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Thermal decomposition processes in polybenzoxazine model dimers investigated by TGA–FTIR and GC–MS

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Abstract

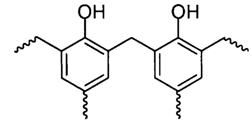
The thermal decomposition processes of a model compound containing Mannich bridge and a series of polybenzoxazine model dimers are investigated using TGA–FTIR and GC–MS. The 2,4-dimethylphenol-based benzoxazine dimers degraded into smaller and highly volatile compounds, leaving no char at the end of degradation. The *p*-cresol-based benzoxazine dimers degraded into smaller and highly volatile products as well, nevertheless some of which are able to undergo crosslinking and aromatization processes and form char. The major decomposition products for modified *p*-cresol-based dimers are amines and ester compounds.

Keywords: Benzoxazine; Polybenzoxazine; Thermal degradation; FTIR; GC–MS

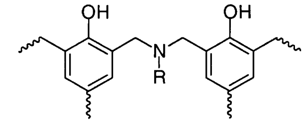
1. Introduction

Polybenzoxazines offer excellent thermal properties, including low flammability. Therefore, elucidating the mechanism of thermal degradation and further improving thermal properties of polybenzoxazines have been our major interests [1–3]. The previous works done in our group mainly focused on the effects of phenols, amines, and reactive functional groups on thermal stability of polybenzoxazines. Little is known on the structures of the decomposition products, nor has the solid evidence for the decomposition pathways been provided. Hence, it is the goal of this work to seek further fundamental insight into the subject, by identifying the structures of pyrolysis products and subsequently proposing the degradation mechanism.

In this study, the thermal decomposition is simplified by using a series of benzoxazine dimers as model compounds for polybenzoxazines. This method not only allows us to study the decomposition processes fundamentally and systematically, but also makes the study less complicated. The identification of degradation products formed during the thermal cleavage of these dimers will be used to illustrate the pathways of thermal decomposition of benzoxazines. In addition to the thermal decomposition processes, the transformation of the phenolic hydroxyl group is included in this study. The idea is similar to the studies of thermal stability of phenolic resins [4,5]. These studies have proven that, for phenolic resins, there is always oxidative degradation whether the atmosphere is inert or oxidative. This is due to the fact that the resin itself has a very high oxygen content. The studies also identified two specific species which are highly susceptible to oxidative degradation in phenolic resins. They are the methylene bridge and phenolic hydroxyl group. A proposed solution to the oxidative susceptibility of these weak points is to have oxidation resistant bonds. One way to make the phenolic hydroxyl groups oxidatively resistant is to apply chemical modification, such as etherification or esterification. Due to the similarity between the structure of phenolic resins and polybenzoxazines, the transformation of phenolic hydroxyl group is, therefore, expected to have some effects on thermal stability of polybenzoxazines.



Phenolic Resin



Polybenzoxazine

For phenolic resins, modification can easily be applied to starting materials, phenols, or to prepolymers. The

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modified phenols or prepolymers will then be polymerized to yield modified phenolic resins; however, the reactivity of phenolic ethers or esters towards formaldehyde is drastically decreased compared to phenols [5]. For polybenzoxazines, the nature of ring-opening makes it impossible to modify the phenols or the monomers prior to polymerization. The modification of the polymers, if desired, must be carried out during the polymerization, since the crosslinked polymers are insoluble and infusible. However, it is possible to modify benzoxazine oligomers, especially the dimers for our model study.

The study will begin with synthesis of a model compound containing a Mannich bridge. The structure of this model compound is similar to that of benzoxazine dimer, except that there is no hydroxyl group. Then a series of polybenzoxazine model dimers will be made. The phenolic hydroxyl group of the dimers will later be modified by esterification reaction. These compounds will be subjected to thermal degradation under inert environment. The mechanism for thermal decomposition of benzoxazine and modified benzoxazine dimers will be proposed according to the structures of the pyrolysis products.

2. Experimental

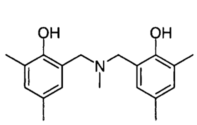
2.1. Starting materials

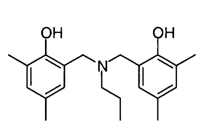
Benzyl bromide (Aldrich, 98%), methylamine (Aldrich, 40%), propylamine (Aldrich, 98%), cyclohexyl amine (Aldrich, 99%), formaldehyde (Aldrich, 37%), 2,4-dimethyl-phenol (Fluka, 99%), *p*-cresol (Aldrich, 99%), benzoyl chloride (Aldrich, 99%), and solvents were used without further purification.

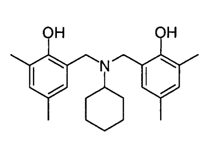
2.2. Synthesis of N,N-dibenzyl-methylamine

Methylamine (0.78 g, 0.01 mol) was added with stirring to a 20 ml solution of benzyl bromide (4.10 g, 0.02 mol) in diethyl ether. The reaction mixture was left at room temperature for about 30 min. To purify the product, the mixture was washed several times by 0.5 N NaOH solution and then rinsed with water. The solvent was then evaporated to yield a very pale yellow liquid product : ^{1}H NMR ($CDCl_3$) δ 7.38–7.23 (10, ArH), 3.51 (4, CH_2), 2.17 (3, CH_3); ^{13}C NMR ($CDCl_3$) δ 138–126 (12, Ar), 61 (2, CH_2), 41 (1, CH_3); MS, m/e 211 (M^+), 134 (M^+-C_6H_5), 120 (M^+-C_7H_7).

2.3. Synthesis of 2,4-dimethylphenol-based benzoxazine dimers

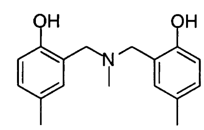

24DMP-m

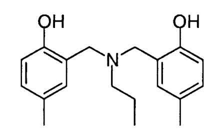

24DMP-p

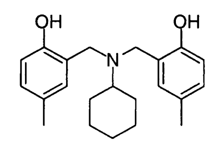

24DMP-c

2,4-Dimethylphenol-based benzoxazine dimers (**24DMP-m**, **24DMP-p**, and **24DMP-c**), were synthesized from the reaction between 2,4-dimethylphenol and 2,4-dimethylphenol-based benzoxazine monomer [6]. The monomer was synthesized from 2,4-dimethylphenol, primary amine (methylamine, propylamine, and cyclohexylamine), and formaldehyde according to the previous study [7,8]. The synthesis and characterization of *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-methylamine, *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-propylamine, and *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)-cyclohexylamine, were described in details in a previous study [9].

2.4. Synthesis of p-cresol-based benzoxazine dimers

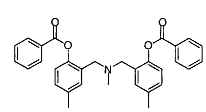

pC-m

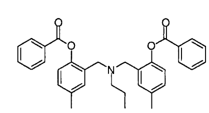

pC-p

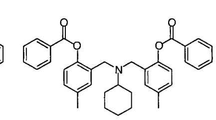

pC-c

The synthesis of *p*-cresol-based benzoxazine dimers (**pC-m**, **pC-p**, **pC-c**) was similar to that of 2,4-dimethylphenol-based benzoxazine dimers. The details of the synthesis and characterization of *N,N*-bis(2-hydroxy-5-methylbenzyl)-methylamine, *N,N*-bis(2-hydroxy-5-methyl benzyl)-propylamine, and *N,N*-bis(2-hydroxy-5-methylbenzyl)-cyclohexylamine were described in the previous study [9].

2.5. Synthesis of modified p-cresol-based benzoxazine dimers


pC-m-B


pC-p-B


pC-c-B

Modified *p*-cresol-based benzoxazine dimers (**pC-m-B, pC-p-B, pC-c-B**), were synthesized from the esterification of *p*-cresol-based benzoxazine dimers with benzoyl chloride. The details of the synthesis and characterization of *N,N*-bis(2-benzoate-5-methylbenzyl)-methylamine, *N,N*-bis(2-benzoate-5-methylbenzyl)-propylamine, and *N,N*-bis(2-benzoate-5-methylbenzyl)-cyclohexyl amine can be found in the previous study [9].

2.6. Characterization

A thermogravimetric analyzer (TGA) from TA Instruments, High Res TGA 2950, was used for thermogravimetric analysis. Thermal degradation experiments were done under nitrogen purge. The flow rate used for all experiments was 90 ml/min. A heating rate of 10 °C/min from ambient temperature to 820 °C was used.

For the TGA–FTIR study, the TGA was interfaced with Bio-Rad Fourier transform infrared (FTIR) spectrometer using Bio-Rad/TGA interface, equipped with a deuterated triglycine sulfide (DTGS) detector. The temperatures of the transfer line and gas cell were both set at 300 °C. Spectra were collected with 4 scans co-added at a resolution of 8 cm^{-1}, resulting in a time resolution of 1 s.

Evolved gas analysis (EGA) was carried out by passing the gases evolved from the TGA furnace through a HPLC grade chloroform. The gases were trapped in the chloroform and the solution was injected into a gas chromatograph coupled with a mass spectrometer (GC–MS.) The GC–MS used was a Hewlett-Packard 6890 gas chromatograph coupled with the 5973 mass selective detector. The GC column used was a capillary column coated with nonbonded 5% phenyl–methyl siloxane. The injection port of the GC was set at 250 °C, while the GC column was programmed from 70 to 250 °C at a heating rate of 5 °C/min. The ionization energy is set at 70 eV. Helium is used as a carrier gas for the GC–MS. When the solvent comes off the GC column and hits the MS detector, the concentration of the solvent can be so high that it can destroy the detector gradually, if not immediately. To prevent this from happening, the detector is programmed to be turned off during the time when the solvent hits the detector. As a result, the detection of the compounds that come 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 Daltons. The assignments are confirmed by either consulting the references [10–12], using the model compounds available or synthesized in our laboratory, or searching the NIST MS library software, Nbs75k.

3. Results and discussion

3.1. Thermal degradation of model compound (N,N-dibenzyl-methylamine)

The model compound is used in this study to represent a molecule with the Mannich bridge in the structure, but without any hydroxyl groups. The TGA thermogram of the model compound in N_2 is shown in Fig. 1. The weight loss of the model dimer without phenolic hydroxyl groups started at about 100 °C. The rate of weight loss reached maximum at approximately 180 °C. After that, the rate of weight loss quickly dropped to zero, and at 200 °C there was nothing left. The infrared spectrum of the gases evolved from degradation in N_2 is shown in Fig. 2. The results from EGA are tabulated in Table 1 for degradation in N_2. The result shows that 97% of the model compound evaporated before it decomposed. Only 3% of the model compound decomposed by the cleavage of the C–N bond.

The model compound did not yield any char residue. This can be explained from the fact that the model compound is a small molecule without any strong intermolecular interactions, such as hydrogen bonding. As a consequence, the boiling point of the model compound is so low that, when exposed to high temperature, it

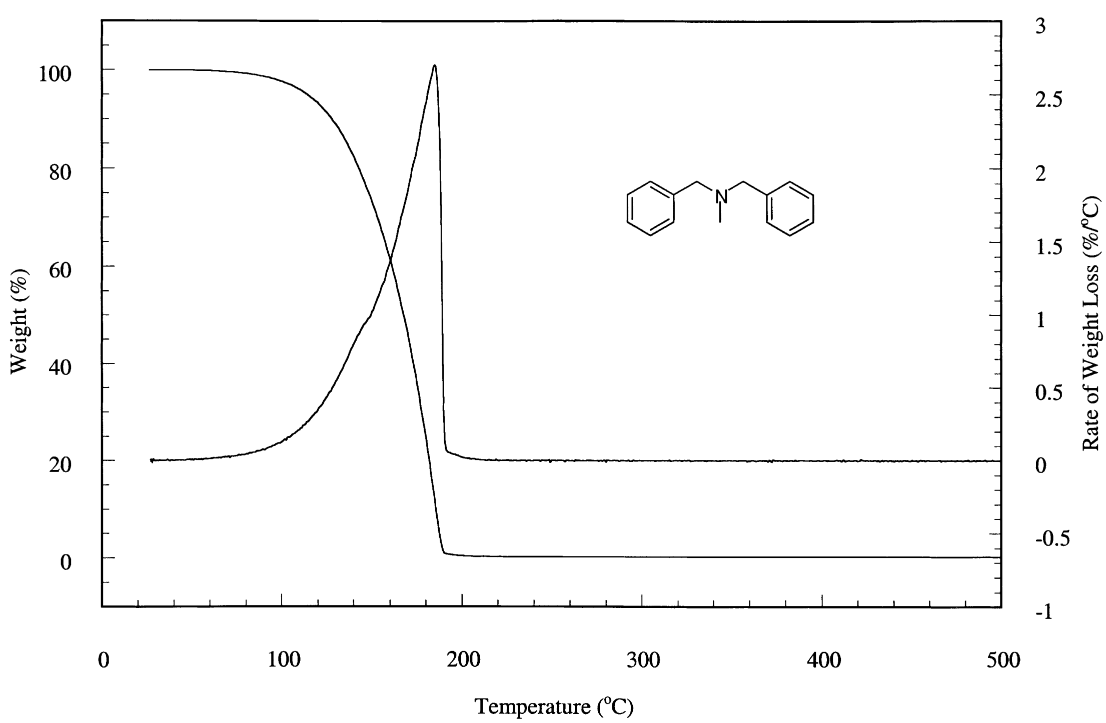


Fig. 1. TGA thermograms of *N,N*-dibenzyl-methylamine in nitrogen.

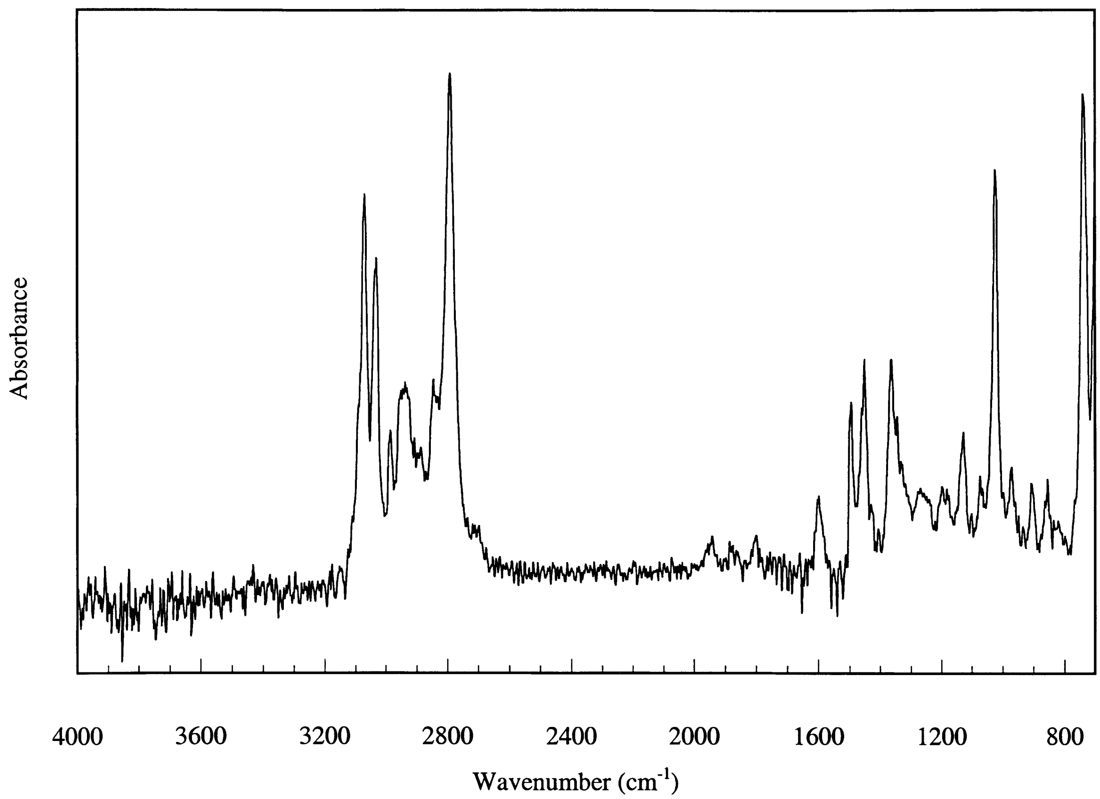
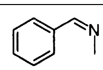
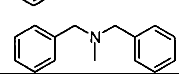


Fig. 2. FTIR spectra of gases evolved (taken at 185 °C) from the degradation of *N,N*-dibenzyl-methylamine in nitrogen.

Table 1
EGA from the degradation of N,N-dibenzyl-methylamine in nitrogen

Retention time (min)	Molecular structure	Molecular weight	Percentage
6.61		119	3%
22.15		211	97%

reached its boiling point and evaporated before it could degrade.

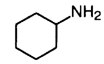
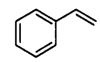
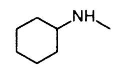
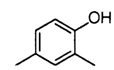
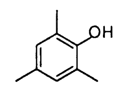
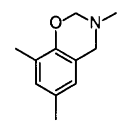
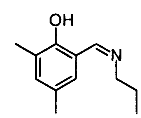
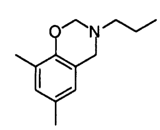
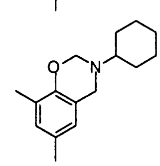
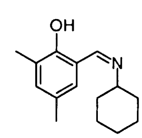
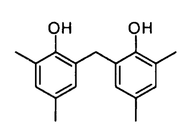
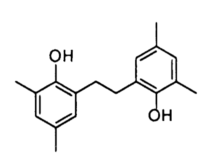
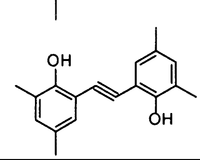
3.2. Thermal degradation of 2,4-dimethylphenol-based benzoxazine dimers

The TGA thermograms of 2,4-dimethylphenol-based dimers in nitrogen are displayed in Fig. 3. The onset of degradation was found at about 160 °C. The thermograms show a highly overlapped two-stage weight loss process, the first one at about 230 °C and the second one at 260 °C. The dimers completely decomposed before 350 °C. Fig. 4 shows the infrared spectrum (taken at 230 °C) of gases evolved from the degradation of **24DMP-m** in N_2. The spectrum shows the presence of a Schiff base, as seen from the sharp band at 1640 cm^{-1} for the C=N stretching vibration. This band is not present in the FTIR spectra of the pure dimers.

The degradation products were identified by GC–MS. The result from the GC–MS analysis of the gases evolved from 2,4-dimethylphenol-based benzoxazine dimers is shown in Table 2. The results indicate that the dimers disintegrated into amines, phenolic compounds, monomers, Schiff bases, and bisphenol compounds. From these results, the mechanism for thermal decomposition of 2,4-dimethylphenol-based benzoxazine dimers has been proposed, as shown in Fig. 5. There are two different fragmentation processes which are happening simultaneously during the decomposition of 2,4-dimethylphenol-based benzoxazine dimers. The first one is the cleavage of the C–N bond, which results in the formation of a Schiff base and 2,4,6-trimethylphenol. The presence of the Schiff base is also obvious from the FTIR result mentioned previously. The second fragmentation process is the cleavage of the C–C bond, resulting in the formation of a 2,4-dimethylphenol-based benzoxazine monomer and 2,4-dimethylphenol.

The reformation of the monomer was confirmed by running the GC–MS of the pure benzoxazine monomer. The result from the pure monomer showed exactly the same retention time and fragmentation pattern. The reformation of the monomer is illustrated graphically in Fig. 6. There is solid evidence showing that benzoxazine dimers posses strong intramolecular hydrogen bonding between the proton of the hydroxyl group and the nitrogen of the Mannich bridge [13,14]. The hydrogen

Table 2
EGA from the degradation of 2,4-dimethylphenol-based benzoxazine dimers in nitrogen

Retention time (min)	Molecular weight	Structure	**24DMP-m**	**24DMP-p**	**24DMP-c**
3.30	99				11%
3.62	104				15%
4.33	113				< 1%
9.01	122		7%	< 1%	< 1%
10.45	136		7%	5%	4%
16.07	177		52%		
19.92	191			17%	
20.02	205			41%	
27.85	245				8%
28.00	231				21%
32.40	256		10%	14%	29%
33.20	270		22%	21%	11%
34.86	266		< 1%	<1%	< 1%

bonding leads to the formation of a six-membered ring. When the dimer degrades, the breaking of C–C bond results in 2,4-dimethylphenol radical and tertiary amine radical. The 2,4-dimethyl radical couples with hydrogen radicals and becomes 2,4-dimethylphenol. For the tertiary amine radical, the nature of hydrogen bonding makes the hydrogen atom transferable between the oxygen atom and the nitrogen atom. At some point,

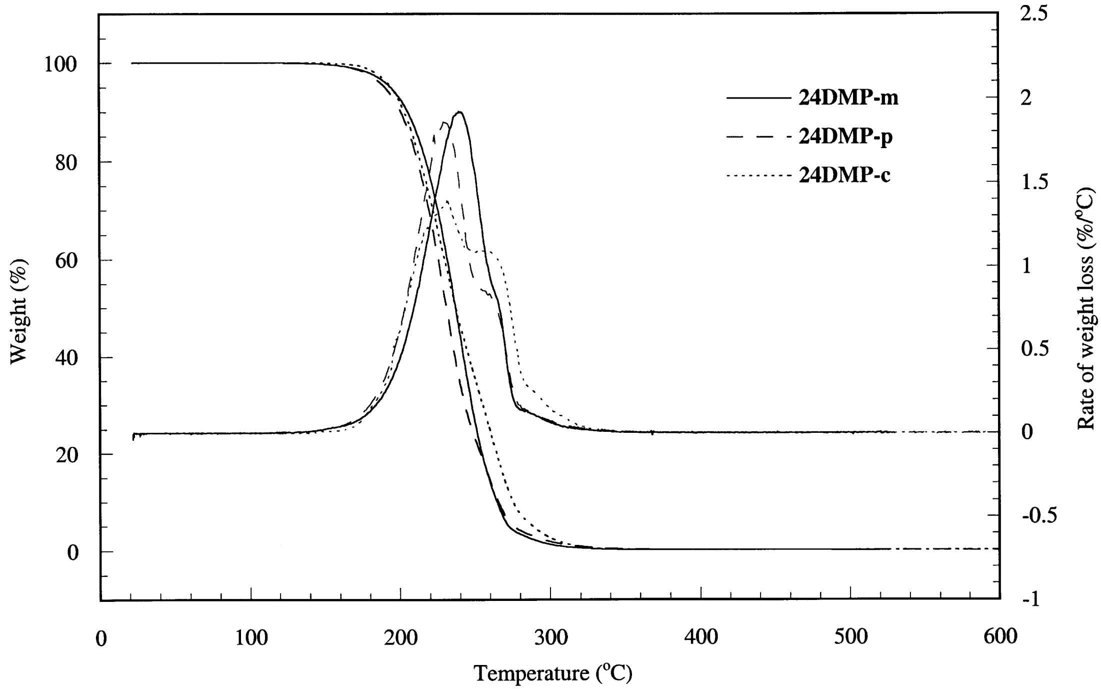


Fig. 3. TGA thermograms of 2,4-dimethylphenol-based benzoxazine dimers in nitrogen.

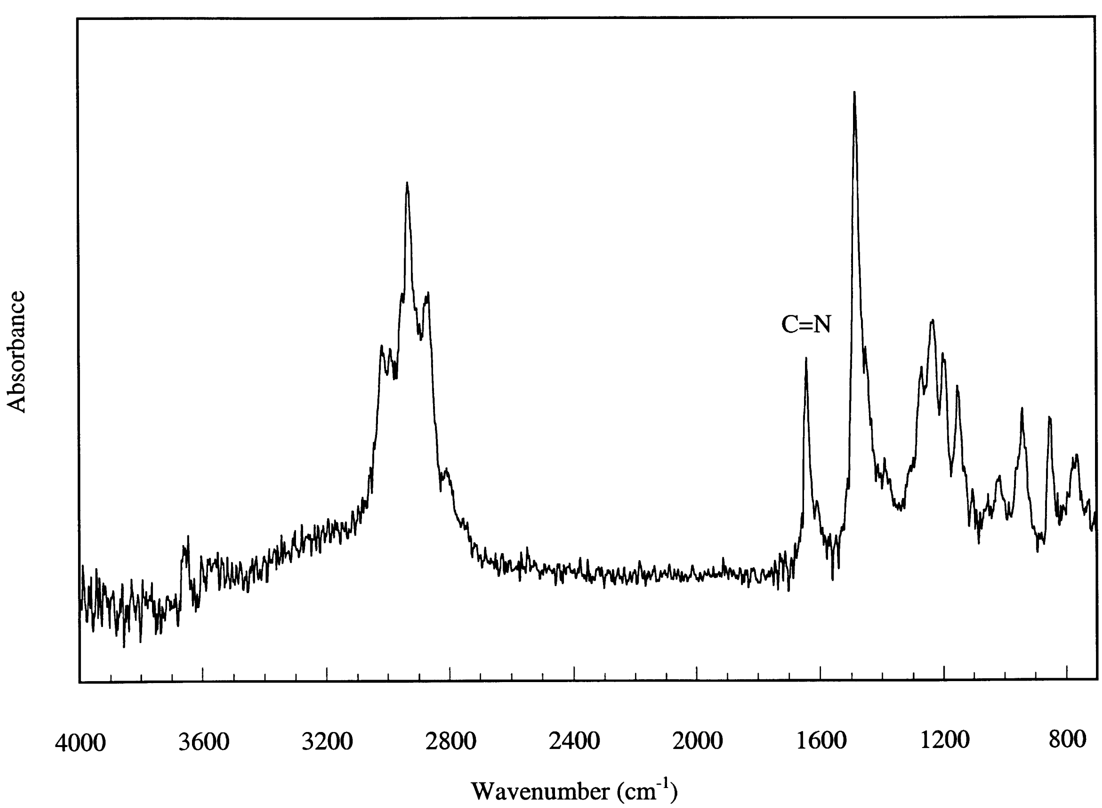


Fig. 4. FTIR spectra of gases evolved (taken at 230 °C) from the degradation of 24DMP-m in nitrogen.

when hydrogen is transferred to nitrogen, the free rotation of the C–N bond makes it possible for the oxygen radical to combine with the methylene radical. As a result, the monomer is formed. At the present time, it is not clear whether or not the monomer formation takes place in the gas phase or in the trapping solvent. The monomer and the Schiff base can then degrade further to yield primary amine, secondary amines, 2,4-dimethyl

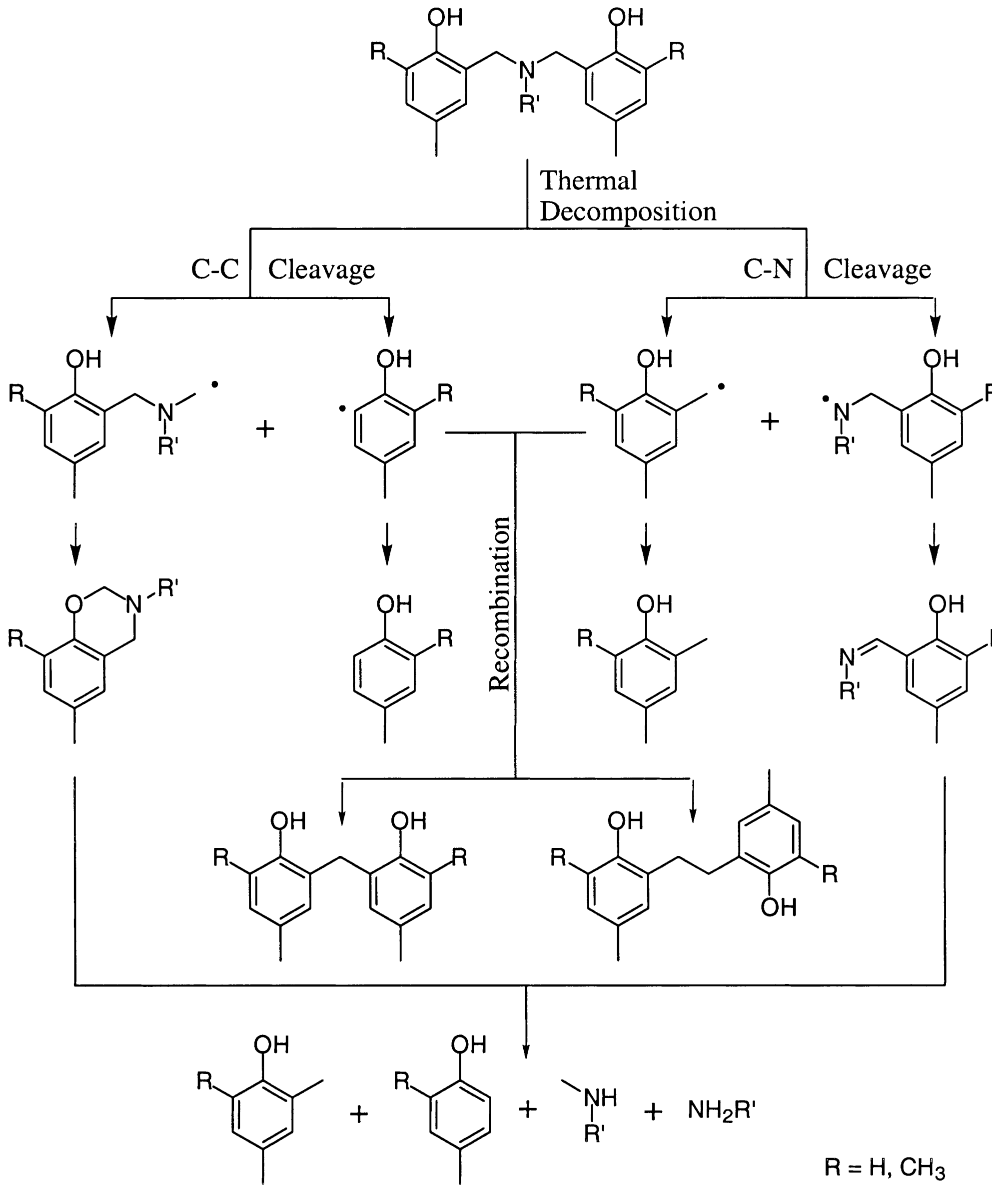


Fig. 5. Proposed mechanism for thermal degradation of benzoxazine dimers.

phenol, and 2,4,6-trimethylphenol. In addition, the 2,4,6-trimethylphenol radicals can combine with themselves or with 2,4-dimethylphenol radicals to form bisphenol compounds as shown in Fig. 5. Note that all the bisphenol compounds formed are occupied at positions *ortho* and *para* to the hydroxyl group.

The GC–MS results from Table 2 also reveal that amine has an effect on the thermal decomposition pattern of the dimers. The percentage of the monomer as one of the degradation products decreases with the increasing size of amines, i.e. 52, 41, and 8% for **24DMP-m**, **24DMP-p**, and **24DMP-c**, respectively. While the percentage of the Schiff base as one of the degradation products increase with increasing size of amines, i.e. 0, 17, and 21% for **24DMP-m**, **24DMP-p**, and **24DMP-c**, respectively. In other words, the small amine tends to undergo C–C cleavage and form monomer, while the large amine tends to undergo C–N cleavage and form a Schiff base. Therefore, the size of the amines plays an important role on how the benzoxazine dimers degrade. It should be noted that small amines such as methylamine and propylamine cannot be detected because they come out at the same time as the solvent, and that is when the detector was turned off.

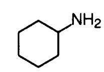
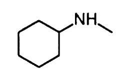
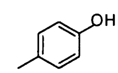
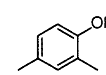
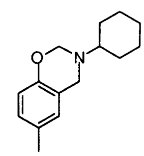
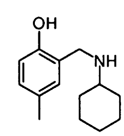
Like *N,N*-dibenzyl-methylamine, the 2,4-dimethylphenol-based dimers gave 0% of char residue at 800 °C. However, unlike *N,N*-dibenzyl-methylamine, these dimers did not simply evaporate during the thermal analysis. In fact, the results from EGA showed that the dimers underwent thermal degradation with no trace of the original dimers. However, this does not mean that evaporation did not occur. When the pure original dimers were injected into GC, the mass selective detector could not detect the presence of the dimers. The hydrogen bonding may be sufficiently strong such that the intact dimers are not volatile enough to go through the GC column and thus could not be detected by GC–MS. The decomposition products formed during the degradation of the 2,4-dimethylphenol-based dimers are small, highly volatile molecules that completely evaporated by 350 °C.

3.3. *Thermal degradation of* p-*cresol-based benzoxazine dimers*

The decomposition behavior of *p*-cresol-based benzoxazine dimers in N_2 is displayed in Fig. 7. It is obvious that the decomposition pattern of *p*-cresol-based benzo xazine dimers is different from that of 2,4-dimethylphenol-based benzoxazine dimers. The latter showed an overlapped two-stage weight loss process, and all the dimers completely decomposed before 350 °C. Instead, *p*-cresol-based benzoxazine dimers showed a well-separated two-stage weight loss process, and all the dimers gave approximately 15% of char yield at 800 °C. The dimers started losing weight at about 160 °C. The rate of weight loss reached a maximum at approximately 200 °C, then slowed and stopped before the temperature reached 300 °C. The first stage of degradation resulted in 40% weight loss. The onset of the second stage of degradation was observed at 320 °C. This process resulted in another 45% of weight loss. The evolved gases collected from the degradation of **pC-p** were detected by FTIR and the result is shown in Fig. 8. The spectrum taken at 180 °C shows only the presence of aliphatic compounds, while that taken at 370 °C starts showing the presence of aromatic compounds. The reason for this will be explained later.

In order to identify the decomposition products of each degradation process by EGA, two additional TGA experiments were performed. To identify the decomposition products from the first stage of degradation,

Table 3
EGA from the degradation of **pC-c** in nitrogen (up to 250 °C)

Retention time (min)	Molecular structure	Molecular weight	Percentage
3.19		99	94%
4.28		113	3%
7.20		108	2%
9.04		122	< 1%
26.65		231	< 1%
27.26		219	< 1%

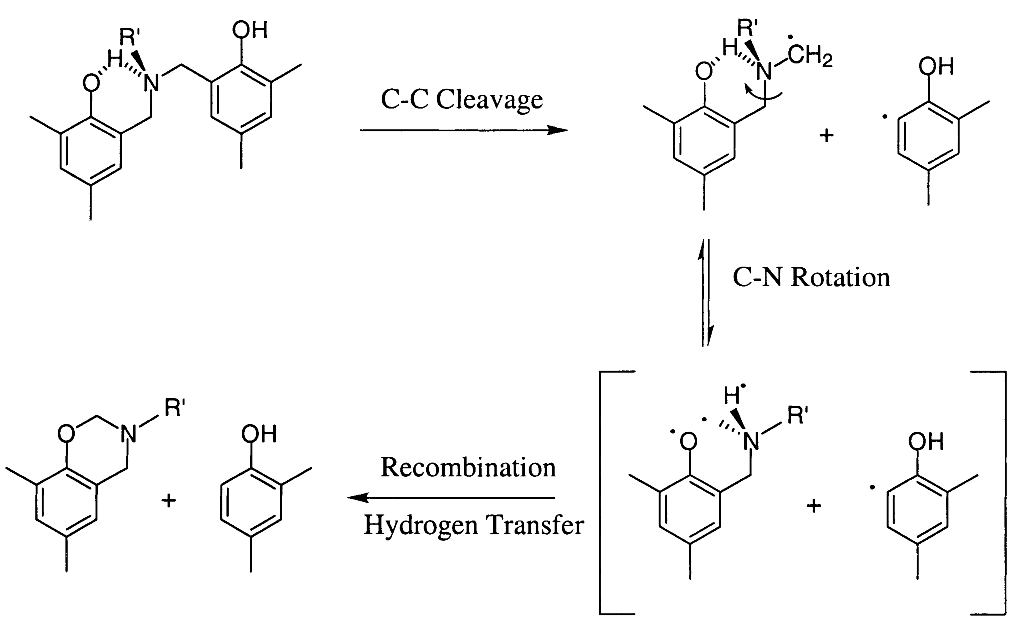


Fig. 6. Proposed mechanism for the reformation of 2,4-dimethylphenol-based benzoxazine monomer.

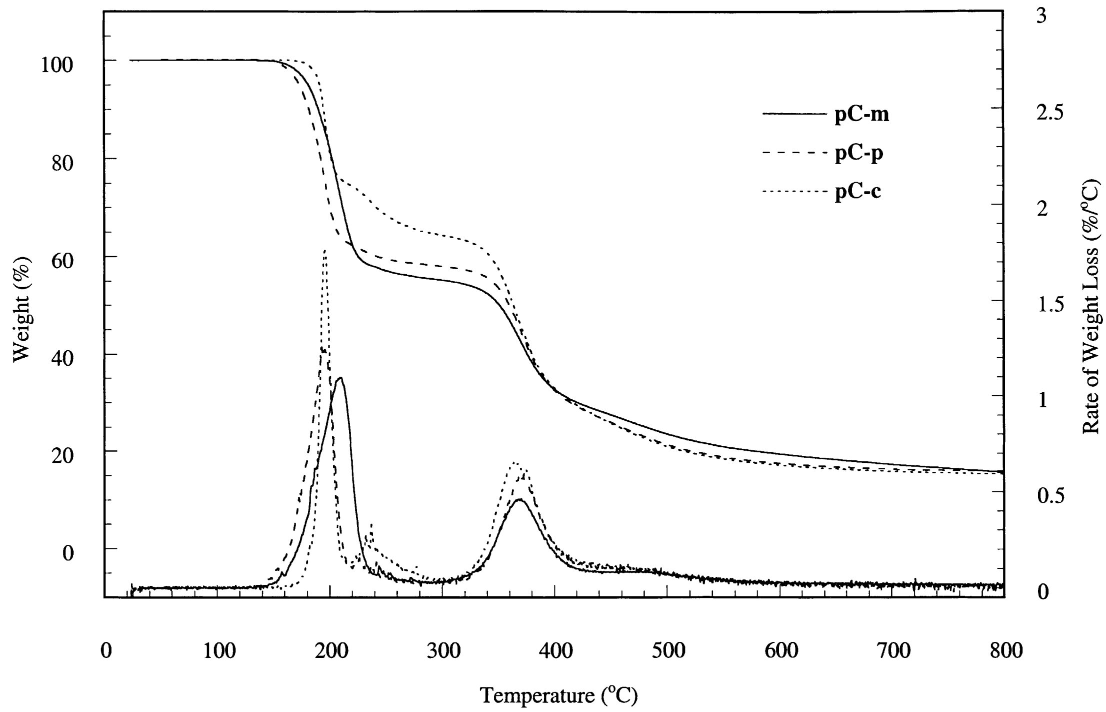


Fig. 7. TGA thermograms of *p*-cresol-based benzoxazine dimers in nitrogen.

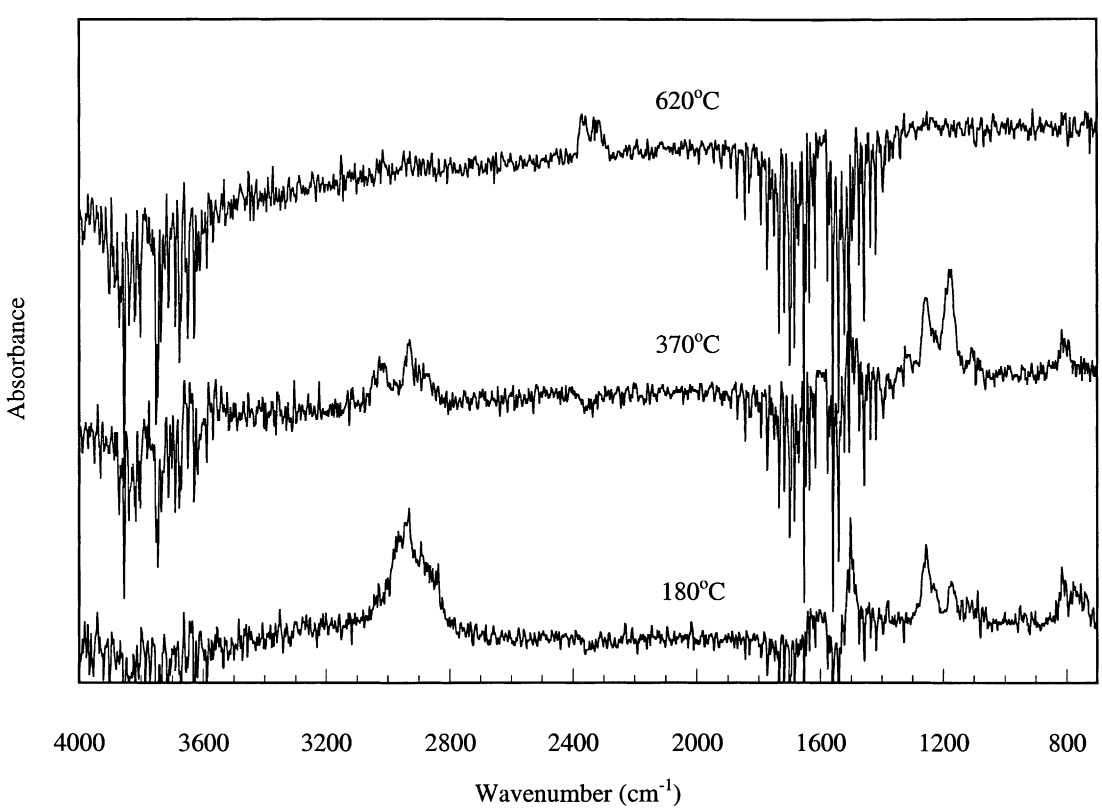
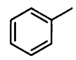
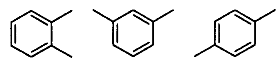
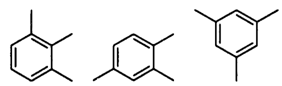
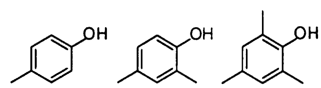
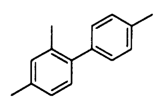
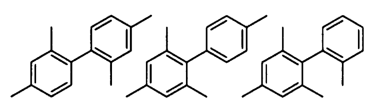
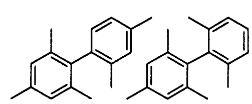
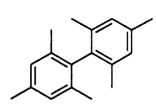
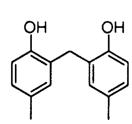
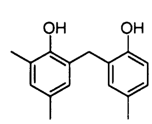
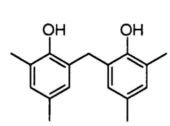
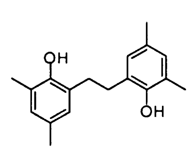
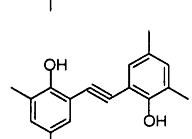


Fig. 8. FTIR spectra of gases evolved from the degradation of **pC-p** in nitrogen.

Table 4
EGA from the degradation of **pC-c** after heat treatment at 250 °C for 1 h

Retention time (min)	Molecule structure	Molecular weight	Percentage
2.44		92	< 1%
3.26, 3.36 and 3.68		106	10%
4.94, 5.50 and 6.10		120	6%
7.18, 9.00 and 10.45		108, 122 and 136	12, 14 and 5%
24.04		196	< 1%
25.61, 25.73 and 26.41		210	2%
27.72 and 27.92		224	7%
29.81		238	5%
31.02		228	13%
31.79		242	18%
32.39		256	4%
33.22		270	< 1%
34.85		266	< 1%

the first TGA experiment was run from room temperature to 250 °C. The temperature was then kept isothermal at 250 °C for 1 h. Only the results from the **pC-c** dimer are presented here, since it is the only dimer whose primary amine can be detected by GC–MS. The EGA from the degradation of **pC-c** from room temperature to 250 °C is presented in Table 3. It is obvious that the major decomposition product is cyclohexyl amine which occupies 94% of the total. Therefore, what happened during the first stage of weight loss for *p*-cresol-based benzoxazine dimers is obviously the evaporation of amines. This is confirmed by the presence of aliphatic compounds from the gases evolved detected by FTIR at 180 °C, as previously mentioned.

To identify the decomposition products during the second stage of weight loss, the second TGA was run from the samples left after the isothermal experiment at 250 °C for 1 h. The evolved gases were collected and analyzed by GC–MS, and the result is shown in Table 4. The EGA shows that the decomposition products are toluene, dimethylbenzenes, trimethylbenzenes, phenols, biphenyl, and bisphenol compounds. Amines were not detected, which confirms that they evaporated during the first decomposition process.

From the EGA result, the mechanism for the degradation of *p*-cresol-based benzoxazine dimers is proposed. The dimers decomposed the same way as the 2,4-dimethylphenol-based dimers, with competitive cleavage of

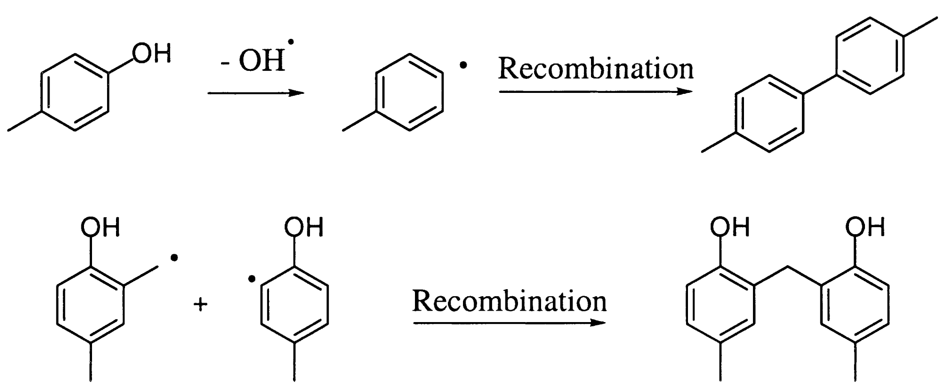


Fig. 9. Formation of biphenyl and bisphenol compounds during the decomposition of *p*-cresol-based benzoxazine dimers.

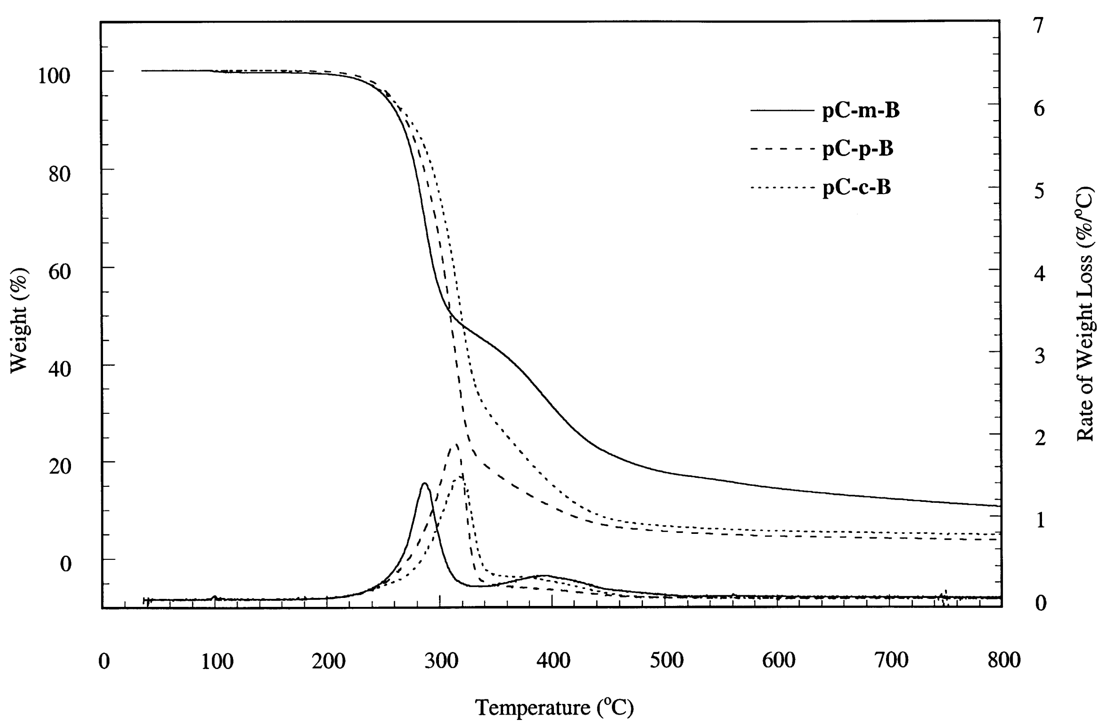
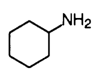
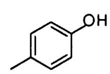
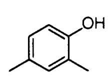
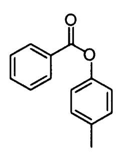
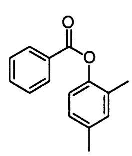
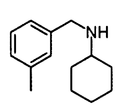
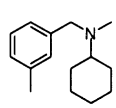
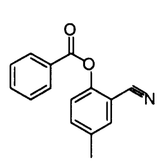
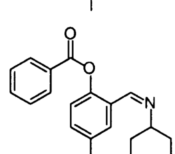


Fig. 10. TGA thermograms of modified *p*-cresol-based benzoxazine dimers in nitrogen.

the C–N and C–C bonds as shown in Fig. 5. The cleavage of the C–N bond brings about the formation of a Schiff base and 2,4-dimethylphenol. The cleavage of the C–C bond leads to the formation of *p*-cresol-based benzoxazine monomer and *p*-cresol. The Schiff base and the monomer can degrade further to yield amines and phenols. The primary amine is highly volatile, and is the first thing that evaporated. After the evaporation of amines, phenols and their radicals remain which may couple with each other to form bisphenol compounds as shown in Fig. 9. In addition to this, the phenols themselves can lose hydroxyl radicals and combine with each other and, hence, form biphenyl compounds. However, this is not the end of decomposition, since about 15% of char was observed at 800 °C.

In the case of 2,4-dimethylphenol-based benzoxazine dimers, all three dimers completely decomposed before 350 °C. But for *p*-cresol-based benzoxazine dimers, each lost approximately 40% of its weight by 300 °C with a final char yield of about 15% at 800 °C. The only obvious reason that can be used to explain this major difference is the absence of the methyl groups at ortho positions in *p*-cresol-based benzoxazine dimers. As seen in Fig. 9, biphenyl and bisphenol compounds are substituent-free at one or both of the ortho-positions. The lack of a substituent at the ortho position makes it possible for

Table 5
EGA from the degradation of **pC-c-B** in nitrogen

Retention time (min)	Molecular structure	Molecular weight	Percentage
3.40		99	< 1%
7.21		108	< 1%
9.00		122	3%
24.15		212	2%
25.50		226	29%
26.31		203	50%
26.50		217	11%
29.81		237	2%
38.56		321	1%

biphenyl and bisphenol compounds, which were formed during the decomposition, to undergo post condensation and crosslinking. These reactions finally lead to the formation of char.

Unlike *N,N*-dibenzyl-methylamine and 2,4-dimethylphenol-based dimers, *p*-cresol-based dimers gave 15% of char residue in N_2 at 800 °C. The reason for this is the presence of an unblocked *ortho* position and a hydroxyl group. The H atoms make the *ortho* position a reactive site for compounds formed during degradation to couple with each other and thereby form larger molecules which are more resistant to increased temperature. It has been reported that hydroxyls and halogens are reactive dehydrogenating groups [15]. These groups are capable of reacting with hydrogen atoms and, therefore, lead to crosslinking. This is the reason why polymers containing hydroxyl groups (or halogens), such as cellulose and poly(vinyl alcohol), tend to give a small char residue [15]. This also seems to be the case for p-cresol-based benzoxazine dimers.

3.4. *Thermal degradation of modified* p-*cresol-based benzoxazine dimers*

The thermal degradation of esterified benzoxazine dimers in nitrogen is shown in Fig. 10. All the dimers show a two-stage weight loss process. The major process is centered at about 220 °C, and reached maximum rate of weight loss near 300 °C, before stopping at 320 °C. Notice that the onset of decomposition shifted to 240 °C, compared to 160 °C for 2,4-dimethylphenol-based and *p*-cresol-based benzoxazine dimers. The second degradation started almost immediately following the first process, with a much slower rate of weight loss. The FTIR spectra of the evolved gases of **pC-p-B** are presented in Fig. 11 and the EGA of **pC-c-B** by GC–MS is tabulated in Table 5. The GC-MS indicated that the major decomposition products are not primary amine nor phenols, but rather secondary amine and ester compounds. Therefore, the mechanism for thermal decomposition of benzoyl chloride modified benzoxazine dimers is proposed and is illustrated in Fig. 12. It is proposed that, in addition to C–N and C–C cleavages, the cleavage of C–O is another pathway for the decomposition of the modified benzoxazine dimers. The driving force for the cleavage of C–O bond is the product stability caused by resonance delocalization. It is the breaking of the C-O bond that results in the formation of aromatic secondary and tertiary amines instead of aliphatic primary amines. This can be used to explain the shift of the onset of degradation of modified dimers, compared to that of the unmodified dimers. However, regardless of the fact that the modified *p*-cresol-based benzoxazine dimers decompose at a higher temperature,

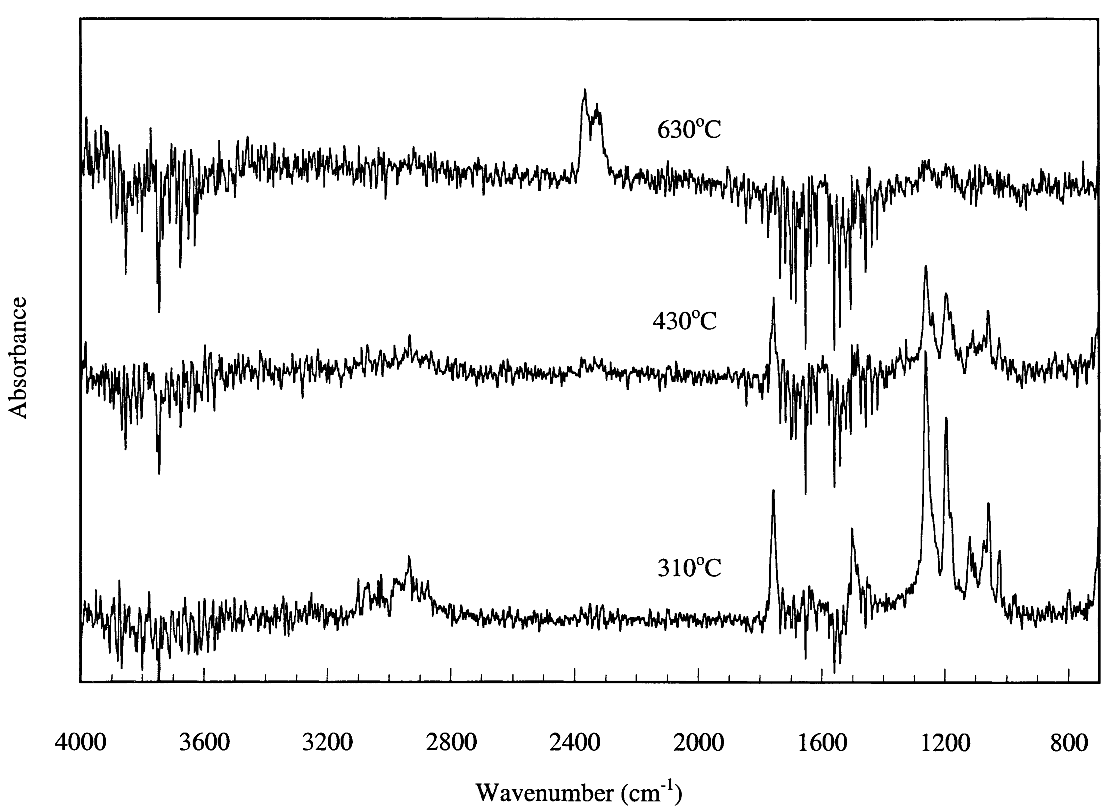


Fig. 11. FTIR spectra of gases evolved from degradation of **pC-p-B** in nitrogen.

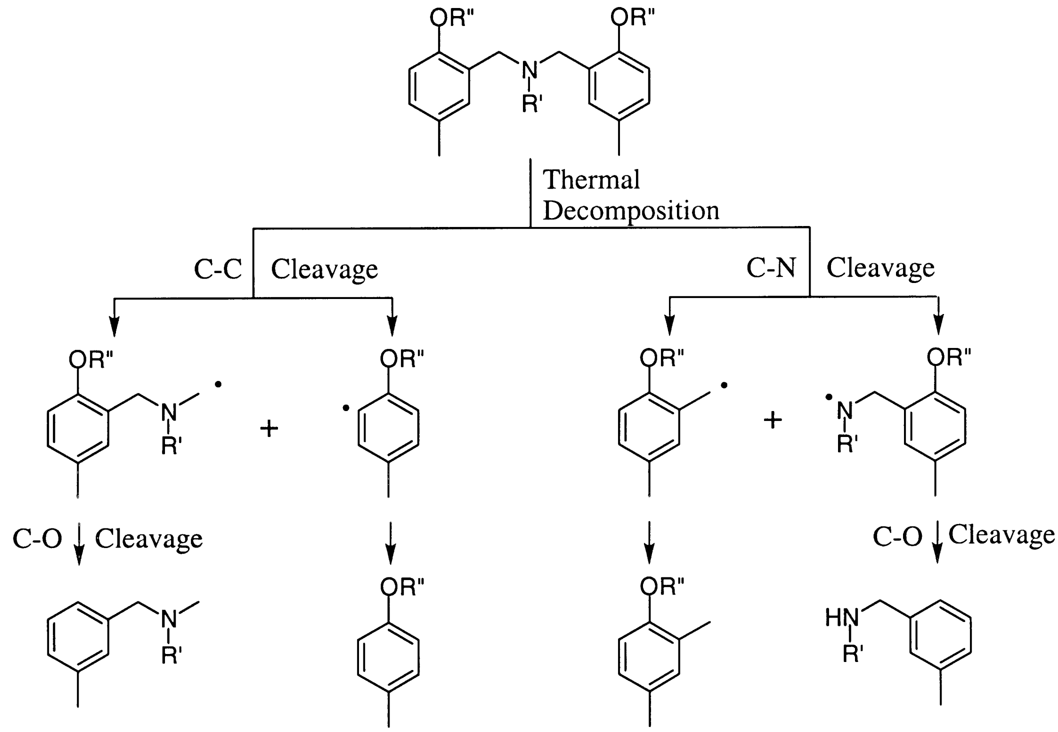


Fig. 12. Proposed mechanism for thermal degradation of the modified *p*-cresol-based benzoxazine dimers (R'' = benzoyl).

each of these dimers gave less char yield than *p*-cresol-based benzoxazine dimers. The reason that can be used to explain this difference is the type of products formed during the decomposition. The major decomposition products for *p*-cresol-based benzoxazine dimers are phenol and bisphenol compounds, while those of modified *p*-cresol-based dimers are amines and ester compounds. The presence of hydroxyl groups makes it possible for phenol and bisphenol compounds to undergo crosslinking and thus form char [15]. In contrast, the amine and ester compounds are not capable of crosslinking, but are likely to disproportionate into volatile substances.

4. Conclusions

A model compound containing a Mannich bridge and a series of polybenzoxazine model dimers have been synthesized. The TGA, TGA–FTIR interface, and TGA–GC–MS were used to study the thermal degradation of the dimers. The majority of the model dimer compounds, which contain Mannich bridges but have no phenolic hydroxyl groups, simply evaporated when exposed to high temperature. For the benzoxazine dimers, there are two different fragmentation processes, the cleavage of C–N and C–C bonds, occurring simultaneously during the thermal decomposition. Both fragmentations result in the evaporation of the amines. The radicals left after the evaporation of amines can combine with each other to form bisphenol and biphenyl compounds. The presence or absence of a substituent at the ortho position to hydroxyl group makes a significant difference in terms of the decomposition pattern and the char formation of the dimer. The unblocked ortho position makes it possible for the radicals to undergo aromatization and crosslinking processes which will finally lead to the formation of char. For the modified benzoxazine dimers, in addition to the cleavages of C–N and C–C bonds, the breaking of the C–O bond was found to be another possible fragmentation during the thermal decomposition. As a result, secondary and tertiary amines were formed, instead of primary amines. This leads to a shift of the onset of degradation to higher temperatures compared to those of the unmodified benzoxazine dimers.

Acknowledgements

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References

[1] Kim HJ, Brunovska Z, Ishida H. Molecular characterization of the polymerization of acetylene-functional benzoxazine resins. Polymer 1999;40:1815–22.

[2] Low H, Ishida H. Structural effects of phenols on the thermal and thremo-oxidative degradation of polybenzoxazines. Polymer 1999;40:4365–76.

[3] Low H, Ishida H. An investigation of the thermal and thermo-oxidative degradation of polybenzoxazines with a reactive functional group. J Polym Sci Part B 1999;37:647–59.

[4] Conley RT, editor, Thermal stability of polymers. New York: Marcel Dekker; 1970.

[5] Knop A, Pilato LA, editors. Phenolic resins : chemistry, applications and performance. Berlin: Springer-Verlag; 1985.

[6] Ishida H, Krus CM. Synthesis and characterization of structurally uniform model oligomers of polybenzoxazine. Macromolecules 1998;31:2409–18.

[7] Ning X, Ishida H. Phenolic materials via ring-opening polymerization: synthesis and characterization of bisphenol-A based benzoxazines and their polymers. J Polym Sci Part A 1994;32: 1121–9.

[8] Ning X, Ishida H. Phenolic materials via ring-opening polymerization of benzoxazines: effect of molecular structure on mehanical and dynamic mechanical properties. J Polym Sci Part B 1994;32:921–7.

[9] Laobuthee A, Chirachanchai S, Ishida H. (in press).

[10] Silverstein RM, Bassler GC, Morrill TC, editors, Spectrometric identification of organic compounds. New York: John Wiley & Sons; 1981.

[11] McLafferty FW, Turecek F, editors. Interpretation of mass spectra. California: University Science Books; 1993.

[12] Heller SR, Milne GWA. EPA/NIH Mass spectral data base, NSR DS-NB S 63. Washington: US Department of Commerce, National Bureau of Standards, US Government Printing Office, 1978.

[13] Dunkers J, Zarate EA, Ishida H. Crystal structure and hydrogen-bonding characteristics of *N,N*-Bis(3,5-dimethyl-2-hydroxybenzyl) methylamine, a benzoxazine dimer. J Phys Chem 1996;100:13514–20.

[14] Schnell I, Brown SP, Low H, Ishida H, Spiess HW. An investigation of hydrogen bonding in benzoxazine dimers by fast magic-angle spinning and double-quantum ^{1}H NMR spectroscopy. J Am Chem Soc 1998;120:11784–95.

[15] Van Krevelen DW. Some basic aspects of flame resistence of polymeric materials. Polymer 1975;16:615.