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Identification of volatile products and determination of thermal degradation mechanisms of polybenzoxazine model oligomers by GC–MS

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Abstract

The polybenzoxazine model trimer and tetramer were utilized to extend the use of model compounds for the decomposition study of polybenzoxazines. The use of polybenzoxazine model dimers was proven to be effective in our previous study. The study of the decomposition of the benzoxazine dimers makes the interpretation for the oligomers as well as that of the polymers simpler. The use of the benzoxazine oligomers shows a good agreement with those of the dimers, and at the same time confirms the mechanisms previously proposed. The fragments containing methyl-substituted at ortho position, such as those at both end groups, make no contribution to char formation. The fragments without methyl-substituted at the ortho position, such as those in the repeating unit in the main chain, contribute considerably to the formation of char residues.

Keywords: Polybenzoxazine oligomer; Thermal degradation; TGA; GC–MS

1. Introduction

The thermal decomposition processes in polybenzoxazine was studied extensively in our previous works [1,2] by using thermogravimetric analyzer interfaced with Fourier transform infrared spectroscopy (TGA–FTIR). The TGA–FTIR provides useful information about the type and functionality of the degradation products according to the infrared fingerprints. Moreover, this technique is a real time analysis capable of giving information at different time and temperature. Nevertheless, this technique does not have the capability to provide the exact chemical structure of all the decomposition products, nor the ability to separate different pyrolysis products coming off at the same time. Therefore another technique that can overcome the limitation of the TGA–FTIR would be useful, so that the combination of both techniques can offer a better insight into the study. Gas chromatography combined with mass-spectrometry (GC–MS) is one of the most appropriate solutions to the problem and has been used widely in the decomposition studies [3–8]. The GC column is able to separate all the degradation products from each other. After the separation, all the compounds will be respectively sent to the MS detector where they are mass selectively identified. The chemical structure of the decomposition products, therefore, can be verified according to the molecular weight and the fragmentation pattern seen in the mass spectrum. The verification can be further confirmed by using model compounds or searching mass spectral libraries.

The level of difficulty for the decomposition study varies according to the complexity of the system under investigation. The study of systems such as clays or minerals where only a few kinds of small molecules are produced can be simple. On the other hand, the interpretation of more complicated systems, such as polymers

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where a large number of decomposition products are being released simultaneously, can be very difficult. Polybenzoxazine, being a thermosetting polymer, is no exception to this statement. Nevertheless, there are a number of methods that can be utilized to help simplify the study of these complex systems, including the use of model compounds. Model compounds can be used to represent a polymer in a much simpler way. In the previous works [9,10], we utilized polybenzoxazine model dimers as the model compounds for the decomposition study of polybenzoxazines. This method not only makes the decomposition study of polybenzoxazines less complicated, but also allows us to study the decomposition processes fundamentally and systematically.

In the present work we expand the use of model compounds to the decomposition study by using the polybenzoxazine model oligomers. The attempt to synthesize and characterize the polybenzoxazine model oligomers has been done successfully [11,12]. Controlled structure oligomers were also used as models for other kinds of study, such as hydrogen bonded network structure of polybenzoxazines [12]. The results were informative and led to the explanation for different properties of various polybenzoxazines.

2. Experimental

All chemicals were used as received. 2,4-Dimethylphenol (98%), *p*-cresol (99%), formaldehyde (37% in water), and methylamine (40% in water) were obtained from Aldrich Chemical Company.

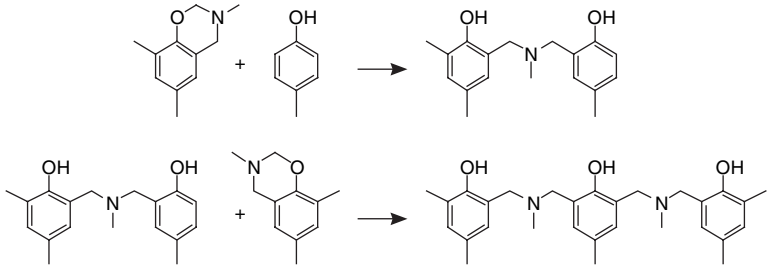
2.1. Synthesis of polybenzoxazine model trimer and tetramer

2,6-Bis[*N*-(3,5-dimethyl-2-hydroxybenzyl)-*N*-methylamino-methyl]-*p*-cresol (trimer) and *N*,*N*-bis{2-hydroxy-5-methyl-3-[(*N*-3,5-dimethyl-2-hydroxy-benzyl)-*N*-methylamino methyl]}-methylamine (tetramer) were synthesized according to the reactions shown in Schemes 1 and 2, respectively. The model oligomers were synthesized using 2,4-dimethylphenol, *p*-cresol, formaldehyde, and methylamine. The starting monomer, 3,4-dihydro-3,6-dimethyl-2H-1,3-benzoxazine, was prepared by the procedure described by Dunkers and Ishida [13]. The synthesis of the intermediate dimers and the characterization of the model trimer and tetramer were described in detail in a previous study [12].

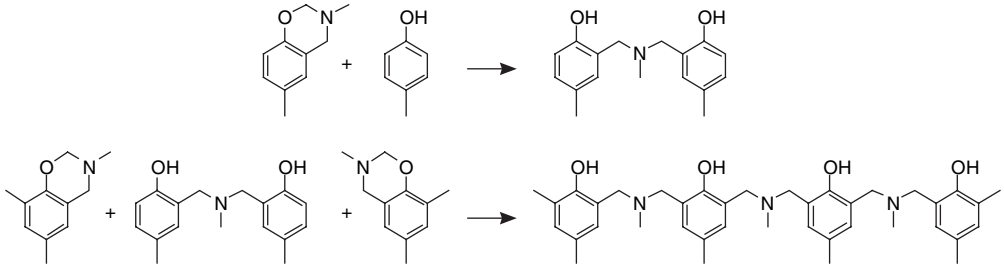
2.2. Characterization

A TGA used for thermogravimetric analysis in this study is a High Res TGA 2950 from TA Instruments. Thermal degradation experiments were done in inert atmosphere using a nitrogen purge at 90 ml/min. The heating rate was 10 °C/min from room temperature to 820 °C.

Evolved gas analysis (EGA) was performed by collecting the gases evolved from a TGA furnace into HPLC grade chloroform. The gases dissolved in the chloroform and the solution was manually injected into a GC coupled with an MS. The GC–MS used for this study was a Hewlett-Packard 6890 Gas Chromatograph coupled with a 5973 Mass Selective Detector. The column inside the GC was a capillary column coated



Scheme 1. Synthesis of polybenzoxazine model trimer.



Scheme 2. Synthesis of polybenzoxazine model tetramer.

with nonbonded 5% phenyl–methyl siloxane. The injection port of the GC was set at 250 °C. The GC column was initially set up at 70 °C and held there for 1 min after the run was started. A heating rate of 5 °C/min was used to heat the column to 250 °C, where the temperature was held for 20 min. This resulted in 57 min of running time for an experiment. The energy used for electron ionization (EI) was 70 eV. The carrier gas used for the GC–MS was helium. The solvent is usually the first thing that comes off from the GC column. Since the MS has microgram sensitivity, the concentration of the solvent reaching the MS detector can be so high that it is detrimental to the instrument. We therefore turn off the detector during the time when the solvent reaches the detector. As a consequence, the detection of the compounds, usually small ones, that comes 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. Nevertheless, the GC–MS may not be able to detect compounds with molecular weight less than the limit, but with low volatility. The identifications of compounds can be confirmed by either consulting the Ref. [14], using the model compounds available or synthesized in our laboratory, or searching the NIST MS library software, Nbs75k.

3. Results and discussion

The polybenzoxazine model trimer and tetramer were successfully synthesized and purified. Both oligomers were thoroughly characterized by Fourier transform infrared spectroscopy (FTIR) along with proton and carbon-13 nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR) as reported in the previous study [12]. Both oligomers were subjected to thermal degradation in TGA. The evolved gases were collected and separated in GC before mass selectively identified by MS.

3.1. Thermal degradation of the benzoxazine trimer and tetramer

The TGA thermograms and their derivatives of the benzoxazine trimer and tetramer are presented in Figs. 1 and 2, respectively. Both oligomers show a well-separated two-stage weight loss process. The onset of degradation was observed at approximately 160 °C for both the trimer and tetramer. After the onset of weight loss, the trimer degraded rapidly and reached the maximum weight loss rate of 1.4%/°C at about 245 °C. After that, the rate of weight loss started decreasing and reached almost zero. The trimer lost 80% of the original weight from the first stage of weight loss. At 300 °C, the onset of the second state of weight loss began and proceeded with the maximum weight loss rate of only 0.1%/°C. The trimer lost another 15% of its original weight from this process. A char yield of 5% for the trimer was determined at 800 °C. As for the tetramer, the overall process was similar to that of the trimer. However, the maximum rate of weight loss during the first process was 1.1%/°C and its temperature was shifted to 250 °C. The tetramer lost about 70% and 20% of its original weight during the first and second weight

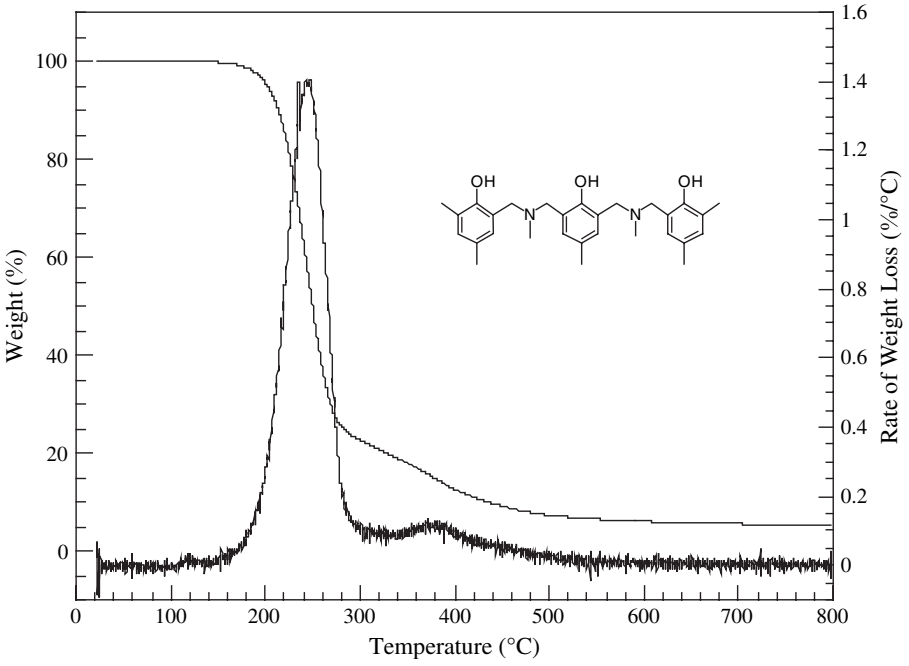


Fig. 1. TGA thermogram and its derivative from the degradation of benzoxazine trimer in nitrogen.

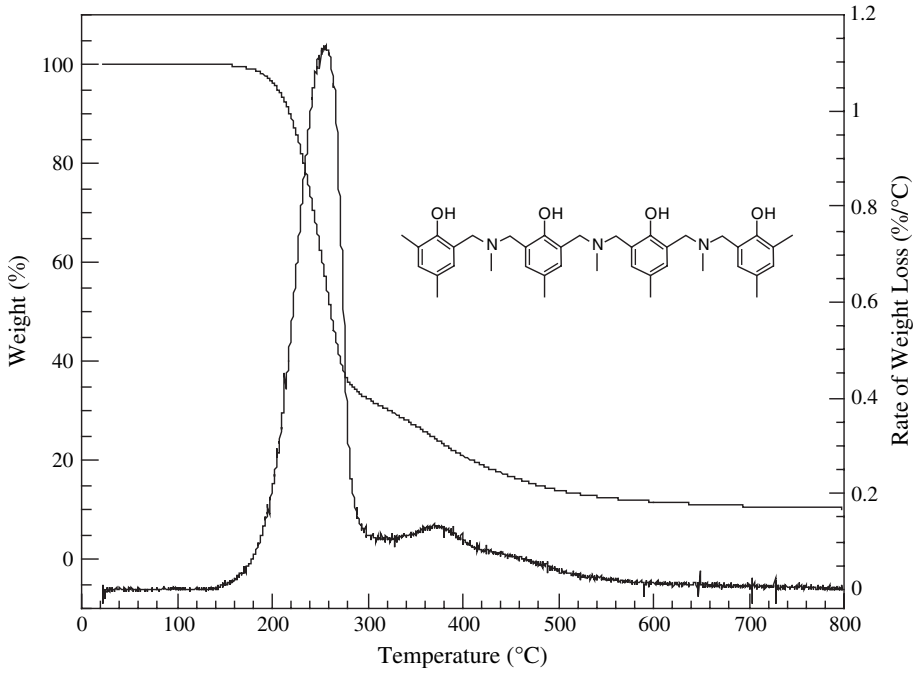


Fig. 2. TGA thermogram and its derivative from the degradation of benzoxazine tetramer in nitrogen.

loss process, respectively. The amount of char left at 800 °C was 10% for the tetramer.

3.2. The EGA from the benzoxazine trimer and tetramer degradation

The gases evolved during the degradation of the trimer and tetramer were collected and subsequently injected into GC–MS. The total ion chromatograms (TIC) of the pyrolyzates of the trimer and tetramer are presented in Figs. 3 and 4, respectively. Both oligomers showed a similar pattern of chromatogram, with the difference being the abundance of the peaks at the same retention time. The structures and percentages of the decomposition products formed during the degradation of the benzoxazine trimer and tetramer in nitrogen are tabulated in Table 1. The oligomers disintegrated into benzene derivatives, phenolic compounds, benzoxazine monomers, Mannich bases, biphenyl compounds, and bisphenol compounds. It should be noted that methylamine is expected to be one of the degradation products,

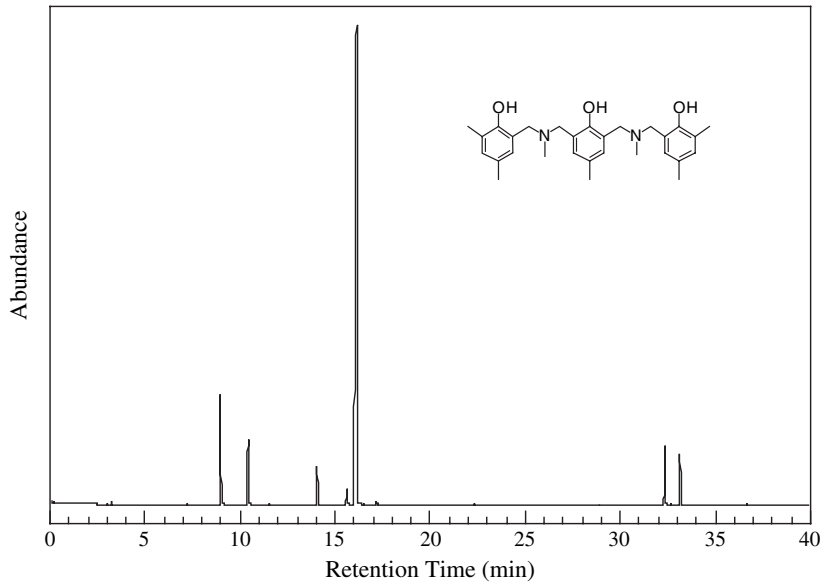


Fig. 3. TIC of evolved gases from the degradation of benzoxazine trimer in nitrogen.

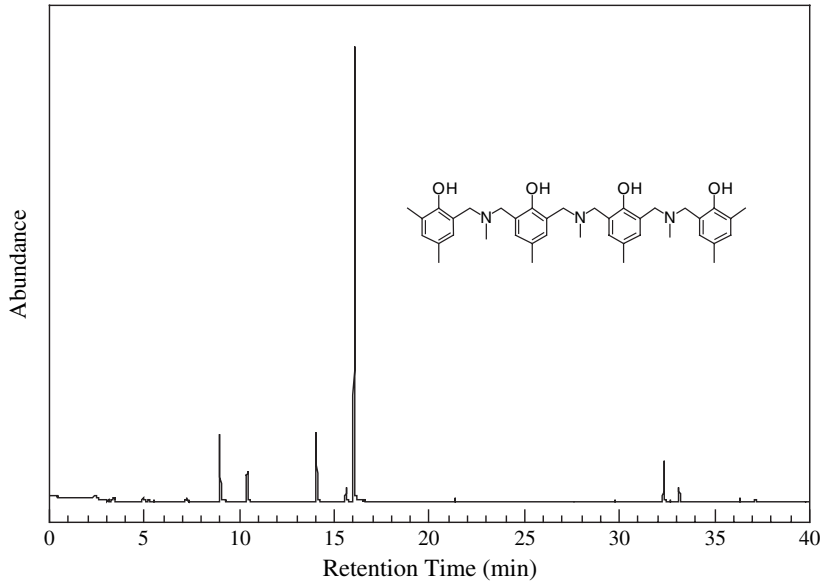


Fig. 4. TIC of evolved gases from the degradation of benzoxazine tetramer in nitrogen.

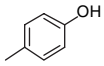
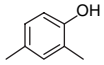
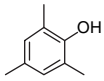
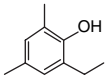
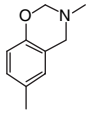
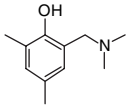
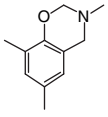
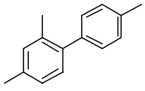
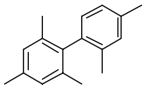
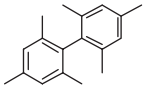
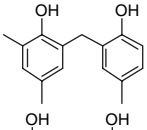
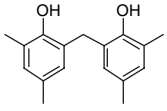
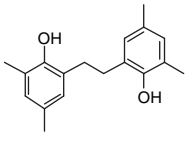
but it would come out when the detector is turned off. The degradation product with the maximum abundance for both the trimer and tetramer is 2,4-dimethylphenol-methylamine-based benzoxazine monomer. This result agrees very well with those found in our previous study of aliphatic amine-based polybenzoxazine model dimers [9], that is the methylamine-based dimers have a tendency to undergo C–C cleavage and form the monomer. The thermal degradation study of the dimers has shown that the presence or absence of a methyl substitution of the end groups, at the ortho position with respect to the hydroxyl group, has a significant effect on the char formation of the dimers. The reason for this was explained in the previous work [9] and will be briefly discussed here shortly after.

3.3. Thermal decomposition processes inferred from the degradation products

The structures of the decomposition products are used to propose the degradation processes happening during the pyrolysis of the benzoxazine trimer and tetramer. Additionally, the proposed mechanisms for the degradation of the benzoxazine dimers are taken into consideration since the dimers can be used as a model for the trimer and tetramer as well. The dimer study has shown that the C–C and C–N cleavages take place simultaneously during the thermal degradation of benzoxazines [9]. When the dimers degrade they disintegrate into smaller molecules which are highly volatile. Depending on the starting dimers some are capable of undergoing recombination reaction to form larger and less volatile compounds. As for the trimer and tetramer, the first C–C and C–N cleavages bring about the formation of smaller fragments including the dimers, as shown in Schemes 3 and 4. These schemes also propose logical radicals and pathways based on the observed products.

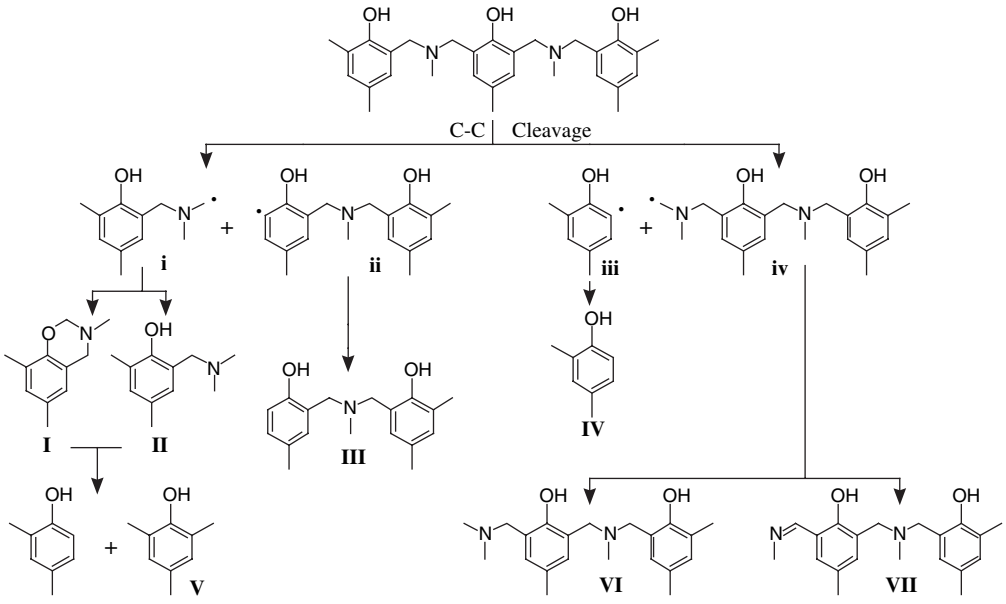
Scheme 3 illustrates the radicals and products formed as a result of the C–C cleavages at the Mannich bridge. The C–C cleavage can take place in two different pathways at the end of the chain or in the middle of it. The breaking of C–C at the middle results in the formation of radicals **i** and **ii**. Radical **i** can undergo either reverse Mannich reaction or hydrogen abstraction to form products **I** (a benzoxazine monomer) and **II** (a Mannich base), respectively. Note that the formation of the benzoxazine monomer was verified and discussed in detail in the dimer study [9]. Both products **I** and **II** can disintegrate further into smaller compounds, i.e. amines and phenolic compounds (**IV** and **V**). Radical **ii** can abstract a hydrogen from the system and becomes product **III**, a benzoxazine dimer. It should be pointed out that the EGA showed no trace of any benzoxazine dimers. This does not mean that the dimers are not present in degradation products. In fact, the benzoxazine dimers have been shown to possess stable hydrogen bonding [15,16]. The intermolecular interaction via hydrogen bonding makes benzoxazine dimers less volatile, unable to go through the GC column and therefore remain undetected. The further decomposition of benzoxazine dimers formed during the degradation of the trimer and tetramer will be discussed in a later section. On the other hand, the C–C cleavage at the terminal group leads to the formation of radicals **iii** and **iv**. Radical **iii** can abstract a hydrogen and form 2, 4-dimethylphenol (**IV**) which can simply evaporate at high temperature. The radical **iii** can also combine with

Table 1
EGA from the degradation of benzoxazine trimer and tetramer in nitrogen

Retention Time (min)	Molecular Weight	Structure	Trimer	Tetramer
2.38	92		< 1%	< 1%
3.46	106		< 1%	< 1%
5.00	120		< 1%	< 1%
7.20	108		< 1%	< 1%
8.97	122		11%	11%
10.42	136		5%	4%
11.51	150		< 1%	< 1%
14.06	163		3%	7%
15.61	179		< 1%	2%
16.13	177		70%	66%
23.75	196		< 1%	< 1%
27.89	224		< 1%	< 1%
29.76	238		< 1%	< 1%
31.70	242		< 1%	< 1%
32.33	256		4%	4%
33.15	270		4%	2%

other phenolic radicals to form bisphenol compounds, as shown in Scheme 4. Radical **iv** can undergo either hydrogen abstraction or elimination to form benzoxazine dimers **VI** and **VII**, respectively.

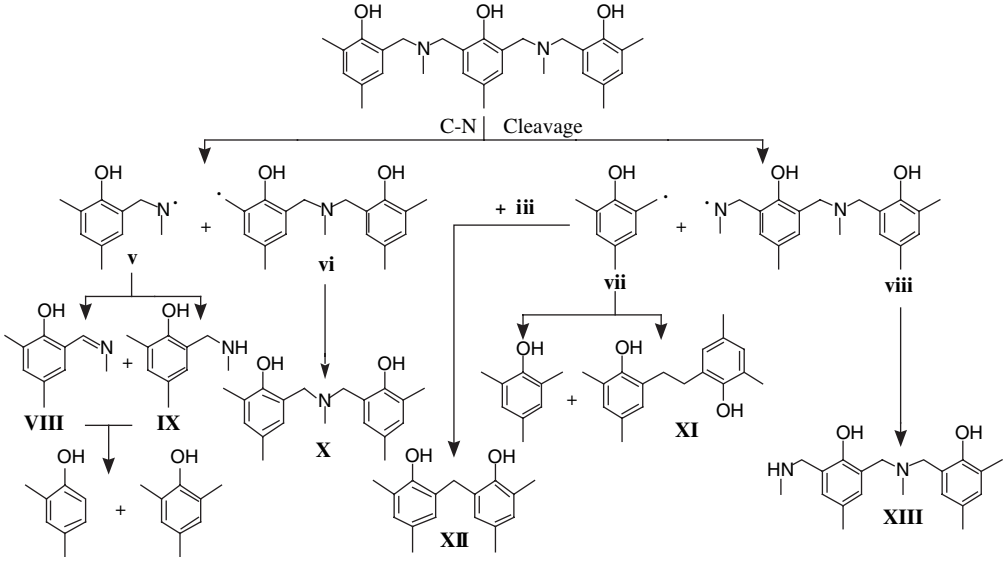
The radicals and products formed as a result of the C–N cleavages are shown in Scheme 4. Like C–C cleavage, the breaking of C–N bonds can take place at either the middle or the end of the chain. Radicals **v** and



Scheme 3. The proposed mechanism for the C–C cleavages at the Mannich bridge during the thermal degradation of the benzoxazine trimer.

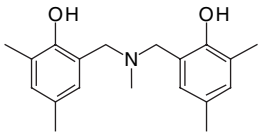
vi are formed when the C–N bond breaks at the middle of the chain. Radical **v** can undergo dehydrogenation or hydrogen abstraction to form a Schiff base (**VIII**) or a Mannich base (**IX**), respectively. Both of which again can continue to decompose to give smaller amines and phenolic compounds. Radical **vi** can abstract a hydrogen atom and become product **X**, another benzoxazine dimer. When the C–N cleaves at the end of the chain, radicals **vii** and **viii** are obtained. Radical **vii** can combine with the H radical, itself or radical **iii** to form products **V**, **XI** and **XII**, respectively, all of which are volatile and have a tendency to evaporate.

From both proposed mechanisms for the C–C and C–N cleavages, five different benzoxazine dimers (**III**, **VI**, **VII**, **X** and **XIII**) should be formed as degradation products of the trimer. All these dimers may evaporate, or as previously mentioned, could remain undetected by GC–MS. However, the dimers can also continue decomposing into smaller fragments. The study of the decomposition of the aliphatic amine-based benzoxazine dimers has been done [9] and proven to be informative as a model for the trimer and tetramer. Therefore, the information from the dimer study will be used here to help interpret the degradation pathways of the oligomers. The two benzoxazine dimers selected as model compounds for the trimer and tetramer are the 2, 4-dimethylphenol-methylamine-based (**24DMP-m**) dimer and the *p*-cresol-methylamine-based (**pC-m**) dimer.

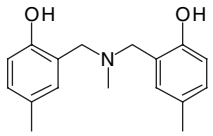


Scheme 4. The proposed mechanism for the C–N cleavages at the Mannich bridge during the thermal degradation of the benzoxazine trimer.

The only structural difference of these two dimers is the presence of methyl group at the ortho position with respect to the hydroxyl group.

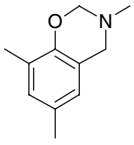


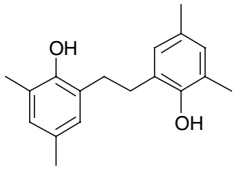
24DMP-m

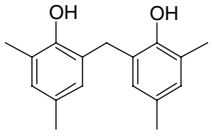


pC-m

The results from TGA, illustrated in Fig. 5, showed that the **24DMP-m** dimer degraded completely and left nothing at 800 °C. While the **pC-m** dimer showed different decomposition pattern and yielded 15% of char residue at 800 °C. The EGA results from the **24DMP-m** dimer showed that the degradation products are small and highly volatile molecules which can completely evaporate below 350 °C. The structures of three major products detected from the degradation of the **24DMP-m** dimer are shown below.

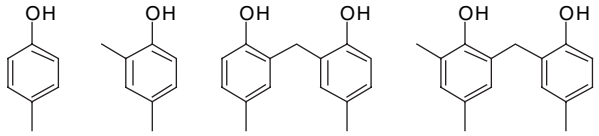




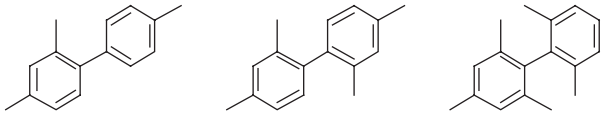


The methyl group at the ortho position prevents the radicals formed during the degradation of the **24DMP-m** dimer to form any products larger than **XI**. Once these compounds are formed, they have a high tendency to evaporate.

On the other hand, the **pC-m** dimer showed two stages of weight loss during the degradation. Note that this degradation pattern is similar to that of the bisphenol-A-methylamine-based (**BA-m**) polybenzoxazine shown in the same Figure. The EGA showed that the first stage of weight loss was mainly due to the evaporation of the primary amine. The second stage of weight loss, in contrast, indicated the release of benzene derivatives, phenolic, biphenyl and bisphenol compounds. The first four major degradation products are shown below.



The last two compounds were not found in the degradation products of the **24DMP-m** dimer. Another type of product that was detected from the degradation of the **pC-m** dimer but not from that of the **24DMP-m** dimer was biphenyl compound, some of which are listed below.



The structure of biphenyl compounds is not present in the **pC-m** dimer, therefore they must be formed during the pyrolysis. The proposed mechanisms for the formation of biphenyl as well as bisphenol compounds are presented in Scheme 5. The existence of these biphenyl and bisphenol compounds is believed to be the reason for char formation of the **pC-m** dimer. At elevated temperatures, the unsubstituted ortho positions on both ends of the **pC-m** dimer make it possible for the biphenyl and bisphenol compounds to undergo successive elimination reactions such as dehydrogenation,

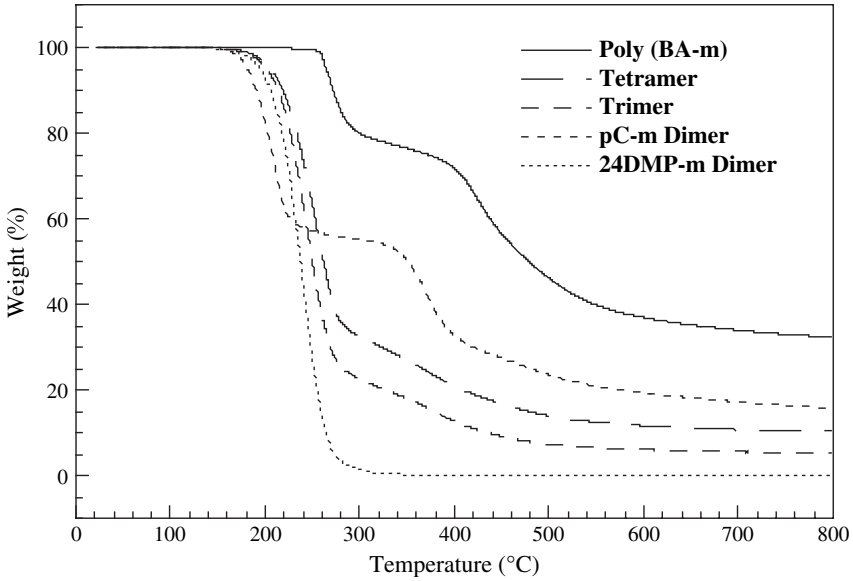
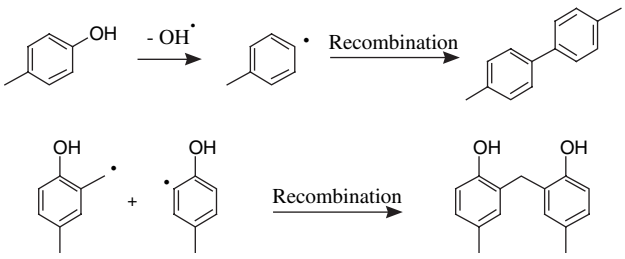


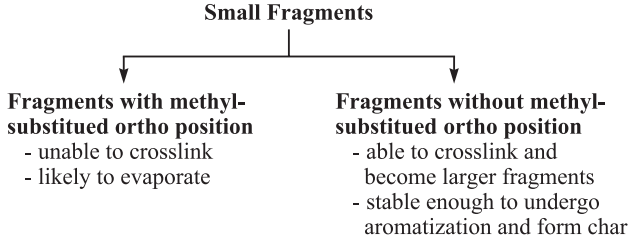
Fig. 5. TGA thermograms of **24DMP-m** dimer (A), trimer (B), tetramer (C), **pC-m** dimer (D), and **BA-m** polybenzoxazine (E).

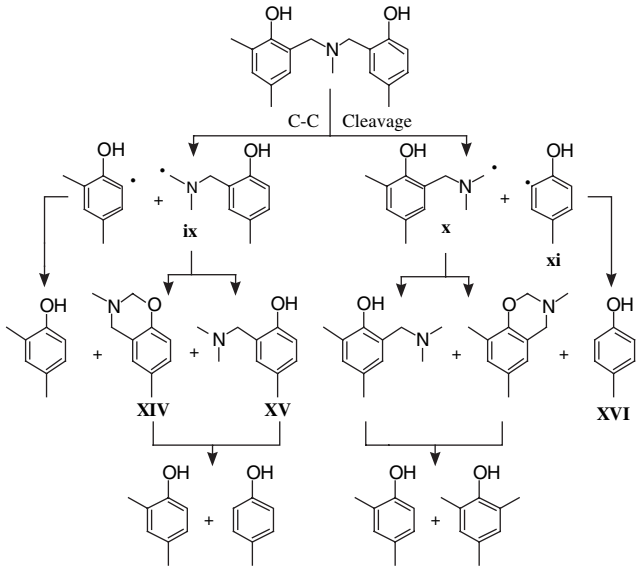


Scheme 5. The formation of biphenyl and bisphenol compounds.

cross-linking and aromatization as shown in Scheme 6. These reactions are known to occur in pyrolysis and capable of generating higher polynuclear aromatic hydrocarbons [8]. Taking this information into account, we can propose how those five dimers, which were formed during the pyrolysis of the trimer, degrade.

Using dimer **III** as an example, it can be seen how the dimer can undergo both C–C and C–N cleavages simultaneously. Schemes 7 and 8 show the mechanism of both types of fragmentation. Both cleavages resulted in further formation of smaller fragments. The char formation of the trimer depends significantly on the structures of the smaller fragments formed as a result of the degradation of the trimer itself and that of the following dimers.

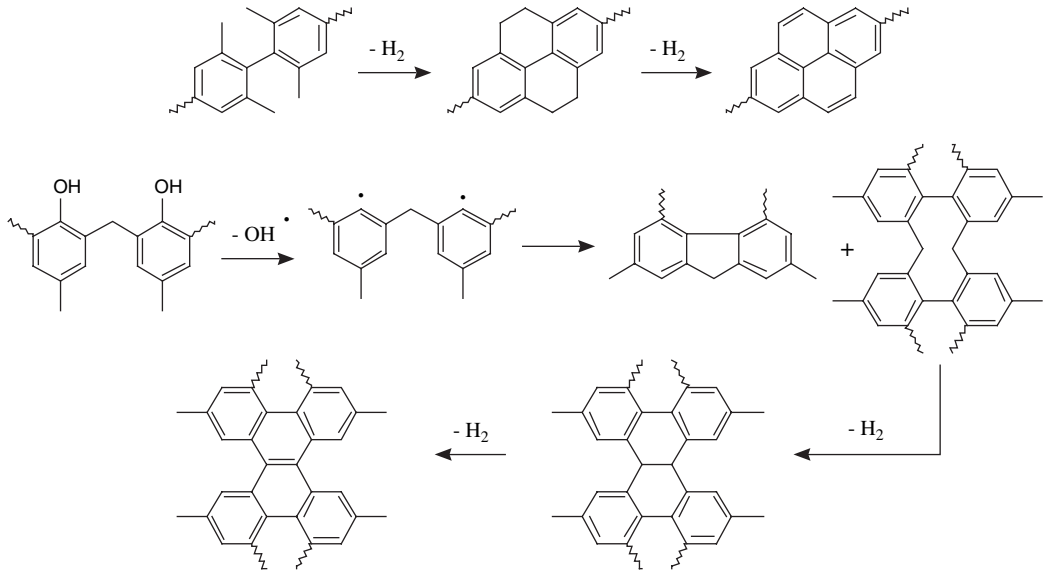




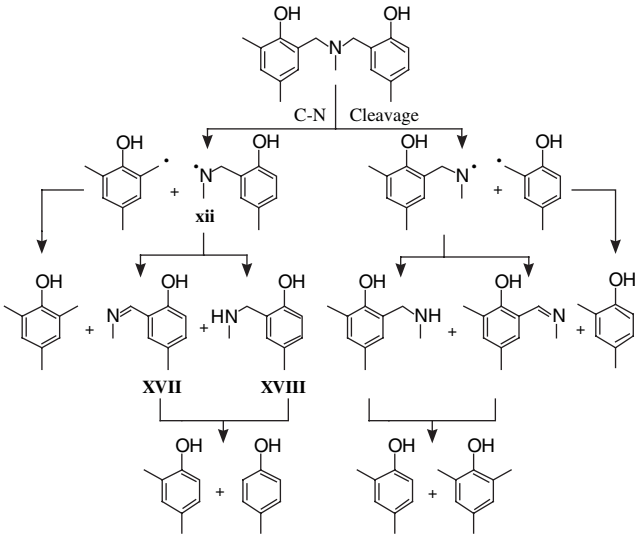
Scheme 7. The proposed mechanism for the C–C cleavages at the Mannich bridge during the thermal degradation of the benzoxazine dimer **III**.

The small fragments can be divided into two groups, as depicted in the above diagram. The first group, in the left of the diagram, represents the fragments containing a methyl group at one or both of the ortho positions. Obviously, the two units at both end of the chain contribute significantly to the formation of these types of fragments. According to the structures of the degradation products, the fragmentation is likely to happen at the methylene bridges rather than at the methyl group. This observation can be explained according to the following reasons.

First of all, the bond energy of C–C (347 kJ/mol) is higher than that of C–N (305 kJ/mol) [17]. Therefore,



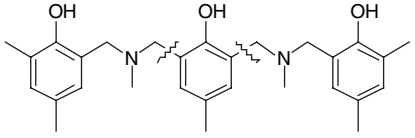
Scheme 6. The char formation as a result of successive dehydrogenation, cross-linking and aromatization.



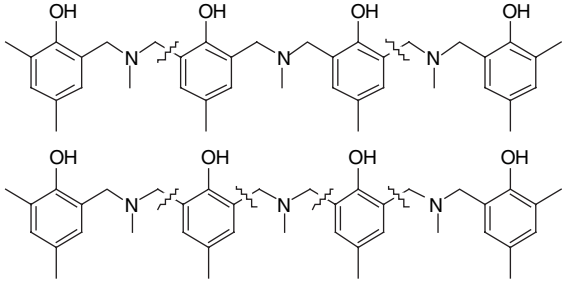
Scheme 8. The proposed mechanism for the C–N cleavages at the Mannich bridge during the thermal degradation of the benzoxazine dimer **III**.

the breaking of C–N bond is more likely to happen than that of C–C bond. Secondly, one of the most important driving forces for fragmentation is the stability of the radicals or products formed. According to the fragmentation and ion chemistry, the fragmentation is governed predominantly by product ion stability [18]. Reactions that lead to conjugation of charge or radical or those that result in stabilized products are more likely to take place. The relative stabilities are based on principles such as octet rule, localization of charge on the most favorable site available, resonance delocalization, and absence of electron unpairing. There are two specific samples which can be used for the explanation of this case. The first principle states that alkyl arenes give $ArCH_2^+$ in strong preference to Ar^+ or $Ar(CH_2)_n^+$. The second principle states that the charge is preferentially localized on the more electronegative element. In this case, N has higher electronegativity than C. As a result, reactions are more likely to happen at the Mannich bridges which contain the N atom. Also, the breaking of C–C bonds of the methylene group results in more stable radicals than that of the methyl group, since the charge can be delocalized at the N atom, too. These two principles are one of the most crucial reasons why methyl group stayed intact throughout the degradation processes. The products **IV**, **V**, **VIII**, **IX**, **X**, **XI** and **XII**, taken from Schemes 3 and 4, are examples of the first group of fragments, containing a methyl group or two in the structure. Most of these degradation products tend to evaporate from the system. The dimer **X**, having the same structure as **24DMP-m** dimer, is a good example of this statement. The dimer yielded no char [9] since the majority of the degradation products contain the methyl group at the ortho position.

The second group contains the fragments without any methyl-substituted ortho position. Product **XVI**, *p*-cresol, is an example of this type of fragment. The *p*-cresol was obtained from both C–C and C–N cleavages of dimer **III**. Similarly, dimers **VI**, **VII** and **XIII** can release *p*-cresol as well, given that the C–C bonds at the methylene bridges were cleaved. The fact that the ortho positions of these fragments are opened for cross-linking is critical to char formation of the trimer. When we look at the structure of the trimer, it is obvious that only the repeating unit in the middle has the possibility to form fragment without methyl group. The only difference between the **24DMP-m** dimer and the trimer is the presence of this repeating unit in the middle. This indicates the effect of the repeating unit on the char formation of benzoxazines. It should be pointed out that, even if the breaking of C–N bonds is more favorable, that does not mean that the C–C cleavage is impossible. The C–C bonds at the methylene bridges can cleave simultaneously, since at elevated temperatures, the energy provided is sufficient for molecules to undergo reactions that do not normally occur at ambient temperatures.



This statement was confirmed by the higher char yield of the tetramer. The tetramer degrades the same way as the trimer does, with the possibility of both the C–C and C–N cleavages. The fact that the tetramer has one more repeating unit than the trimer gives the tetramer higher chances of char formation. The degradation of the tetramer can result in two kinds of fragments without methyl group, the **pC-m** dimer and *p*-cresol.



The **24DMP-m** and **pC-m** dimers can be viewed as a representative for the end group and repeating unit in the main chain of benzoxazines, respectively. The first yields no char residues, while the latter is capable of forming char. The presence of the repeating unit is obviously responsible for the char forming capability of the oligomers.

3.4. The thermal degradation of the trimer and tetramer compared with those of the dimers and methylamine-based polybenzoxazine

Polybenzoxazines are well known to yield a large amount of char residue during the thermal degradation in inert atmosphere. This stems from the fact that polybenzoxazines contain hydroxyl group which is proven to be an active group capable of forming char upon pyrolysis [19]. The results from the trimer and tetramer further confirm this statement. Despite being small molecules, the benzoxazine trimer and tetramer yield high amounts of char. Our previous works have shown that even benzoxazine dimers can produce char residues [9,10]. The results from the study of the benzoxazine dimer and methylamine-based polybenzoxazine [10] from our previous works are shown here for the purpose of comparison. The TGA thermograms of the trimer and tetramer are shown together in Fig. 5, along with those of two different methylamine-based dimers and the bisphenol-A-methylamine-based (**BA-m**) polybenzoxazine.

In spite of the fact that the structure of the trimer and tetramer is rather similar to that of **24DMP-m** than the **pC-m** dimer, both oligomers yield a certain amount of char at 800 °C. This can be explained from the fact that when the oligomers degraded it is likely to have degradation products with structure similar to that of the **pC-m** dimer. As mentioned earlier, the **pC-m** dimer represents the repeating unit in the main chain of polybenzoxazines or benzoxazine oligomers, and is capable of forming char. The trimer is the first oligomer with two end groups and one repeating unit in the main chain. The repeating unit in the middle, with methylene bridges on both sides, is the available site for cross-linking. This is why the trimer did not degrade completely the way **24DMP-m** dimer did, but rather formed 5% of char. The amount of char from the tetramer is slightly more than twice that of the trimer. This can be explained from the fact that there are two end groups and two repeating units in the main chain of the tetramer. The number of the repeating units in the main chain obviously is a key parameter in char formation. The char yield of the **BA-m** polybenzoxazine and polybenzoxazine model dimers, trimer and tetramer are compared altogether in Fig. 6. The **pC-m** dimer, having no end group characteristics in the structure, has higher char yield than both the trimer and tetramer. The **BA-m** polybenzoxazine gives the highest char yield of 32%. The high viscosity of the polymeric system is one of major factors that differentiate the polymers from small model compounds. For the polymers, the degradation and the reaction products can also be of extreme diversity [8]. To highlight the differences, the decomposition products of the polybenzoxazines [10,20], the polybenzoxazine model dimers [9,10], and oligomers are all compared and listed in Table 2. Note that a number of interesting facts can be delineated from this comparison. First of all, the model dimers and oligomers yielded similar decomposition products, whereas the polymers released some additional products. Secondly, all the oligomers yielded bisphenol compounds as one of the degradation products, while the polybenzoxazines did not. Thirdly, the monomer was not found in any of the aromatic amine-based benzoxazines. The formation of monomer was explained in detail in terms of the capability of hydrogen bond formation of the amines [10].

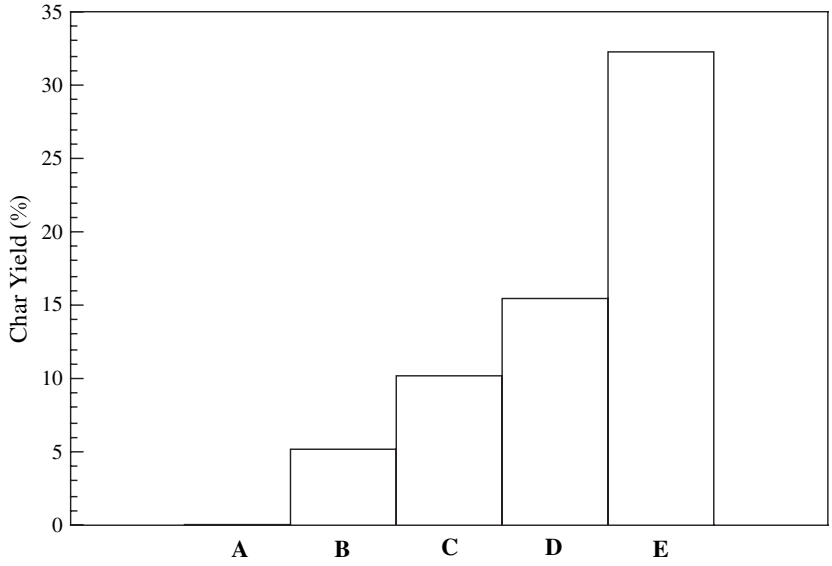


Fig. 6. The char yield of **24DMP-m** dimer (A), trimer (B), tetramer (C), **pC-m** dimer (D), and **BA-m** polybenzoxazine (E).

Table 2
Thermal decomposition products of polybenzoxazines and polybenzoxazine model dimers and oligomers

Degradation products	Dimers			Oligomers	Polymers	
	Aliphatic		Aromatic	Aliphatic	Aliphatic	Aromatic
	24DMP	*p*-Cresol				
Amine	O	O	O	O	O	O
Phenolic	O	O	O	O	O	O
Benzene		O	O	O	O	O
Bisphenol	O	O	O	O		
Biphenyl		O	O	O	O	O
Monomer	O	O		O	O	
Mannich base		O	O	O		O
Schiff base (Imine)	O		O		O	
Heterocyclic			O		O	O
Benzofuran					O	O
Triazene					O	

4. Conclusion

The thermal decomposition processes in the aliphatic amine-based polybenzoxazine model trimer and tetramer were investigated by TGA and GC–MS. The degradation products found from the higher oligomers were similar to those of the aliphatic amine-based polybenzoxazine model dimers previously studied. The study of the dimers has shown to be informative and can be used as model compounds for both the trimer and the tetramer. The end groups containing methyl-substituted ortho position with respect to the hydroxyl group has no contribution to the char formation. On the other hand, the repeating units in the main chain have a profound effect on the char yield. The ability of both oligomers to form char is contributed to the presence of the degradation products without methyl-substituted ortho position. In addition to the products found from the degradation of the dimers and higher oligomers, the aliphatic amine-based polybenzoxazine released some extra products. The decomposition study of the benzoxazine trimer and tetramer has shown to be useful as well as those of the dimers. The information obtained simplifies the interpretation and eliminates the complications for the decomposition study of the highly complex polymeric systems.

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