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Study on thermal degradation mechanism of a cured aldehyde-functional benzoxazine

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Cured product of aldehyde-functional benzoxazine has a good heat-resistant performance. The thermal degradation process of this polybenzoxazine was actively studied by TGA-FTIR and Py-GC/MS. The temperature range of pyrolysis and the major products were determined by TGA-FTIR. A stepwise-temperature testing method based on Py-GC/MS was employed to identify the structures and contents of the pyrolysis products in different temperature stages. Transformation and chemical structures of polymer bulk during the pyrolysis process were speculated. The results showed that the reactions of the aldehyde groups can form special crosslinking structures which effectively prevent the release of phenols during the pyrolysis process. Additionally, benzophenone compounds and carbon monoxide were detected.

1. Introduction

Benzoxazine is a novel class of high-performance thermosetting resin. Polybenzoxazines formed by ring-opening polymerization have various unique properties such as high mechanical strength, low water absorption, good flame-resistance and excellent thermal stability[1-3]. They can be used in several fields. With the development of aerospace technology, ablative-resistant materials are widely used leading to increasing requirements of the thermal stability of the materials.

Studying the pyrolysis of polybenzoxazines can help us to understand the essence of the thermal stability and guide us to design new structures to further improve the thermal resistance of materials. Ishida investigated the thermal decomposition processes of aromatic amine-based polybenzoxazines by TGA and GC/MS[4], and proposed that the thermal degradation products of this polybenzoxazine can be grouped into two categories including primary decomposition products originated from polybenzoxazines itself and secondary decomposition products resulted from the combination or further decomposition of those primary decomposition products. Although GC/MS test can give the structure information of decomposition products during the entire process, this test fails to tell the exact time and temperature of the appearance of the decomposition products. TGA-FTIR can give the structure information at some time and temperature, but it is hard to distinguish the decomposition products because of the complexity of IR spectra. To solve this problem, a stepwise-temperature testing method based on Py-GC/MS has been applied by our research group to study the thermal degradation processes of two polybenzoxazines containing sulfone groups[5]. This method can give lots of information about degradation products and the variation of chemical structures in bulk.

Reactive functional groups are usually employed to increase crosslinking densities and the thermal stability of polybenzoxazines. It has been shown that the thermal stability of the cured benzoxazine monomers containing acetylene, nitrile, furan, and maleimide groups can be greatly improved[6-15]. A novel aldehyde-functional benzoxazine monomer (Ald-B) has been synthesized in our group and its polymer has superior thermal stability[16]. Also, its curing reaction has been investigated in detail[17]. It was inferred that the aldehyde groups reacted with *ortho* positions of phenol and participated in oxidation and decarboxylation reactions to create new crosslinking structures. But it is unclear for the effect of these new structures on the degradation process.

In this study, the thermal degradation process of cured Ald-B was studied as a part of our research series on this resin. The temperature range of pyrolysis and main products were determined by TGA-FTIR. A stepwise-temperature testing method based on Py-GC/MS was employed. Several temperatures were selected to divide the main weight-losing temperature range into small ones. Structures and contents of the degradation products at different temperatures were obtained. The entire process of thermal degradation was discussed in detail involving the structure evolution of gas phase and bulk phase. Chemical structure of polybenzoxazine (poly-A) was further speculated from the perspective of the degradation.

2. Experimental

2.1 Materials

3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbaldehyde(Ald-B, Fig. 1.) was synthesized according to the reference[16].

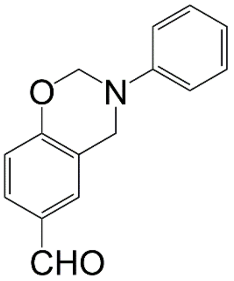


Figure 1 Chemical structure of Ald-B.

2.2 Preparation of polymers

Ald-B was melted in mold at 130 °C. The resin-filled mold was initially degassed at 130 °C for 3hr to remove trace solvent from the resin. Then a stepwise curing process was adopted as follows: 140 °C/2h, 160 °C/4h, 180 °C/2h and 200 °C/4h. After that, a dark red-brown porous polybenzoxazine was obtained and marked poly-A.

2.3 Characterization

TGA-FTIR was performed on a TA Instruments TA-Q500 thermogravimetric analyzer interfaced to a Nicolet 6700 Fourier transform infrared spectrometer. Thermal degradation of the sample was under nitrogen atmosphere from 30 to 800 °C at a heating rate of 20 °C/min. The spectral resolution of the spectrometer was 8 cm^{-1} and about 20 mg powder of poly-A was used.

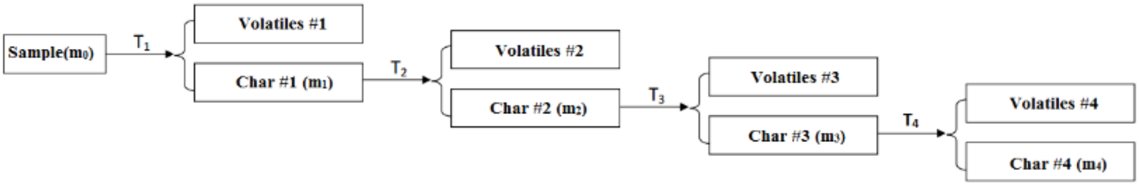


Figure 2 Stepwise-temperature method conducted by Py-GC/MS.

Py-GC/MS analysis was carried out using a combination of single-point pyrolyzer PY-2020i (Frontier, Japan) and chromatograph-mass spectrometer GC/MS QP2010 (Shimadzu, Japan) equipped with a pyrolysis injection system. About 1 mg of sample was pyrolyzed at setting temperature immediately. Helium was used as a carrier gas. The energy of MS used for electron ionization (EI) was 70 eV .Masses were scanned from m/z 29 to 500. Identification of compounds was performed with a Nist11 MS library.

The process of stepwise-temperature method by Py-GC/MS is described in Fig. 2. As shown below, the sample poly-A first degraded in pyrolyzer at T_1 to obtain Volatiles #1 and Char #1. Volatiles #1 were separated and characterized by GC/MS, while Char #1 was weighted and recorded as $\boldsymbol{m_1}$. After that, Char #1 degraded further at next temperature T_2 similarly and degradation at T_3 and T_4 would be conducted by analogy.

3. Results and discussion

3.1 TGA-FTIR

3.1.1 Thermal stability of poly-A

TGA thermogram and its derivative DTA curve from poly-A are shown in Fig.3. Three obvious peaks centered at 310 °C, 449 °C and 563 °C were observed on the derivative curve. The main weigh-losing temperature interval ranged from 300 to 650 °C. It is generally considered that the thermal degradation process of polybenzoxazine has two stages including low temperature stage for the release of amines and high temperature stage for phenols, which is because the C-N bond in the network of polybenzoxazine is easy to break when it suffers a high temperature. For poly-A, 449 °C and 563 °C represented the release of amines and phenols respectively, while 310 °C was probably due to reactions of aldehyde groups. The char yield at 800 °C of poly-A was 55.4% which is higher than that of cured Ph-a (35%) whose monomer has no reactive functional groups[4]. It is proved that the aldehyde groups can effectively improve the thermal stability of polybenzoxazine.

3.1.2 FTIR spectra of volatiles

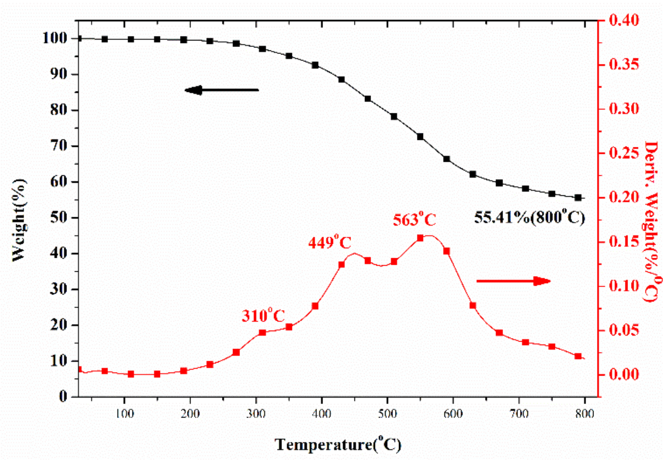


Figure 3 Thermal degradation pattern of poly-A.

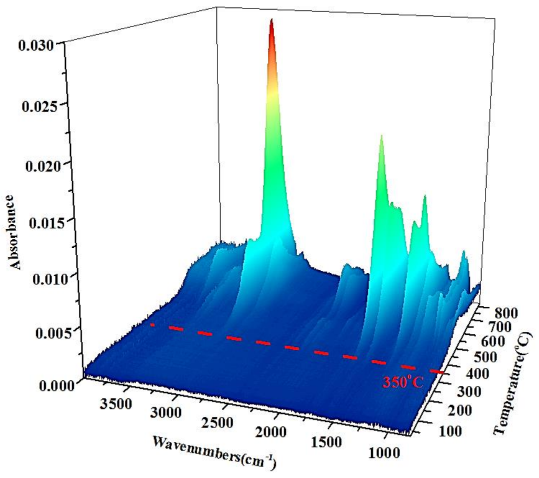


Figure 4 Three-dimensional FTIR spectra of volatiles from the thermal degradation for poly-A.

Fig. 4 gives the three-dimensional FTIR spectra of the volatiles from the thermal degradation of poly-A. The height of the peaks represents the strength of absorbance. The dotted line in Fig.4 represents 350 °C. It can be seen clearly that the degradation of poly-A began to occur around 350 °C. Eight IR spectra between 100 and 800 °C with an interval of 100 °C (5 min) in Fig. 4 were picked up and collected in Fig. 5. Main absorption bands were assigned and classified. As a result, some kinds of volatiles involving amines (1265cm^{-1}), phenols (3648cm^{-1}), and carbon monoxide (2179, 2117cm^{-1}) were detected during the thermal degradation of poly-A. To clearly analyse the evolution of these volatiles, the absorbance of the characteristic bands at 1265cm^{-1}, 3648cm^{-1} and 2117cm^{-1} *vs* temperature was plotted in Fig.6.

As seen from Fig. 5 and 6, at the beginning of thermal degradation (350-400 °C), the absorption band at 1265cm^{-1} assigned to amines was obviously strong, while 3648cm^{-1} belonging to phenols was still weak. Phenols began to evolve till about 500 °C and reached the maximum at 600 °C. This result suggested that the release of phenols was greatly delayed. It is inferred that the reactive aldehyde groups which located in *para* position of phenolic hydroxyl may participate in some kinds of special crosslinking reactions during the polymerization process, and these crosslinking structures can "lock" phenols firmly in polybenzoxazine.

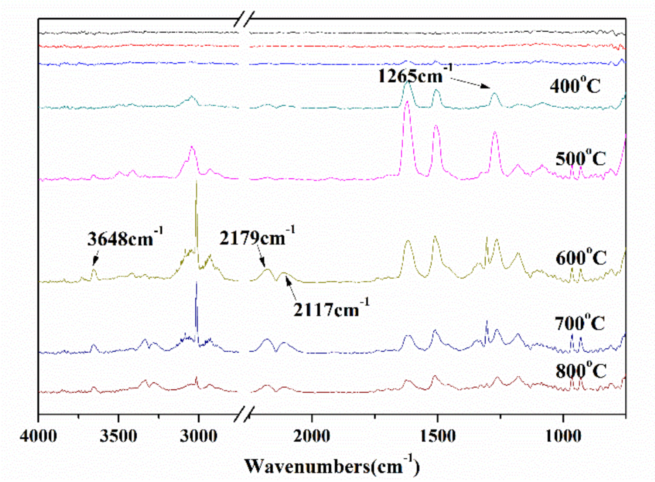


Figure 5 FTIR spectra of volatiles from 100 to 800 °C.

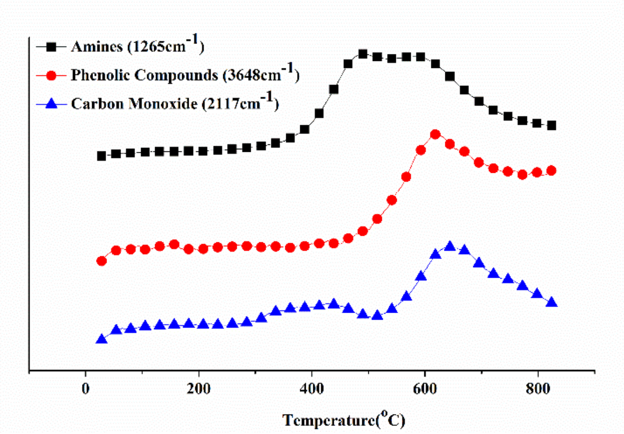


Figure 6 Release of amines, phenolic compounds and carbon monoxide.

Furthermore, the absorption bands at 2179cm^{-1} and 2117cm^{-1} assigned to carbon monoxide started to evolve approximately at 500 °C and reached the maximum at 600 °C as phenolic compounds. As we know, oxygen elements in polybenzoxazine originate from phenolic hydroxyl and no carbon monoxide could be detected during the thermal degradation of those polybenzoxazines without reactive functional groups[4, 18, 19]. In addition, for poly-A, few volatiles containing aldehyde groups were detected during the thermal degradation. So, it is believed that carbon monoxide probably come from the degradation of the crosslinking structures formed by aldehyde groups. Moreover, the release of the phenols and carbon monoxide showed the similar tendency meaning a close relationship between them.

3.2 Py-GC/MS

A stepwise-temperature testing method based on Py-GC/MS was employed to identify the chemical structures and contents of the volatiles in different thermal degradation stages. According to the TGA results of poly-A, the main degradation stage was from 300 ºC to 650 ºC. Four temperatures, 350 ºC (T_1), 400 ºC (T_2), 500 ºC (T_3) and 600 ºC (T_4), were selected. The original sample and the chars at different temperatures were weighted, and losing-weight percentage Δm_n was calculated using **Formula.1**. All the results are shown in Tab.1.

$$\Delta m_n = \frac{m_{n-1} - m_n}{m_0} \times 100\% \quad (n = 1,2,3,4) \qquad \textbf{Formula.1}$$

In this formula, m_0 is the original sample weight while m_n represents the weight of the char at different temperature stage like 350 ºC, 400 ºC, 500 ºC and 600 ºC. For example, "m_1-m_2" means the difference value of the weight of the char at 350 ºC and 400 ºC, it also means the mass of volatiles at 400 ºC.

Table 1 Char weights and losing-weight percentages at different temperatures.

	25 ºC	350 ºC	400 ºC	500 ºC	600 ºC
m_n	1.410 mg	1.357 mg	1.265 mg	1.076 mg	0.984 mg
Δm_n	-	3.8%	6.5%	13.4%	6.5%

Based on the results of MS and the classification method used before[4], volatiles were grouped into eleven types (Tab.2) including small molecule gases (abbr. as Gas), phenolic compounds (-OH), amines (-NH), Mannich bases (Mannich), Schiff bases (Schiff), benzene derivatives (Ph), biphenyl compounds (Biph), 2,3-benzofuran derivatives (Bf), isoquinoline derivatives (Iq), phenanthridine derivatives (Pd) and benzophenones derivatives containing carbonyl groups (Bp).

These eleven types of volatiles were further grouped into three categories in Tab.3 named primary degradation products, secondary degradation products (aromatic and heterocyclic compounds) and benzophenones derivatives containing carbonyl groups. The primary degradation products are obtained directly from the cleavage of the original networks of polybenzoxazines, while the secondary degradation products come from some structures which are resulted from the further reactions during the degradation. Restricted to the Py-GC/MS method, only content percentages (abbr. as CP_n) of the volatiles at a certain temperature can be obtained by gas chromatography. Considering the weight-losing amounts are different at each temperature stage, we introduced the percentage Δm_n to get absolute release percentages by **Formula 2 and 3**. All the results can be found in Tab. 3.

$$EMP_n = \Delta m_n \times CP_n \quad (n = 1,2,3,4) \qquad \textbf{Formula.2}$$

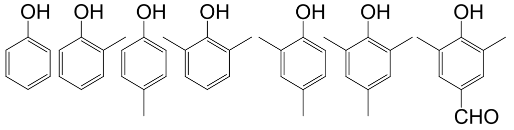
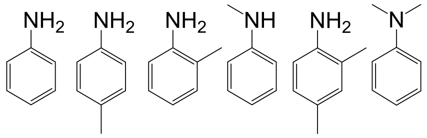
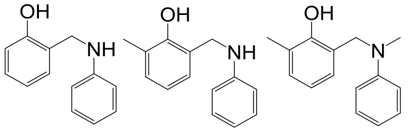
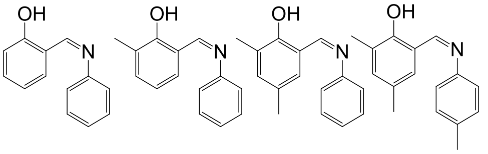
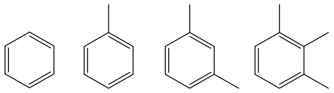
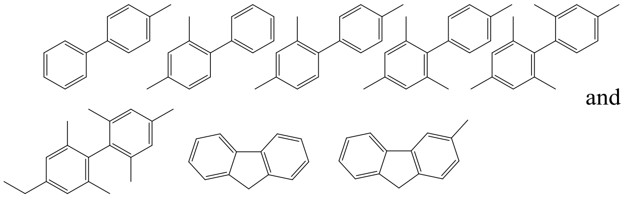
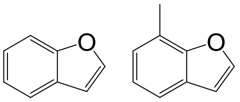
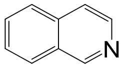
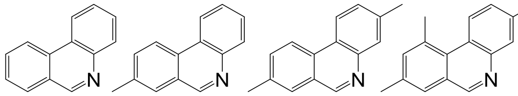
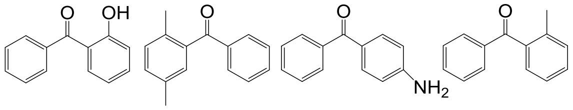
$$TMP = \frac{\sum_{n=1}^{4} EMP_n}{\sum_{n=1}^{4} \Delta m_n} \times 100\% \qquad \textbf{Formula.3}$$

EMP_n above represents mass percentage of each volatile type at a certain temperature when we regard the original sample mass as 100% .While ***TMP*** represents the total mass percentage of a type during the whole temperature stage (350 ºC to 600 ºC) when we regard the total losing weight as 100%. Taking the Gas for example, "EMP_1=0.092%", it means that at 350 ºC the mass of the released Gas accounts for 0.092% of the original sample mass, while "***TMP***=6.9%", it means during the whole temperature stage the content of the released Gas accounts for 6.9% of the total losing weight or total mass of the volatiles. "n=1, 2, 3, 4" here corresponds to 350 ºC, 400 ºC, 500 ºC and 600 ºC, respectively.

As we can see from Tab.3, the primary degradation products including Gas, -OH, -NH, Mannich and Ph accounted for 84% of the total amount meaning the primary degradation products are the main volatiles during the whole degradation process. These products were obtained directly from the cleavage of C-C and C-N bonds in the Mannich bridge of polybenzoxazine which usually began around 350ºC. Among these primary degradation products, -OH and -NH had the biggest release amount with 72%, and showed a similar release tendency. Both of them formed at 350ºC and their ***EMP*** values increased with temperature and reached the peak at 500 ºC. After that the values decreased sharply. However, it should be noted that the ***EMP*** values of -OH compounds at 350 and 400ºC were 0.148% and 0.631%, respectively, which were no more than one ninth of those of -NH compounds (2.854% and 5.037%). This result suggests that the release of phenolic compounds has been greatly delayed, which is also observed in the results of TGA-FTIR. Combining with the MS results that main released phenolic compounds are disubstituted and trisubstituted phenols, we can deduce that lots of new crosslinking sites in poly-A are formed on the phenol rings because of the reactions of aldehyde groups.

Additionally, the ***TMP*** values of Mannich and Ph compounds were quite small and only accounted for 1.2% and 4.5%, respectively. For Mannich compounds, they were only detected at 400 and 500 ºC. The release of Ph needs higher

Table 2 Chemical structures of volatiles detected by the stepwise temperature testing method using Py-GC/MS.

Classification of volatiles	Chemical structures
Small molecule gas (Gas)	CO,CH_4,NH_3,H_2O
Phenolic compounds (-OH)	
Amines (-NH)	
Mannich bases (Mannich)	 and isomers
Schiff bases (Schiff)	 and isomers
Benzene derivatives (Ph)	
Biphenyl compounds (BiPh)	 and isomers
2,3-benzofuran derivatives (Bf)	
Isoquinoline derivatives (Iq)	
Phenanthridine derivatives (Pd)	 and isomers
Benzophenone derivatives containing carbonyl groups (Bp)	 and isomers

temperatures like 500 ºC or 600 ºC because of the requirement of the fracture of Ar-O and Ar-N bonds. Furthermore, Gas showed an increasing trend and reached the maximum at 600 ºC. They accounted for 6.9% of the total volatiles during the whole degradation process. Overall, it should be noted that not all the primary degradation product species released directly in form of gas, some were kept in the end of the molecular chain and may release gradually as temperature rises.The formation and volatilization of the secondary degradation products need higher temperature. So, in the Tab. 3 most of them were detected at 500 ºC and 600 ºC except for small amount of Schiff and Pd derivatives. The Schiff bases appeared only at 350 ºC which are probably formed by the recombination of amines and phenols containing aldehyde. While the Phenanthridine (Pd) derivatives detected at each temperature were the most secondary degradation products with a ***TMP*** of 7.9%. They are probably generated from further degradation of the Mannich base compounds. Moreover, the Biph compounds were detected at 400, 500 and 600 ºC with a similar ***EMP*** value. 2,3-benzofuran (Bf) and isoquinoline (Iq) derivatives were found at 500 ºC or the higher temperature. Overall, the secondary degradation

Table 3 Contents of thermal degradation volatiles at different temperatures.

Degradation Volatiles		350 °C		400 °C		500 °C		600 °C		TMP (%)
		CP_1 (%)	EMP_1 (%)	CP_2 (%)	EMP_2 (%)	CP_3 (%)	EMP_3 (%)	CP_4 (%)	EMP_4 (%)	
Primary degradation products	**Gas**	2.4	0.092	4.4	0.283	2.1	0.279	22.0	1.432	6.9
	-OH	3.9	0.148	9.7	0.631	32.4	4.347	27.6	1.791	22.9
	-NH	75.1	2.854	77.5	5.037	48.9	6.554	4.8	0.314	48.9
	Mannich	0.0	0.000	0.8	0.051	2.3	0.302	0.0	0.000	1.2
	Ph	0.2	0.008	0.8	0.051	2.5	0.336	15.0	0.974	4.5
Secondary degradation products	**Biph**	0.0	0.000	2.5	0.159	1.1	0.151	2.3	0.151	1.5
	Schiff	5.4	0.206	0.0	0.000	0.0	0.000	0.0	0.000	0.7
	Iq	0.0	0.000	0.0	0.000	0.0	0.000	0.6	0.036	0.1
	Bf	0.0	0.000	0.0	0.000	1.4	0.193	10.9	0.710	3.0
	Pd	12.5	0.474	1.2	0.081	5.6	0.745	16.8	1.093	7.9
Bh		0.5	0.019	3.2	0.206	3.7	0.493	0.0	0.000	2.4

products had a high percentage at high temperatures, but their absolute quantities were very low because of less weight loss of polymer in this temperature stage. Compared with the primary products throughout the pyrolysis process, the total mass percentage of the secondary degradation products was less and only accounted for 13%. This is because most secondary product species contain thermal stable aromatic heterocyclic or polymer structures with a large molecular weight and a high boiling point. These species in the bulk are vital to form chars.

In addition, several benzophenone (Bh) derivatives containing carbonyl groups were generated mainly at 400 and 500oC with a total mass percentage of 2.4%. They don't come from primary or secondary degradation process, but rather probably from direct fracture of the original structures of polybenzoxazine. So we inferred that the benzophenone structures existed originally in polybenzoxazine.

3.3 Thermal degradation process of poly-A

Time and temperature information was introduced by a stepwise-temperature testing method using Py-GC/MS. Based on these information, we can know the chemical structures and their respective contents of degradation products at different temperatures. Furthermore, combined with the information of small molecule gas got from TGA-FTIR results, polymer structures and degradation process of poly-A could be speculated.

The chemical structure of poly-A has been inferred by investigating the polymerization process in previous study by our group[17]. As supplement, the results of studying thermal degradation process were used to further speculate the structure from the other side. As shown in Fig.7, the Mannich bridge is a basic structure of polybenzoxazine, which is closely related to the formation of primary and secondary degradation products of polybenzoxazine. Beyond this, phenolic compounds containing aldehyde group could be detected in Py-GC/MS, indicating that poly-A still contains some aldehyde groups without participating in any reactions.

Furthermore, hydroxymethyl groups and carboxyl groups also exist in poly-A. These two groups are obtained through reductive or oxidation reactions of aldehyde groups. Additionally, there exists a special crosslinking structure

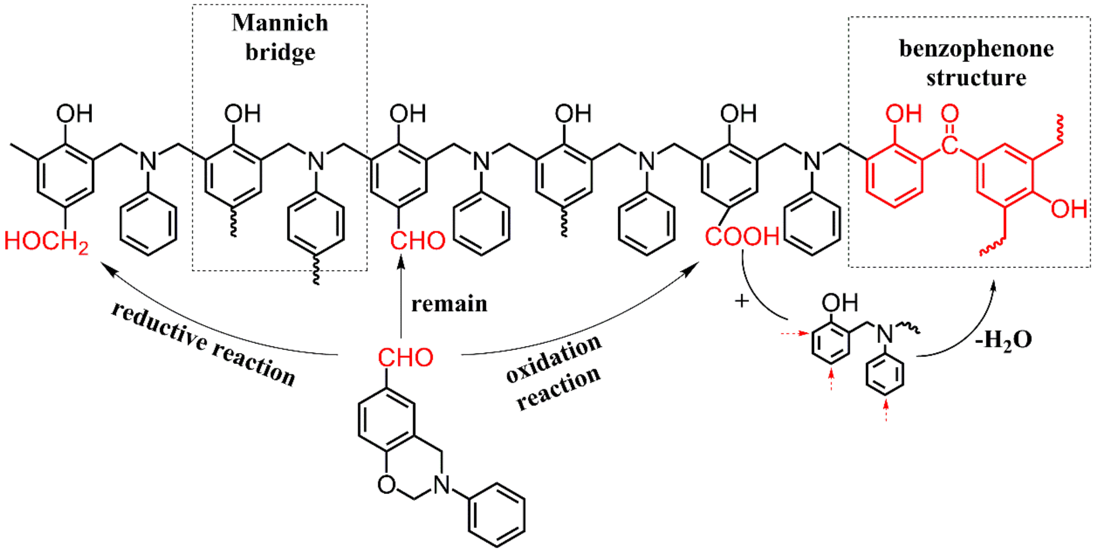


Figure 7 Chemical structure of poly-A and formation of benzophenone structure.

containing benzophenone species in poly-A, which is closely related to aldehyde groups. It's reasonable that some carboxyl groups can be generated from the oxidation of aldehyde groups. It is believed that a part of carboxyl groups take part in the decarboxylation reactions to create new reactive crosslinking points on the *para* positions of phenolic hydroxyls. Other carboxyl groups which do not involve in any reactions may react with the *ortho* or *para* position of phenolic hydroxyls to generate benzophenone structures with the removal of the water. Besides that, *para* positions of aniline may be also involved in this reaction. Formation of this structures may also exist in the early stage of degradation. The small weight loss at 310 °C in TGA is probably attributed to the decarboxylation and dehydration reactions.

The thermal degradation process of poly-A is described in Fig. 8 and divided into four parts. The evolution of bulk structures is presented on the left and the variation of volatiles is on the right.

During 350-400 °C of the thermal degradation process, the weakest C-N and Ar-C bonds in polybenzoxazine break first. Molecular weight rapidly decreases and lots of small molecule radicals are generated. These radicals catch hydrogen to form homologous primary degradation products such as amines, phenolic compounds and Mannich base. This is a main reason for weight-loss. Due to the generation of more thermal stable structures like carbonyl groups on phenolic rings from the crosslinking reactions of the aldehyde groups as mentioned above, the amount of phenolic compounds is really small. The weak bonds adjacent to benzophenone structure may break to release a small amount of benzophenone compounds, and most of them are still remained in bulk. Moreover, some polymer chain fragments terminated with primary degradation product species have enough good thermal stability and also are kept in bulk.

During 400-500 °C, polymer chain fragments further degrade to release amines, phenolic compounds and other primary products. Rising temperature increases the breaking possibility of adjacent chemical bonds, so Ar-O and Ar-N bonds may be broken and create the ammonia and benzene derivatives. At the same time, some primary degradation products can either combine each other to form the secondary products like biphenyl compounds and phenanthridine derivatives or further degrade. Those polymer chain fragments terminated with primary products can also react like this and make the species of biphenyl and phenanthridine to remain in the bulk. These species are vital to the carbonization reaction at higher temperature.

During 500-600 °C, the release of primary products becomes slow. This means that the basic skeleton of Mannich bridges in polybenzoxazine nearly disappears. The secondary products recombine each other to generate aromatic heterocyclic or fused rings structures. Dehydrogenize and aromatization of these structures carries on further. Additionally, high temperature makes Ar-O bonds in the benzophenone structure break to release "locked" phenolic species.

Above 600 °C, the weight loss of the bulk almost reaches equilibrium. Aromatization and dehydrogenation in the bulk are main reactions at this temperature range, and the char is formed finally.

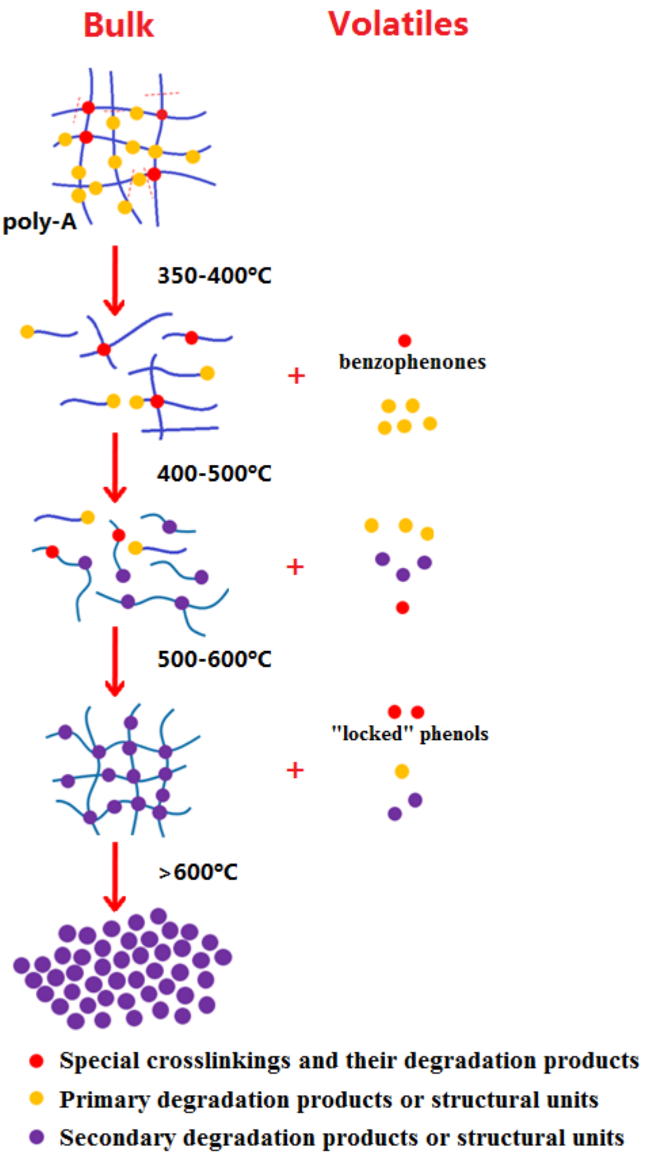


Figure 8 Evolution of gas and bulk during thermal degradation of poly-A.

4. Conclusion

The thermal degradation of a polybenzoxazine containing aldehyde groups was studied by TGA-FTIR and a stepwise-temperature testing method based on Py-GC/MS. The entire process of thermal degradation was discussed in detail and the crosslinking structures of poly-A were further proved from the perspective of the degradation. The results indicate that special crosslinking benzophenone structures caused by aldehyde groups exist in poly-A. These extra crosslinking structures improve the thermal stability of poly-A. During the thermal degradation process, the primary degradation products involving amines, Mannich base and phenolic compounds were detected and the release of phenolic compounds significantly delayed. These primary products and polymer chain fragments terminated with these species can recombine each other to generate secondary degradation products or further degrade. The second degradation products and their species are vital to form chars at higher temperature. In addition, the segments containing benzophenone structures may degrade at a high temperature to release carbon monoxide and unlock the phenolic species at the same time.

5. Acknowledgement

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