

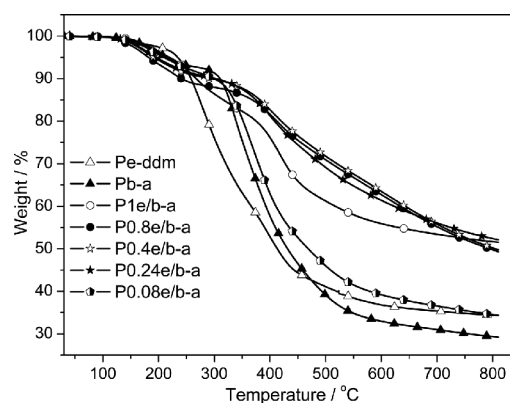
Improving the Thermal Stability of Polybenzoxazines Through Incorporation of Eugenol-Based Benzoxazine

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Abstract: To introduce the para-position of phenol or aniline moiety into the cross-linked network of polybenzoxazine and improve its thermal stability, benzoxazine based on eugenol and 4,4'-diaminodiphenylmethane (e-ddm) was copolymerized with bisphenol A-aniline-based benzoxazine (b-a) or phenol-aniline-based benzoxazine (p-a). The differential scanning calorimetry and Fourier transform infrared spectroscopy (FTIR) results show that the carbenium ion intermediate from e-ddm could react with the para-position of phenol or aniline in b-a and p-a during the ring-opening polymerization process, resulting in that the aniline and phenol moieties were introduced into cross-linked structures of polybenzoxazines. The thermogravimetric analysis (TGA) and TGA interfaced with FTIR results indicate that the thermal stability of polybenzoxazines increased with the incorporation of e-ddm, due to that the volatilization of phenol, aniline and their derivatives was restrained during the thermal degradation processes. Thereby, introducing e-ddm into benzoxazine is a better method of increasing the thermal stability of polybenzoxazine.



Keywords: eugenol, benzoxazine, para-position, copolymerization, thermal stability.

1. Introduction

Benzoxazine, synthesized via the Mannich condensation reaction of primary amine, phenol and formaldehyde, can form polybenzoxazine with the structure characteristics of cross-linked phenolic resin through ring-opening polymerization (ROP) mechanism. As a novel kind of phenolic resin, polybenzoxazine possesses lots of fascinating properties such as good mechanical performance, thermal stability, flame retardance, low surface energy and wide molecular design flexibility. Thereby, polybenzoxazine has gained great interests from both academia and industry.¹⁻⁶ However, its thermal stability need to be further improved to the application in the harsh fields. Introducing polymerizable group such as allyl, acetylene and nitrile groups could make aniline moiety incorporated into cross-linked network and thus improve thermal properties of polybenzoxazines.⁷⁻⁹ Nevertheless, those primary amine or phenolic compounds with polymerizable groups are usually expensive. Thereby, it is very meaningful to find out some new and more economical ways to introduce aniline and phenol moieties into the cross-linked network of polybenzoxazines.

The dwindling of fossil resources coupling with the increasing in polymer consumption has encouraged research interests in alternative and bio-based polymers. At the present, various

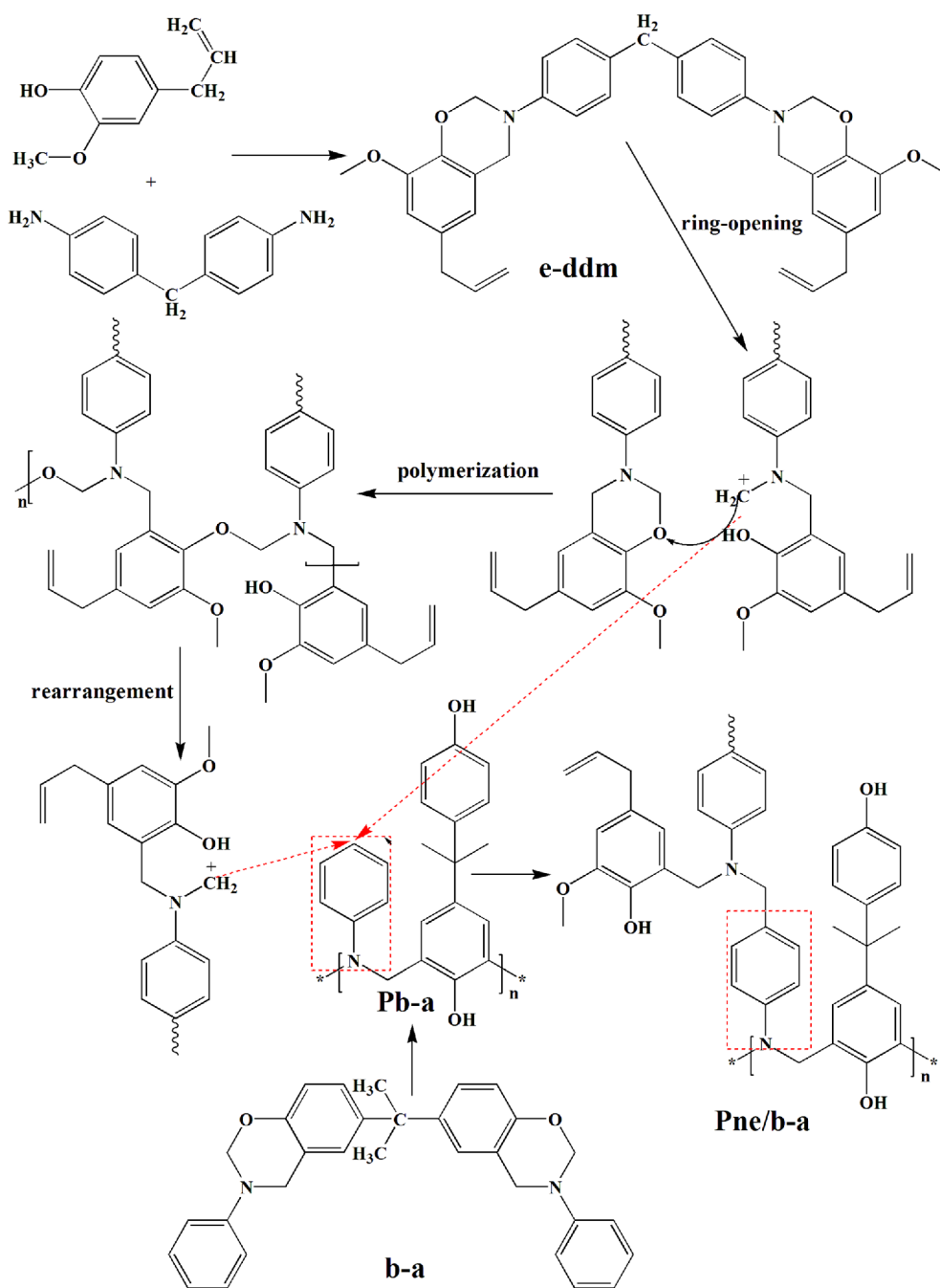
benzoxazines from renewable resources such as cardanol,¹⁰ rosin, guaiacol,¹¹ vanillin,¹² diphenolic acid,¹³ furfuryl amine^{14,15} and eugenol (4-allyl-2-methoxy phenol)¹⁶⁻²² have been synthesized. Thereinto, eugenol has attracted great interests owing to its abundant, cheap and naturally occurring characteristics. However, the homopolymerization of eugenol-based benzoxazine hardly occur theoretically due to the occupied ortho and para positions of hydroxyl and the resulting polymer even could disaggregate in chloroform,¹⁹⁻²² resulting from that preferential polymerization site of benzoxazine is the ortho position of hydroxyl though the para-position of phenol and aniline also shows some reactivity.²³⁻²⁵

With regard to benzoxazine based on eugenol and 4,4'-diaminodiphenylmethane (e-ddm, shown in Scheme 1), carbenium ion intermediate formed during ROP process could only attack the hydroxyl and form the unstable N,O-acetal-type structure, due to the occupied ortho and para positions. Moreover, this structure could rearrange at elevated temperature and the carbocation would generate once again.²⁶ Accordingly, the carbocations from e-ddm could react with unoccupied para-position of arylamine or phenolic moiety when e-ddm polymerizes with benzoxazine based on aniline or (and) phenol. That would make aniline or phenol moiety be introduced into crosslinked structures (Scheme 1 and 2) and increase the thermal stability of polybenzoxazine.

Thereby, e-ddm was mixed and copolymerized with bisphenol A-aniline-based benzoxazine (b-a) or phenol-aniline-based benzoxazine (p-a) in this work. Then, differential scanning cal-

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Scheme 1. Ring-opening Polymerization process of e-ddm and b-a mixture.

orimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were utilized to study the reaction between the carbenium ion intermediate of e-ddm and the para-positions of aniline and phenol in b-a or pa, thermogravimetric analysis (TGA) and TGA interfaced with FTIR (TGA-FTIR) were performed to investigate the effect of copolymerization between e-ddm and b-a or pa on the thermal properties of polybenzoxazine.

2. Experimental

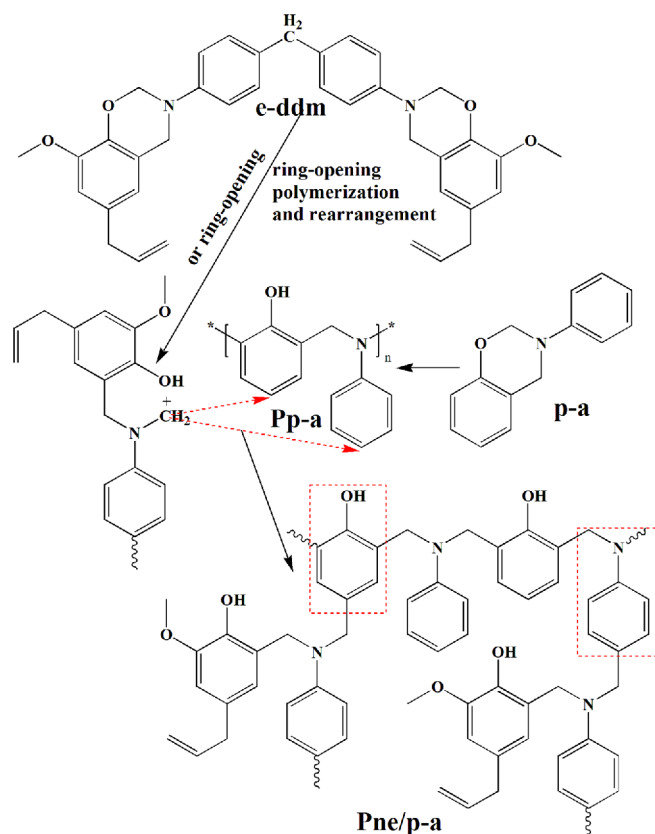
2.1. Materials

Eugenol, phenol, paraformaldehyde, 4,4'-diaminodiphenylmeth-

ane and ethanol were purchased from Sinopharm chemical reagent Co. Ltd. (Shanghai, China). Bisphenol A, aniline, sodium hydroxide, toluene and trichloromethane were purchased from Damao chemical reagent factory (Tianjin, China). All these materials were used as received. B-a and p-a were synthesized according to the previous researches.^{27,28}

2.2. Synthesis of e-ddm

Eugenol (13.14 g, 0.08 mol), 4,4'-diaminodiphenylmethane (7.92 g, 0.04 mol) and paraformaldehyde (5.28 g, 0.176 mol) were put into a 100 mL round-bottom flask equipped with a reflux condenser. The mixture was stirred and refluxed at 110 °C for 1 h,



Scheme 2. Ring-opening Polymerization process of e-ddm and p-a mixture.

then, it was cooled to room temperature and dissolved in toluene. The solution was washed with 0.1 mol/L NaOH aqueous solution and water, respectively, until pH of aqueous solution was 7. Finally, solvents were removed and the mixture was further dried under vacuum to yield an orange viscous product (yield: 83%).

2.3. Preparation of polybenzoxazine

The mixture of e-ddm and b-a was stirred at 80 °C for 1 h to obtain e-ddm/b-a (abbreviation as ne/b-a, e represented e-ddm), then it was degassed under vacuum oven and cured in an air-circulating oven to get polybenzoxazine (Pne/b-a). The preparation of e-ddm/p-a mixture (abbreviation as ne/p-a) and the corresponding polymer (Pne/p-a) was similar to that of e-ddm and p-a. In ne/b-a and ne/p-a, n means the molar ratio of e-ddm and b-a or p-a. The specific polymerization approaches were as follows:

Pne/b-a: 110 °C/2 h in vacuum, then, 120 °C/1 h, 130 °C/1 h, 140 °C/1 h, 150 °C/1 h, 160 °C/1 h, 170 °C/1 h, 180 °C/2 h and 190 °C/4 h in air-circulating oven.

Pne/p-a: 110 °C/1 h in vacuum, then, 130 °C/1 h, 150 °C/1 h, 170 °C/1 h, 180 °C/2 h and 190 °C/2 h in air-circulating oven.

The cured e-ddm, b-a and p-a were defined as Pe-ddm, Pb-a and Pp-a, respectively. The curing procedure of Pb-a and Pp-a was identical with that of Pne/b-a and Pne/p-a, respectively.

Preparation of Pe-ddm: e-ddm was degassed under vacuum at 110 °C for 1 h and then it was placed in an air-circulating oven as

the following: 130 °C/1 h, 140 °C/1 h, 150 °C/1 h, 160 °C/1 h, 170 °C/5 h, 180 °C/3 h and 190 °C/2 h.

2.4. Characterization

Nuclear magnetic resonance (NMR) spectra (¹H NMR and ¹³C NMR) were obtained through a Bruker AVANCE 300 MHz NMR spectrometer, using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as internal standard.

FTIR spectrum was recorded on a Nicolet IS 10 Fourier transform spectrometer in the range of 4000–400 cm⁻¹.

DSC test was performed on a TA Instruments Q20 with a heating rate of 10 °C/min under nitrogen flow (50 mL/min) from 40 to 320 °C.

TGA was performed on a TA Instruments Discovery with a heating rate of 10 °C/min under nitrogen flow (25 mL/min) from 40 to 810 °C.

For TGA-FTIR, A Perkin-Elmer STA6000 synchronized thermal analyzer was interfaced with a Perkin-Elmer Frontier FTIR. The gas cell and the transfer line were set at a temperature of 280 °C. The experiment was carried out with a heating rate of 10 °C/min under nitrogen flow (50 mL/min) from 40 to 810 °C.

3. Results and discussion

3.1. Synthesis of e-ddm

The structure of e-ddm was demonstrated by FTIR and NMR. The FTIR spectrum of e-ddm is shown in Figure 1. The bands at 3073, 3056 and 3005 cm⁻¹ were due to the =C-H stretching vibration of benzene ring and allyl. The bands at 2935, 2900 and 2832 cm⁻¹ were owing to the stretching vibration of methyl and methylene. The band at 1639 cm⁻¹ was corresponded to -CH=CH₂ of allyl. The bands at 1226 and 1027 cm⁻¹ were assigned to the asymmetric and symmetric stretching vibration of Ar-O-C. The characteristic absorption peak of oxazine ring was located at 941 cm⁻¹. The band at 843 cm⁻¹ was from 1,2,4,6-tetrasubstituted benzene of eugenol moiety, the absorption peak at 818 cm⁻¹ was due to 1,4-disubstituted benzene of amine moiety.

The NMR spectra are displayed in Figure 2. In ¹H NMR spec-

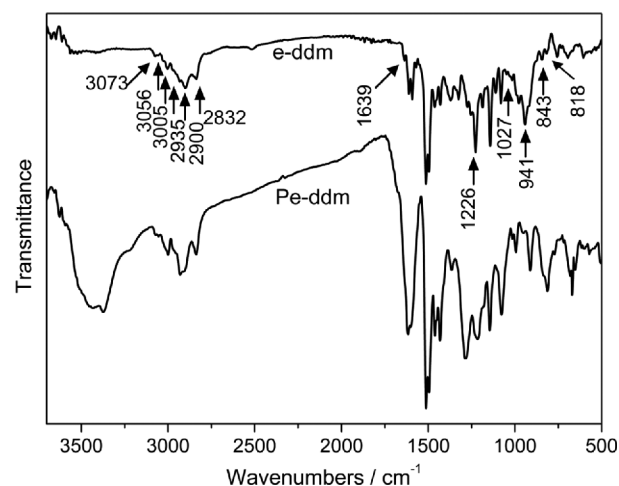


Figure 1. FTIR spectra of e-ddm and Pe-ddm.

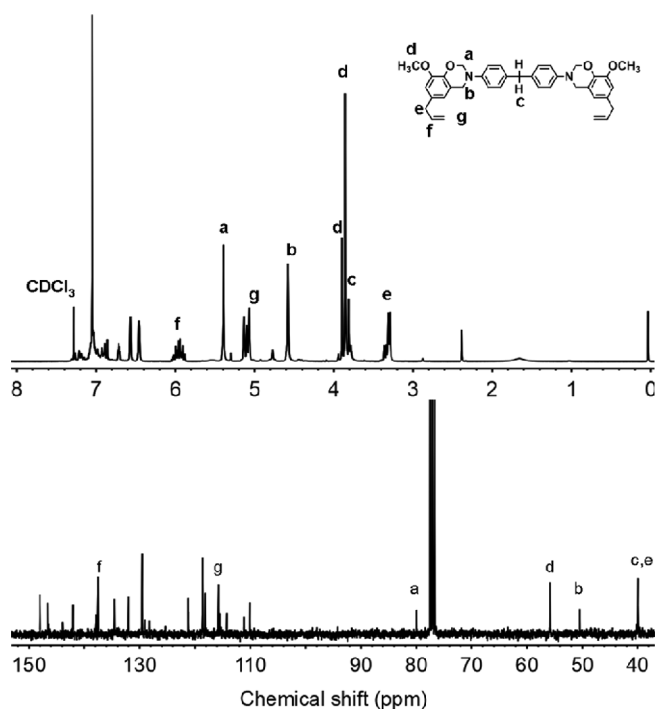


Figure 2. NMR spectra of e-ddm.

trum, the resonances appearing at 5.39 and 4.58 ppm were owing to the methylene protons of oxazine ring. The resonances emerging at 5.94 and 5.10 ppm were from hydrogens of $-\text{CH}=\text{CH}_2$. The signal located at 3.90 ppm was due to protons of $\text{CH}_3\text{O}-$. In ^{13}C NMR spectrum, the resonances corresponding to carbons of $\text{Ar}-\text{CH}_2-\text{N}$ and $\text{O}-\text{CH}_2-\text{N}$ appeared at 50.67 and 79.98 ppm, the peak at 55.81 was assigned to carbon of $-\text{OCH}_3$. The signals located at 115.75, 137.53 and 39.93 ppm were attributed to the carbons of $-\text{CH}_2-\text{CH}=\text{CH}_2$, respectively. These results confirm the successful synthesis of e-ddm.

3.2. Polymerization behavior of ne/b-a and ne/p-a

3.2.1. Polymerization ability of e-ddm

The dark red viscous product was obtained when e-ddm was heated as the following procedures: 130 °C/1 h, 140 °C/1 h, 150 °C/1 h, 160 °C/1 h, 170 °C/5 h, 180 °C/3 h and 190 °C/2 h. Then, it was kept heating at 250 °C for 1 h and still could flow. However, Figure 1 shows that the absorption peaks at 1226, 1027 and 941 cm^{-1} of e-ddm had vanished through the above heat treatment, implying that oxazine ring had opened completely. These results indicate that e-ddm could not form cross-linked structure although the ring-opening reaction had took place, resulting from the occupied ortho and para positions of phenol and arylamine moieties.

3.2.2. DSC analysis

To investigate the reaction between e-ddm and b-a or p-a, DSC tests of ne/b-a and ne/p-a were performed.

3.2.2.1. ne/b-a

As shown in Figure 3, the ROP of b-a happened at lower temperature compared with e-ddm. Moreover, the initial temperature (T_i) of ROP of ne/b-a was also lower than that of e-ddm, due

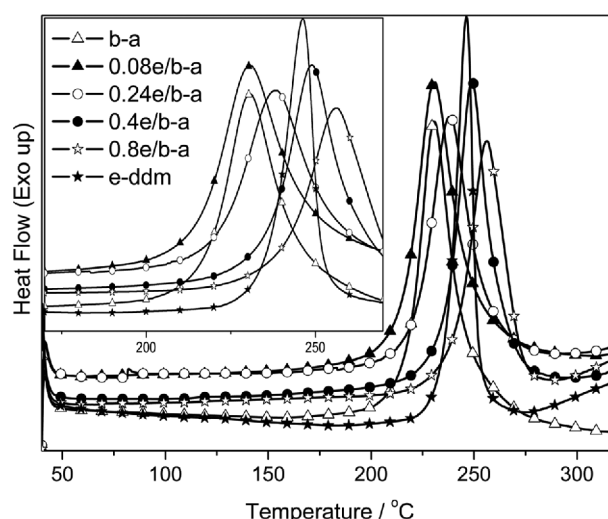


Figure 3. The DSC curves of b-a, e-ddm and ne/b-a.

to that the hydroxyl from b-a catalyzed the ROP of e-ddm. However, the peak temperature (T_p) of ne/b-a gradually shifted to higher one with the increasing of e-ddm, and the T_p of 0.4e/b-a and 0.8e/b-a was even more than that of e-ddm. These imply that there was some new reaction occurring in ne/b-a, which was more difficult and needed higher temperature compared with the homopolymerization of e-ddm or p-a. It should be assigned to electrophilic substitution reaction of the carbenium ion intermediate from e-ddm and para-position of aniline in p-a, resulting from that the reactivity of para-position of aniline is low and its electrophilic substitution is inclined to happen at a higher temperature. The carbenium ion could be from the ring-opening of e-ddm or the rearrangement of N,O-acetal structure at elevated temperature (shown in Scheme 1). Furthermore, only an exothermic peak could be observed in the ne/b-a, also suggesting that the copolymerization of e-ddm and b-a had occurred.

3.2.2.2. ne/p-a

To further investigate the reaction of carbenium ion from e-ddm and the para-positions of aniline or phenol moiety in benzoxazine, ne/p-a was also tested by DSC and the results are dis-

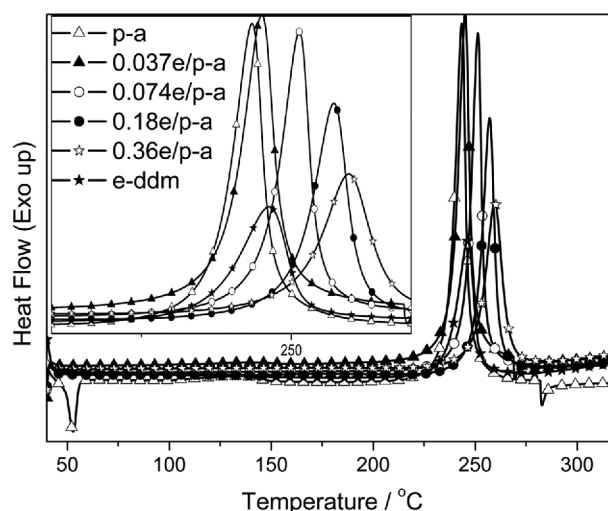


Figure 4. The DSC curves of p-a, e-ddm and ne/p-a.

played in Figure 4. As can be seen, the T_p of ne/p-a gradually shifted to higher temperature with the increase of e-ddm, it was even more than that of p-a and e-ddm as e-ddm in ne/p-a was beyond 0.037/1. It should be attributed to the new electrophilic substitution reactions between the carbenium ion from e-ddm and para-positions of phenol and aniline moieties in p-a (shown in Scheme 2), which was same as that of ne/b-a.

According to the above DSC results, it can be concluded that the carbenium ion intermediates, formed during the ROP processes of e-ddm, could react with the para-positions of phenol and aniline moieties in benzoxazine. It implies that there should be more 1,4-disubstituted and 1,2,4,6-tetrasubstituted benzenes in Pne/b-a and Pne/p-a compared with Pb-a and Pp-a (shown in Scheme 1 and 2). Thereby, the following FTIR measurements of Pne/b-a and Pne/p-a were performed to further testify the occurrence of copolymerization.

3.2.3. FTIR analysis

3.2.3.1. Pne/b-a

The FTIR spectra of Pb-a, Pe-ddm and Pne/b-a are shown in Figure 5. The peaks located at 750 and 689 cm^{-1} were due to mono-substituted benzene, the bands in the range of 1621 and 1470 cm^{-1} were attributed to skeleton vibration of benzene ring. With the incorporation of e-ddm, the absorption peak at 750 cm^{-1} gradually became weak compared with those between 1621 and 1470 cm^{-1} , implying the decrease of mono-substituted benzene. That is to say, the para-positions of aniline had reacted with the methylene of e-ddm, resulting in the formation of arylamine Mannich bridge structure (shown in Scheme 1). Moreover, the bands between 1621 and 1470 cm^{-1} of Pne/b-a were not summation of those of Pb-a and Pe-ddm, which also illustrated the difference of substituted benzenes and occurrence of copolymerization between e-ddm and b-a. Except the above changes, the other bands of Pne/b-a were almost identical with those of Pb-a and Pe-ddm.

However, the bands at 750 and 689 cm^{-1} always existed even if the ratio of e-ddm and b-a was 1/1 (the stoichiometry of e-ddm and b-a in copolymerization is 1/1), possibly resulting from the low reactivity of para-position of aniline.

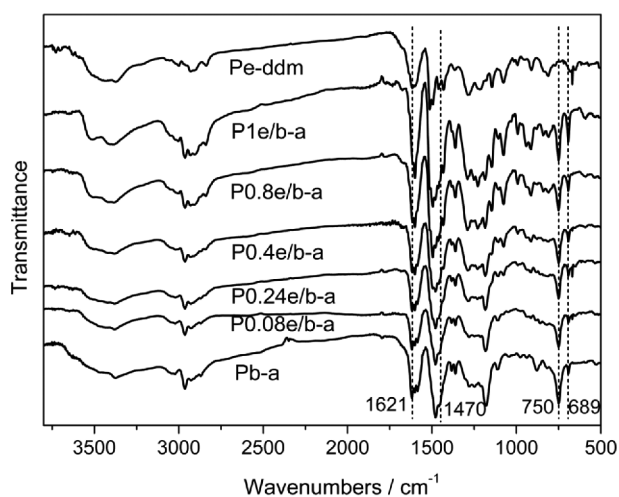


Figure 5. FTIR spectra of Pe-ddm, Pb-a and Pne/b-a.

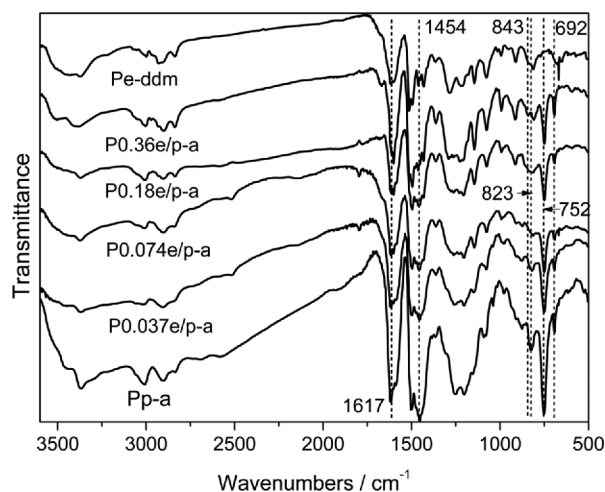


Figure 6. FTIR spectra of Pe-ddm, Pp-a and Pne/p-a.

3.2.3.2. Pne/p-a

The FTIR spectra of Pne/p-a and Pp-a are shown in Figure 6. It could be seen that the absorption peak appeared at 752 cm^{-1} gradually became weak and that at 843 cm^{-1} assigned to 1,2,4,6-tetrasubstituted benzene gradually grew strong with the incorporation of e-ddm into p-a. Moreover, the intensity of peak at 843 cm^{-1} in P0.36e/p-a even exceeded that in Pe-ddm, implying that there were more 1,2,4,6-tetrasubstituted benzene structures in P0.36e/p-a than those in Pe-ddm. Namely, the carbenium ion from e-ddm had reacted with that para-position of phenolic moiety in p-a. The above results of Pne/b-a suggest that para-position of aniline could react with e-ddm. Thus, the decrease of peak intensity at 752 cm^{-1} implies the decrease of 1,2,6-trisubstituted and mono-substituted benzenes, due to that the peak of 1,2,6-trisubstituted benzene overlapped with that of the mono-substituted benzene at 752 cm^{-1} . In other words, the carbenium ion from e-ddm could react simultaneously with that para-position of phenolic and aniline moieties in p-a, bringing about the formation of 1,2,4,6-tetrasubstituted and 1,4-disubstituted benzene structures (shown in Scheme 2). In addition, the peaks intensity and position in the range of 1617 to 1454 cm^{-1} of Pne/p-a were different from those of Pp-a and Pe-ddm, also suggesting the formation of 1,2,4,6-tetrasubstituted and 1,4-disubstituted benzenes.

But the peaks of mono-substituted benzene ring located at 752 and 692 cm^{-1} could be always detected in all Pne/p-a, further illustrating the low reactivity of para-position of aniline. Except the above differences, the other bands of Pne/p-a were similar to those of Pp-a and Pe-ddm.

3.3. The effect of e-ddm on the thermal stability of Pb-a and Pp-a

3.3.1. TGA analysis

3.3.1.1. Pne/b-a

The TGA results of Pb-a, Pe-ddm and Pne/b-a are shown in Figure 7. TG curves indicate that the char yield at 800 $^{\circ}\text{C}$ of Pne/b-a was obviously more than that of Pb-a and Pe-ddm. DTG curves suggest that the weight loss rate of Pne/b-a in the range of 270-

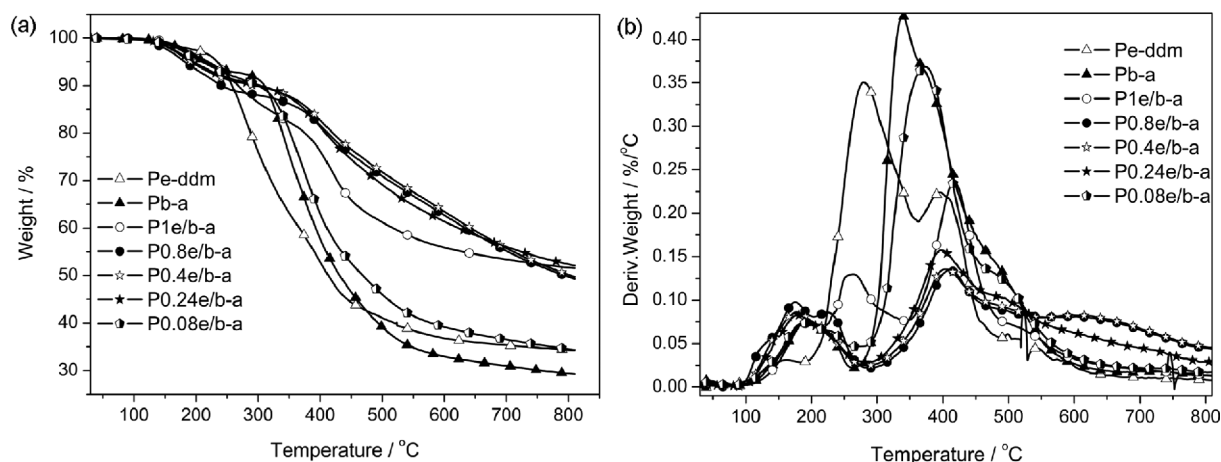


Figure 7. TG (a) and DTG (b) curves of Pe-ddm, Pb-a and Pne/b-a in nitrogen.

550 °C remarkably decreased and their maximum weight loss peak shifted to higher temperature compared with Pb-a. These imply that the thermal stability of Pb-a increased with the incorporation of e-ddm.

The degradation gases between 270 and 450 °C mainly included aniline, phenol, benzene and their derivatives during the thermal degradation of Pb-a.²⁹ The above DSC and FTIR results indicate that the addition of e-ddm made the unstable 'hang' aniline moiety be introduced into crosslinked network, which would make the evaporation of amine and benzene compounds be restricted during thermal degradation processes of polybenzoxazine. Accordingly, the weight loss rate of Pne/b-a at 270-550 °C decreased and their maximum one was shifted to higher temperature compared with Pb-a. However, the weight loss rate of P1e/ba at 230-360 °C was obviously more than that of Pb-a and other Pne/b-a and similar to that of Pe-ddm. These imply that only parts of e-ddm could react with para-position of aniline in b-a and the others homopolymerized into oligomers, which was also identical with FTIR results.

3.3.1.2. Pne/p-a

The TGA results of Pp-a and Pne/p-a are displayed in Figure 8. TG curves show that the char yield at 800 °C of Pne/p-a was remarkably more than that of Pp-a, indicating that the addition

of e-ddm improved the thermal stability of Pp-a.

DTG curves suggest that Pne/p-a showed a three-stage weight loss process. The first weight loss event in the range of 100-200 °C was similar to that of Pp-a, mainly resulting from the evaporation of oligomers and other low-molecular-weight compounds. The second weight loss event, occurring at 200-350 °C, was corresponded to the maximum one of Pe-ddm, chiefly due to the evaporation of e-ddm oligomers and their degradation products. Nevertheless, the weight loss rate of Pne/p-a was remarkably lower than that of Pe-ddm, possibly resulting from that the cross-linked networks of Pne/p-a inhibited the volatilization of oligomers and their degradation products. The third weight loss event centering at the range of 300-650 °C overlapped with the maximum one of Pp-a and the third one of Pe-ddm, in which the weight loss rate of Pne/p-a was obviously lower than that of Pp-a. It should be due to that the volatilization of phenolic and amine degradation gases was restricted with the para-positions of phenol and aniline moieties being introduced into crosslinked networks (shown in Scheme 2), which would be demonstrated by the following TGA-FTIR tests.

The thermal stability of P0.037e/p-a was the best in all Pne/p-a, and that of Pne/p-a gradually became worse with the increase of e-ddm in ne/p-a. It could be assigned to that p-a volatilized

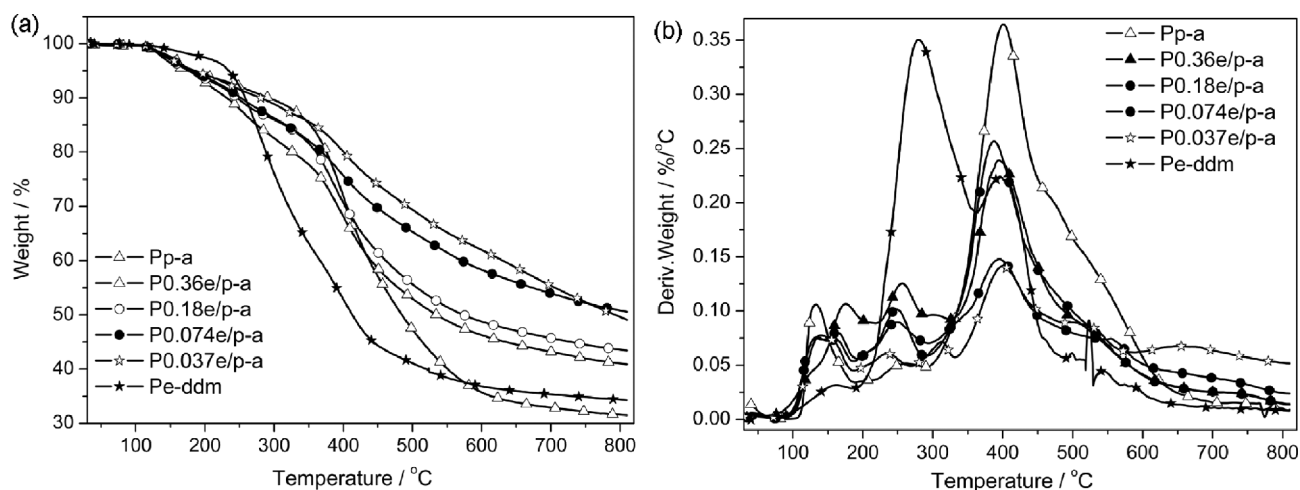


Figure 8. TG (a) and DTG (b) curves of Pe-ddm, Pp-a and Pne/p-a in N₂.

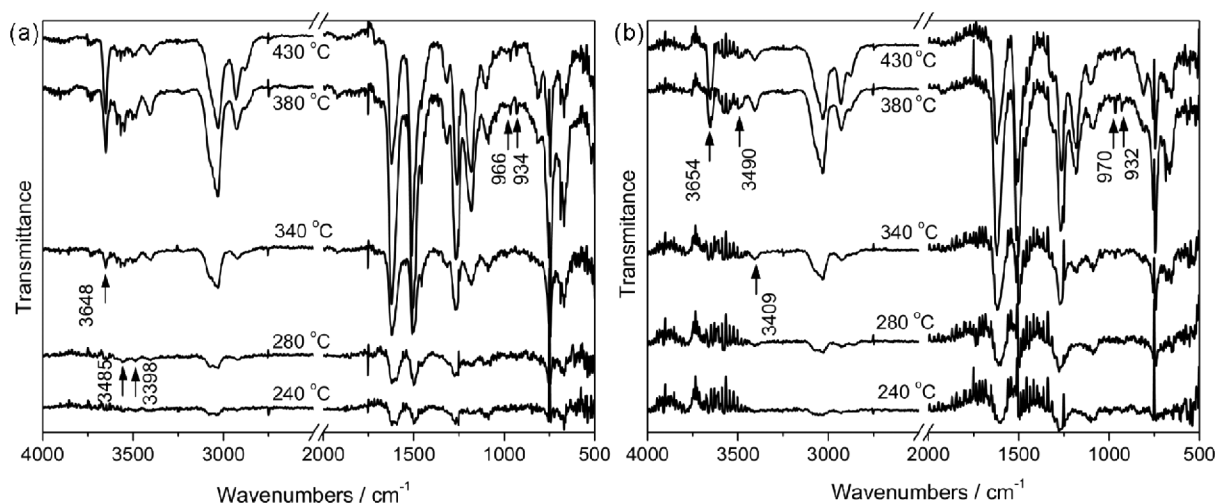


Figure 9. FTIR spectra of the evolved gases from the thermal degradation of Pp-a (a) and P0.037e/p-a (b) in N_2 .

very easily at higher temperature and the reactivity of para-positions of phenol and aniline was lower, leading to that the ratio of e-ddm in Pne/p-a was far more than that in initial ne/p-a. Therefore, most of e-ddm in ne/p-a homopolymerized into oligomers which degraded and evaporated at lower temperature (corresponding to the maximum weight loss peak of Pe-ddm), bringing about that the thermal stability of Pne/p-a decreased with the increase of e-ddm.

3.3.2. TGA-FTIR tests of Pp-a and P0.037e/p-a

The para-positions of phenol and aniline in b-a and p-a could react with methylene cation of e-ddm, which would inhibit the evaporation of benzene, amine, phenol and their derivatives during the thermal degradation processes of Pb-a and Pp-a. At the following, the TGA-FTIR measurements of Pp-a and P0.037e/p-a as representatives were performed to further demonstrate the above conclusion.

The FTIR spectra of evolved gases during the thermal degradation process of Pp-a are shown in Figure 9(a). A pair of bands at 3485 and 3398 cm^{-1} assigned to primary amine were detected at 280 °C, the band at 3648 cm^{-1} due to phenolic hydroxyl appeared at 340 °C, and the absorption peaks of ammonia located at 966 and 934 cm^{-1} could be observed at 380 °C.

The FTIR spectra of degradation gases of P0.037e/p-a in the range of 240–430 °C are shown in Figure 9(b). As can be seen, a pair of bands at 3409 and 3490 cm^{-1} owing to primary amine could be observed until 340 °C, the band at 3654 cm^{-1} attributed to phenolic hydroxyl appeared at 380 °C, and the characteristic peaks at 970 and 932 cm^{-1} assigned to ammonia could also be detected at 380 °C.

These results suggest that the volatilization of phenolic and amine compounds during thermal degradation processes was delayed with the introduction of e-ddm into p-a, further confirming that the para-positions of phenol and aniline moieties in benzoxazine had reacted with carbenium ions from e-ddm and been introduced into cross-linked networks of polybenzoxazine.

4. Conclusions

The FTIR and NMR results demonstrate the successful preparation of e-ddm. The DSC, FTIR, TGA and TG-FTIR results show that the carbenium ions intermediates from e-ddm could react with the para-positions of phenol and aniline moieties in b-a and p-a during the ROP process, which made phenol and aniline structure be further introduced into cross-linked networks of polybenzoxazine. Thereby, the volatilization of phenolic, amine and benzene compounds was restrained during the thermal degradation process of polybenzoxazines, resulting in that the thermal stability of Pb-a and Pp-a increased with the addition of e-ddm.

Furthermore, it could be speculated that the other benzoxazines, with unoccupied para-positions in phenolic or amine moieties, also could react with e-ddm during the ROP process, leading to that the thermal, mechanical properties and cross-linked density of polybenzoxazines would increase with the introduction of e-ddm. Thereby, it can be a new method to improve the performances of polybenzoxazine.

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