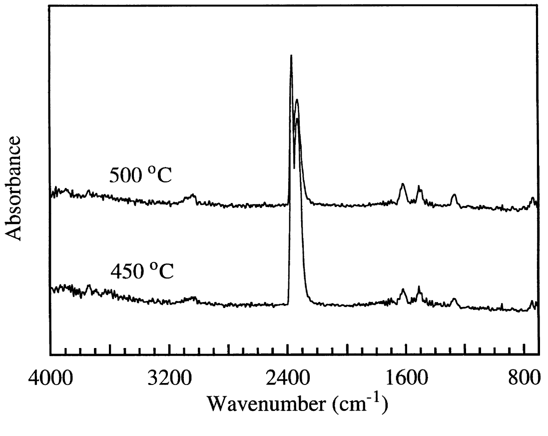


Fig. 14. FTIR spectra of the evolved gases from the thermal oxidation of 15N-a.

Table 5
GC-MS analysis of the initial thermo-oxidative degradation products of selected polybenzoxazines. Temperatures up to which these gases were collected are in parentheses

Retention time (min)	BA-a (500°C)	22P-a (400°C)	44O-a (550°C)
3.61	–	–	*p*-Xylene
4.93	Isocyato-benzene	–	Isocyanato-benzene
5.17	Phenol	–	Phenol
5.24	Aniline	Aniline	Aniline
6.51	2-Methylphenol	–	2-Methylphenol
6.83	*N*-methylaniline	–	*N*-methylaniline
6.87	–	–	4-Methylphenol
6.95	*p*-Aminotoluene	–	*p*-Aminotoluene
7.54	2,6-Dimethyphenol		

show that only simple phenol and amine are detected from the decomposition of 15N-a. This is due to the stabilizing effect of the fused benzene linkage of 1,5-naphthol. As shown in the FTIR analysis, the only major degradation product of 15N-a under oxidative environment is CO_2 even in the early stage of degradation.

From the above results, it is seen that fragmentation and possibly char formation of polybenzoxazines occur between 260°C and 600°C. In this temperature regime, the effects of the phenolic linkage are evident from the amount of residual weight and the different degradation behavior of the corresponding polybenzoxazine. However, it is important to point out that the type of amines released as a consequence of thermal oxidation is similar for these polybenzoxazines. These degradation components are very similar to the degradation under nitrogen environment except for a small amount of isocyanato-benzene.

As mentioned earlier the production of isocyanato-benzene is a result of the oxidation of the Mannich base. A proposed oxidation of the Mannich base is shown in Scheme 3. In the presence of intramolecular hydrogen bonding, the most likely site for oxygen attack is the methylene carbon that is not part of the six-membered ring (see Scheme 3). On the other hand, if the nitrogen of the Mannich base is not hydrogen bonded, then both the methylene carbons are equally likely to be attacked by the oxygen. However, there is no evidence of such reaction from the products of thermal oxidation. Therefore, in the absence of intramolecular hydrogen bonding, thermal cleavage of the Mannich base occurs as in the degradation under nitrogen. Both aniline and *n*-methylaniline are indeed detected from the thermal oxidation of polybenzoxazines.

4. Conclusions

The char yield of polybenzoxazines is found to be significantly affected by the various phenol linkages under an inert environment. However, the degradation mechanism of the Mannich base is consistent with all the polybenzoxazines studied. The analysis on the TGA derivative curves has allowed the distinction of the thermal degradation patterns of these polybenzoxazines. It is further found that the initial rate of weight loss is influenced by the phenolic structure. Under oxidative degradation, the effect of the various phenols is found to be significant below 600°C. A mechanism of the Mannich base cleavage under oxidative environment is proposed.

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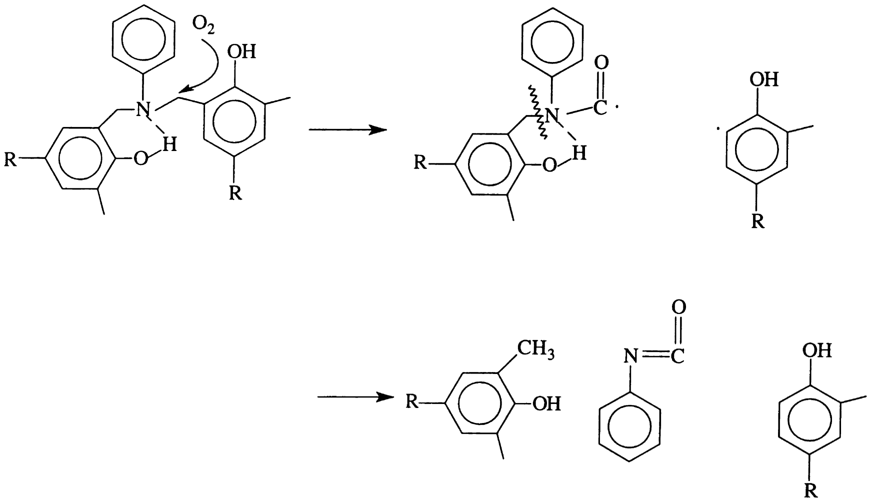
Table 6
GC-MS analysis from thermo-oxidative degradation of polybenzoxazines to 800°C. In parenthesis is the relative concentration of the compound

Retention time (min)	B-a	22P-a	44O-a	15N-a
3.61	–	–	*p*-Xylene (4%)	–
4.94	Isocyanato-benzene (1%)	Isocyanato-benzene (3%)	Isocyanato-benzene (1%)	–
5.17	Phenol (7%)	Phenol	Phenol (22%)	–
5.24	Aniline (56%)	Aniline (40%)	Aniline (22%)	Aniline (80%)
6.53	2-Methylphenol (8%)	–	2-Methylphenol (9%)	–
6.82	*N*-methylaniline (3%)	*N*-methylaniline (2%)	*N*-methylaniline	
6.88	–	–	4-Methylphenol	4-Methylphenol (3%)
6.95	*p*-Aminotoluene (3%)	*p*-Aminotoluene (2%)	*p*-Aminotoluene (4%)	*p*-Aminotoluene (2%)
7.53	2,6-Dimethylphenol (3%)	–	–	–



Scheme 3.

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