

Studies on nitrile substituted bisphenol-F and bisphenol-Z based benzoxazines with enhanced thermal and hydrophobic properties

Subasri Appasamy¹, Arumugam Hariharan¹, Govindraj Latha¹, Rathika G², Krishnasamy Balaji^{1*}, Muthukaruppan Alagar^{1*}

¹Polymer Engineering Laboratory, PSG Institute of Technology and Applied Research, Neelambur, Coimbatore – 641062, India.

²Department of Chemistry, PSG College of Arts and Science, Coimbatore–641014, India.

*Corresponding authors: muthukaruppanalagar@gmail.com, balaji.psgtech@yahoo.co.in

Abstract:

Two types of structurally different benzoxazines (BF-abn and BZ-abn) have been developed using bisphenol-F and bisphenol-Z with 4-aminobenzonitrile and paraformaldehyde through Mannich condensation reaction under an appropriate experimental conditions. Molecular structure of benzoxazine was confirmed by FTIR and ¹H-NMR spectral analyses. Cure behaviour and thermal stability were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) respectively. The results from DSC analysis indicated that these benzoxazines exhibit marginally lower polymerization temperature than that of conventional benzoxazines. Further, the curing behaviour of both benzoxazine samples were studied at two different heating rates viz. 10°C/min and 20°C/min to ascertain their heat releasing properties. The formation of polybenzoxazine was confirmed by FTIR analysis after the thermal curing through the cleavage of benzoxazine ring and subsequently led to the formation of three dimensional cross-linked network structure. Results from TGA infers that among the benzoxazines studied, poly(BF-abn) possess better thermal stability than that of poly(BZ-abn). Further, the values of LOI calculated using char yield obtained at 850°C from TGA for poly(BF-abn) and poly(BZ-abn) are 41% and 30% respectively. The values of water contact angle obtained for poly(BF-abn) and poly(BZ-abn) are 138° and 140° respectively. Both benzoxazine samples exhibit an excellent hydrophobic behaviour.

Keywords: Nitrile substituted benzoxazines, curing temperature, thermal stability, char yield, limiting oxygen index, water contact angle, hydrophobic behaviour.

Introduction

Polybenzoxazines are one of the most important and versatile classes of thermosetting high performance resinous materials, which possess good thermo-mechanical properties, good resistance to moisture, flame and microbial attack uptake, enhanced hydrophobic behaviour, low dielectric constant, excellent design flexibility and cures in the absence of catalysts and/or any curatives.^[1-3] These properties make them useful as sealants and encapsulants in electronic device fabrications, adhesives, coatings and matrices for different industrial and engineering applications.^[4] Though, the benzoxazines possess excellent properties suitable for different industrial applications and some of their deficient characteristics like brittle behaviour and the requirement of high temperature for curing limit their utility.^[5] Hence, in order to overcome these drawbacks and to widen their area of applications, the development of benzoxazine matrices with varying molecular structure and capable of contributing high performance characters are warranted. An improvement of polybenzoxazines with enhanced thermo-mechanical and electrical properties^[6] are the major challenges to expand their applications under harsh environments. Different approaches have been made to enhance their physico-chemical properties; low temperature curing behaviour, impact properties, thermal stability and desirable hydrophobicity by the skeletal modifications of benzoxazine matrices.^[7]

Sijing and Lin *et.al.*^[8, 9] reported a benzoxazine-based resin containing nitrile groups and allyl possessed satisfactory properties in curing processing and structural applications. Allyl-functional phthalonitriles-containing benzoxazine was successfully prepared with excellent properties like wide process temperature, high modulus, high T_g and high thermal stability. Unfortunately, benzoxazine-base resin exhibits brittleness, insufficient toughness, poor resistance to impact and stress cracking, which limit its wide applications in structural

materials with high toughness. To improve the brittleness of thermosetting composites, various methods were attempted, including the physical blending of thermoplastic and thermosetting resins, the chemical bonding of long molecular segments into the thermosetting resin by molecular designing.

Considering the above, the present investigation focuses on the development of new type of nitrile substituted reactive benzoxazines using bisphenol-F and bisphenol-Z and 4-aminobenzonitrile capable of curing at low temperature with enhanced thermal stability and desirable hydrophobicity through appropriate skeletal modifications of benzoxazine matrices. The properties of structurally modified benzoxazines were characterized by appropriate analytical techniques. With this in view, the present work is proposed to synthesize new bi-functional benzoxazine monomers through Mannich condensation using an appropriate phenolic compound, amino derivatives with paraformaldehyde under suitable experimental conditions. The molecular structure of the synthesized benzoxazines was ascertained from FTIR and $^1\text{H-NMR}$ analyses and curing behaviour, thermal stability and hydrophobic properties are studied using differential scanning calorimetry, thermogravimetric analysis and goniometer respectively. Data obtained from different studies are correlated, discussed and reported.

Experimental

Materials

In this work, the materials required for the synthesis of benzoxazines were bisphenol-F and bisphenol-Z procured from Rotopolymers, Chennai, India. Paraformaldehyde and 4-aminobenzonitrile were obtained from Sigma-Aldrich (India) and used as such. 1,4-dioxane and ethyl acetate were purchased from Thomas Bakers, Mumbai, India.

Measurements

FTIR spectra measurements were carried out with Agilent Cary 630 FTIR Spectrometer. NMR spectra were obtained with Bruker (400 MHz) using deuterated chloroform (CDCl_3) as a solvent and tetramethylsilane (TMS) as an internal standard. DSC measurements were recorded using NETZSCH STA 449F3 under N_2 purge (60 mL min^{-1}) at scanning rate of $10^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was obtained using NETZSCH STA 449F3 taking 5 mg of sample under N_2 flow (260 mL min^{-1}) and controlling the heating rate at $20^\circ\text{C min}^{-1}$. Contact angle measurements were obtained using a Kyowa Goniometer with $5\mu\text{l}$ of water as probe liquid.

Synthesis of bisphenol-F/ 4-aminobenzonitrile based benzoxazine (BF-abn)

5.6 g (0.05 mol) of 4-aminobenzonitrile was mixed with 5.0 g (0.025 mol) of bisphenol-F and 3.0 g (0.1 mol) of paraformaldehyde were added in portion into 100 ml double necked round bottomed flask. To this mixture 10 ml of 1,4-dioxane was added under constant stirring. Then, the temperature was raised to 110°C and maintained for about 4h until the completion of formation of benzoxazine. The progress of the reaction was monitored with thin layer chromatography (TLC) (7:3 hexane: ethyl acetate solvent). After completion of the reaction, the resinous crude product obtained was dissolved in 50 ml of ethyl acetate and washed twice with 2N NaOH for removal of unreacted phenolic compounds. Further, the organic layer was washed twice with 100 ml of distilled water. Then, the organic phase was dried over anhydrous Na_2SO_4 and ethyl acetate was removed using the rotary evaporator and the product resulted was recovered. The synthesized bisphenol-F based benzoxazine was labelled as BF-abn (Scheme 1).

Synthesis of bisphenol-Z / 4-aminobenzonitrilebenzoxazine (BZ-abn)

4.73 g (0.04 mol) of 4-aminobenzonitrile was mixed with 5.40 g (0.02 mol) of bisphenol-Z and 2.40 g (0.08 mol) of paraformaldehyde were added in portion into 100 ml double necked round bottomed flask. To this mixture 10 ml of dioxane was added and kept under constant

stirring. Rest of the steps had been followed according to the synthesis procedure adopted for BF-abn. The synthesized bisphenol-Z based benzoxazine was labelled as BZ-abn (Scheme 2).

Synthesis of BF and BZ-based polybenzoxazines

The bisphenol-based polybenzoxazines (Schemes 3 and 4), poly(BF-abn) and poly(BZ-abn) were prepared through thermal ring opening polymerization. In brief, the respective benzoxazines were separately dissolved in 1,4-dioxane and sonicated to obtain the homogenous products. The resultant products obtained were separately heated at 80°C for 8 h in an oven to remove the solvent. After the removal of solvent, the temperature was gradually raised to 230°C at a heating rate of 20°C/h. The heating was further continued for another 3 h at 230°C for complete curing. The polymerization of benzoxazine samples were confirmed from infrared spectroscopic analysis. At this temperature, the benzoxazine monomers undergo ring-opening polymerization to form polybenzoxazines with three dimensional cross-linked network structure^[10] (Figure S1).

Results and discussion

The new types of benzoxazine monomers were synthesized via one-step Mannich condensation reaction of bisphenol-F and bisphenol-Z with 4-aminobenzonitrile and paraformaldehyde under suitable experimental conditions. The molecular structure of the synthesized benzoxazine monomers namely BF-abn and BZ-abn and their respective polybenzoxazines, poly(BF-abn) and poly(BZ-abn) were confirmed from FTIR and ¹H-NMR spectral analyses.

FTIR spectral analysis

The FTIR spectra of benzoxazines (BF-abn and BZ-abn) are presented in Figure 1. The band appeared at around 1221 cm⁻¹ represents the C–O–C asymmetric stretching and a band appeared at 1083 cm⁻¹ was attributed to the symmetric stretching vibrations of C–O–C bond present in the benzoxazines.^[11] The appearance of a peak at 1115 cm⁻¹ confirms the presence of asymmetric stretching of C–N–C. Similarly, the appearance of the band at around 964 cm⁻¹

ascertains the formation of benzoxazine ring structure.^[12] Further, the band appeared at around 3100–2950 cm⁻¹ corresponds to C–H stretching vibrations of the benzene ring and absorption peaks appeared at around 2950 and 2850 cm⁻¹ represent the asymmetric and symmetric stretching vibrations of oxazine ring as well as –CH₂– of bisphenol-F and bisphenol-Z moiety respectively.

¹H-NMR spectral analysis

The molecular structures of BF-abn and BZ-abn benzoxazines were confirmed by ¹H-NMR spectra. The ¹H-NMR spectra of BF-abn and BZ-abn benzoxazines are given in Figures 2 and 3 respectively. In the ¹H-NMR spectrum, the aryl-substituted benzoxazine monomer (BF-abn) and (BZ-abn) exhibits two characteristic resonance signals at around 4.5 ppm (singlet, 2H) for aryl substituted methylene group of oxazine ring -N-CH₂-Ar and 5.5 ppm (singlet, 2H) for oxygen and nitrogen bonded methylene group of benzoxazine molecule^[13] -N-CH₂-O-.

Curing behaviour of benzoxazine monomers

The curing behaviour of BF-abn and BZ-abn benzoxazines were studied by DSC analysis at two different heating rates viz., 10°C/min. and 20°C/min. under a nitrogen atmosphere. The DSC thermograms of BF-abn and BZ-abn shows that the exothermic peaks shifted to higher temperatures with an increase of heating rate (Figures 4 and 5)^[14]. From Figure 4 (10°C/min), an exothermic peak maximum observed for benzoxazine ring opening polymerisation and the cyclotrimerization of cyano groups. The curing temperature of the benzoxazine monomers BF-abn and BZ-abn are 223°C and 237°C respectively (Figure 4)^[10] (Schemes 3 and 4). Similar curing trend was also reported by Yanfang Liu et al. on bisphenol-A and aminobenzonitrile based benzoxazine (BA-abn).^[15] BF-abn and BZ-abn benzoxazine curing temperature is lesser than BA-abn (T_p ~260°C). Nitrile substituted benzoxazines shows higher curing temperature than aniline based benzoxazines (Table 1).^[15–17]

FTIR analysis of polybenzoxazine

The absorption bands of N–C–O appeared at 964 cm^{-1} (oxazine ring) disappeared after thermal curing at 250°C for 2h infers the cleavage of benzoxazine ring and the formation of polybenzoxazine (Figure 6). Upon thermal curing, the bond exists between oxymethylene and nitrogen gets cleaved followed by the rearrangement with ortho hydrogen present in the neighbouring oxazine ring by the reactive methylene group and thus facilitates the occurrence of polymerization.^[18] The schematic representation for the synthesis of polybenzoxazines are presented in Schemes 3 and 4.

Thermal stability of polybenzoxazine

The thermal stability of the cured BF-abn and BZ-abn benzoxazines was studied by TGA at the heating rate of $20^{\circ}\text{C}/\text{min}$. under nitrogen atmosphere and the results obtained are presented in Figure 7. The data obtained from TGA studies are presented in Table 2. It was noticed that, there was no weight loss below 150°C which infers the complete removal of solvents/water from the samples. The 5% weight loss of cured polybenzoxazines viz., poly(BF-abn) and poly(BZ-abn) was noticed at above 320°C , respectively and the values of the 10% weight loss observed are 350 and 345°C respectively. The values of maximum degradation temperature (T_{max}) were observed at 450 and 420°C for poly(BF-abn) and poly(BZ-abn) respectively. The yield of residual char obtained at 850°C for polybenzoxazines [poly(BF-abn) and poly(BZ-abn)] are 58% and 32%, respectively. All the nitrile substituted benzoxazines possesses better thermal stability than aniline based benzoxazines (Table 2),^[15–17] due to the presence of triazine cross-linkages in the matrix system.^[19] Among the benzoxazine samples studied, the poly(BF-abn) possesses better thermal properties than that of poly(BA-abn)^[15] and poly(BZ-abn).

Flame retardant behaviour

The flame retardant behaviour of the cured benzoxazines is also ascertained by using the value of residual char yield. Limiting oxygen index (LOI) value is calculated from van Krevelen equation^[20] [eq. 1] and the results obtained are presented in Table 2.

$$\text{LOI}=17.5+0.4(\theta) \text{ ----- (1)}$$

Where θ is the percentage char yield of materials remains at 850°C.

The char yield of the polybenzoxazines poly(BF-abn) and poly(BZ-abn) was found to be high in the range of 58% and 32% respectively indicating their high flame retardant behaviour, which is expressed in terms of their LOI value. The LOI values of the polymers should be above the threshold value of 26, to render them self-extinguishing and for their qualification for many applications requiring good flame resistance^[21]. It was found that the LOI increases with increasing char yield as expected. The polybenzoxazines synthesized in the present work show the LOI value greater than 26 confirming their good flame retardant properties. The values of LOI obtained for poly(BF-abn) and poly(BZ-abn) are 41 and 30 respectively. Specifically, poly(BF-abn) possesses the higher LOI value than that of poly(BZ-abn), due to the presence of triazine based cross linked network structure.

Water contact angle studies

The water contact angle images and values of water contact angle of poly(BF-abn) and poly(BZ-abn) are presented in Figure 8. The values of water contact angle obtained for poly(BF-abn) and poly(BZ-abn) are 138° and 140° respectively. The lower affinity of the developed polybenzoxazines towards water indicates its hydrophobic nature. These benzoxazines possess better hydrophobic behaviour than that of existing conventional organic matrices. Among the benzoxazine samples developed in the present work, the poly(BZ-abn) possesses better hydrophobic character than that of poly(BF-abn), due to the presence of cyclohexane (alicyclic) moiety.^[22]

Conclusion

An attempt has been made in the present work to develop a structurally different benzoxazines using bisphenol-F and bisphenol-Z with 4-aminobenzonitrile and paraformaldehyde through Mannich condensation reaction in order to study and compare their cure behaviour, thermal stability and hydrophobic properties. The results from thermal analysis indicated that these materials exhibit the marginally lower polymerization temperature than that of conventional benzoxazines with improved thermal stability. Among, the benzoxazines synthesized, the bisphenol-F based benzoxazine possesses lower curing temperature and better thermal stability than those of bisphenol-Z based benzoxazine. Both benzoxazines exhibit excellent hydrophobic behaviour nearing super hydrophobicity. Data obtained from different studies suggests that the benzoxazine developed in the present work can be conveniently used in the form sealants, adhesives, encapsulants, and matrices where application demands high thermal stability, flame resistance and resistant to moisture.

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Conflict of interest

The authors declare no conflict of interest.

References

1. Shukla, S.; Yadav, N.; Lochab, B. Cardanol-Based Benzoxazines and Their Applications; Elsevier Inc. **2017**, 451-472. DOI.org/10.1016/B978-0-12-804170-3.00024-X

2. Low, H.Y.; Ishida, H. Improved thermal stability of polybenzoxazines by transition metals. *Polym. Degrad. Stab.* **2006**, 91, 805–815.
<https://doi.org/10.1016/j.polymdegradstab.2005.05.030>
3. Arumugam, H.; Mohamed, I. A. A.; Govindraj, L.; Muthukaruppan, A. Development of bio-based benzoxazines coated melamine foam for oil-water separation. *Prog. Org. Coatings* **2021**, 153, 106128. DOI:org/10.1016/j.porgcoat.2020.106128
4. Lin, C. M.; Chen, C.H.; Lin, C.H.; Juang, T. Y. High-performance bio-based benzoxazines derived from phosphinated biphenols and furfurylamine. *Eur. Polym. J.* **2018**, 108, 48–56. DOI:org/10.1016/j.eurpolymj.2018.08.024
5. Krishnadevi, K.; Devaraju, S.; Sriharshitha, S. et al. Environmentally sustainable rice husk ash reinforced cardanol based polybenzoxazine bio-composites for insulation applications. *Polym. Bull.* **2020**, 77, 2501–2520. DOI.org/10.1007/s00289-019-02854-4
6. Zhu, C.; Gao, X.; Fan, W.; Fu, X. Synthesis, characterization, and properties of a novel aromatic ester-based polybenzoxazine. *RSC Adv.* **2020**, 10, 6953–6959.
DOI.org/10.1039/c9ra10191h
7. Zhang, D.; Wang, L.; Qian, H.; Li, X. Superhydrophobic surfaces for corrosion protection: a review of recent progresses and future directions. *J. Coatings Technol. Res.* **2016**, 13, 11–29. DOI.org/10.1007/s11998-015-9744-6
8. Chen, S.; Ren, D.; Li, B. et al. Benzoxazine containing fluorinated aromatic ether nitrile linkage: Preparation, curing kinetics and dielectric properties. *Polymers* **2019**, 11, 1036- 1054. DOI.org/10.3390/polym11061036
9. Chen, L.; Ren, D.; Chen, S. et al. Improved thermal stability and mechanical properties of benzoxazine-based composites with the enchantment of nitrile. *Polym. Test.* **2019**, 74:127–137. DOI.org/10.1016/j.polymertesting.2018.11.032
10. Arslan, M.; Kiskan, B.; Yagci, Y. Ring-opening polymerization of 1,3-benzoxazines via borane catalyst. *Polymers* **2018**, 10, 1–13. DOI.org/10.3390/polym10030239

11. Minigher, A.; Benedetti, E.; De Giacomo, O. et al. Synthesis and Characterization of Novel Cardanol Based Benzoxazines. *Nat. Prod. Commun.* **2019**, *4*, 521-528.
DOI.org/10.1177/1934578x0900400416
12. Dumas, L.; Bonnaud, L.; Olivier, M. et al. Eugenol-based benzoxazine: From straight synthesis to taming of the network properties. *J. Mater. Chem. A* **2015**, *3*, 6012–6018.
DOI.org/10.1039/c4ta06636g
13. Calò, E.; Maffezzoli, A.; Mele, G. et al. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. *Green Chem.* **2007**, *9*, 754-759. DOI.org/10.1039/b617180j
14. Zhang, K.; Liu, Y.; Han, L. et al. Synthesis and thermally induced structural transformation of phthalimide and nitrile-functionalized benzoxazine: toward smart ortho-benzoxazine chemistry for low flammability thermosets. *RSC Adv.* **2019**, *9*, 1526–1535. DOI.org/10.1039/C8RA10009H
15. Liu, Y.; Zhao, S.; Zhang, H. et al. Synthesis, polymerization, and thermal properties of benzoxazine based on p-aminobenzonitrile. *Thermochim. Acta* **2012**, *549*, 42–48.
DOI.org/10.1016/j.tca.2012.09.017
16. Hariharan, A.; Srinivasan, K.; Murthy, C.; Alagar, M. A Novel Imidazole-Core-Based Benzoxazine and Its Blends for High-Performance Applications. *Ind. Eng. Chem. Res.* **2017**, *56*, 9347–9354. DOI.org/10.1021/acs.iecr.7b01816
17. Sasi Kumar R.; Ariraman, M.; Alagar, M. Studies on dielectric properties of GO reinforced bisphenol-Z polybenzoxazine hybrids. *RSC Adv.* **2015**, *5*, 23787–23797.
DOI.org/10.1039/c5ra00472a
18. Lochab, B.; Varma, I. K.; Bijwe, J. Thermal behaviour of cardanol-based benzoxazines: Monomers and polymers. *J. Therm. Anal. Calorim.* **2010**, *102*, 769–774.
DOI.org/10.1007/s10973-010-0736-6
19. Abuzeid, H. R.; El-Mahdy, A.F.M.; Ahmed, M.M.M.; Kuo, S.W. Triazine-

functionalized covalent benzoxazine framework for direct synthesis of N-doped microporous carbon. *Polym. Chem.* 2019, 10, 6010–6020.

DOI.org/10.1039/c9py01231a

20. van Krevelen, D. W. Some basic aspects of flame resistance of polymeric materials. *Polymer* **1975**, 16, 615–620. DOI.org/10.1016/0032-3861(75)90157-3
21. Chen, T.; Wang, X.; Peng, C. et al. Efficient Flame Retardancy, Smoke Suppression, and Mechanical Enhancement of β -FeOOH@Metallo-Supramolecular Polymer Core–Shell Nanorod Modified Epoxy Resin. *Macromol Mater Eng.* 2020, 305, 2000137. DOI.org/10.1002/mame.202000137
22. Arumugam, H.; Pichaimani, P.; Manickam, M.; Muthukaruppan, A. Studies on heterocyclic amines based cardanol-benzoxazine for oil-water separation. *Polym. Engg. Sci.* **2020**, 60, 1494-1506. <https://doi.org/10.1002/pen.25396>

DRAFT

Scheme Captions

Scheme 1. Synthesis of bisphenol-F /4-aminobenzonitrile benzoxazine (BF-abn)

Scheme 2. Synthesis of bisphenol-Z/4-aminobenzonitrile benzoxazine (BZ-abn)

Scheme 3. Synthesis of poly(BF-abn)

Scheme 4. Synthesis of poly(BZ-abn)

Scheme 5. The general curing mechanism of benzoxazines

Figure Captions

Figure 1. FTIR spectra of benzoxazine monomers

Figure 2. ¹H-NMR spectrum of BF-abn benzoxazine

Figure 3. ¹H-NMR spectrum of BZ-abn benzoxazine

Figure 4. DSC traces of benzoxazines at the heating rate of 10°C/min

Figure 5. DSC traces of benzoxazines at the heating rate of 20°C/min

Figure 6. FTIR spectra of polybenzoxazines and their respective monomers

Figure 7. TGA traces of polybenzoxazines

Figure 8. The water contact angle of (a) poly(BF-abn) (b) poly(BZ-abn)

Table Captions

Table 1. The curing behaviour of bisphenol based benzoxazines

Table 2. Thermal stability of bisphenol based polybenzoxazine

Tables

Table 1. The curing behaviour of bisphenol based benzoxazines

Bisphenol based benzoxazines	Curing behaviour at different heating rate					
	10°C/min			20°C/min		
	T _i	T _p	T _f	T _i	T _p	T _f
BA-a [15]	165	223	284	--	--	--
BF-a[15]	159	212	278	--	--	--
BZ-a [16]	175	215	275	--	--	--
BA-abn [14]	200	260	310	--	--	--
BF-abn	143	223	278	212	246	288
BZ-abn	201	237	283	225	257	302

T_i initial peak temperature

T_p exothermic peak maximum temperature

T_f final peak temperature

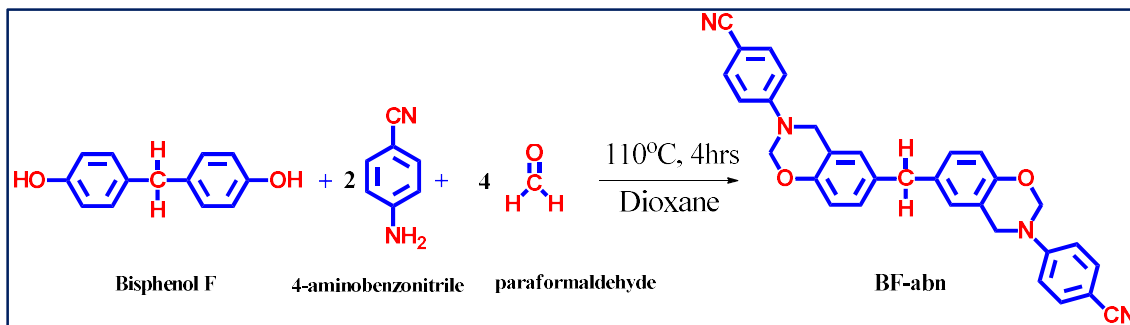
Table 2. Thermal stability of bisphenol based polybenzoxazine

Bisphenol based benzoxazines	Thermal stability				
	5% wt loss (°C) ¹	10% wt loss (°C) ¹	T _{max} (°C) ¹	Char ¹ yield % at 850°C	LOI ² (%)
Poly(BA-a)[15]	332	351	419	28	29
Poly(BF-a)[15]	316	343	440	25	28
Poly(BZ-a)[16]	200	316	430	12	22
Poly(BA-abn)[14]	300	325	425	43	35
Poly(BF-abn)	320	350	450	58	41
Poly(BZ-abn)	324	345	420	32	30

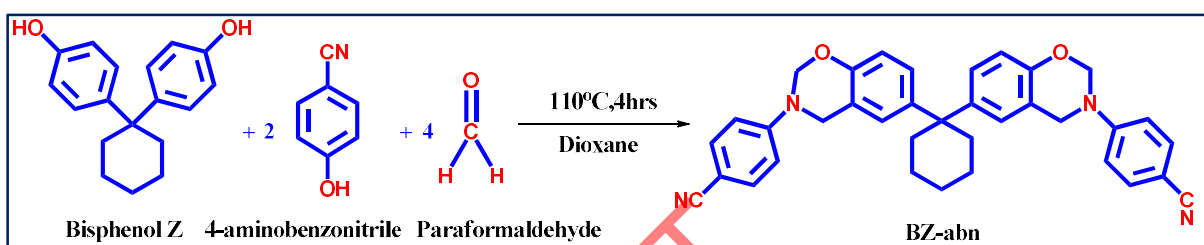
¹The values were determined by TGA at a heating rate of 20°C/min in nitrogen atmosphere

²Determined using van Krevelen's equation

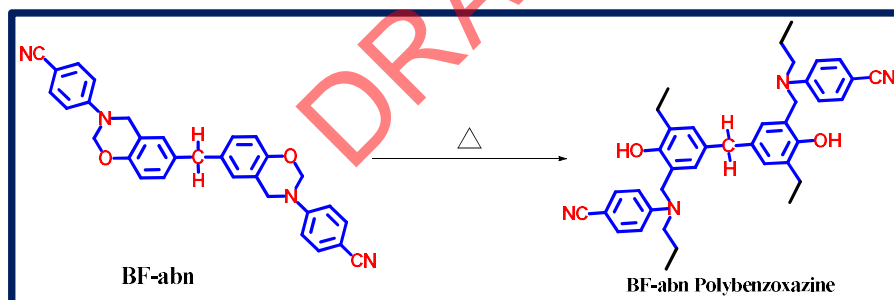
Schemes and Figures



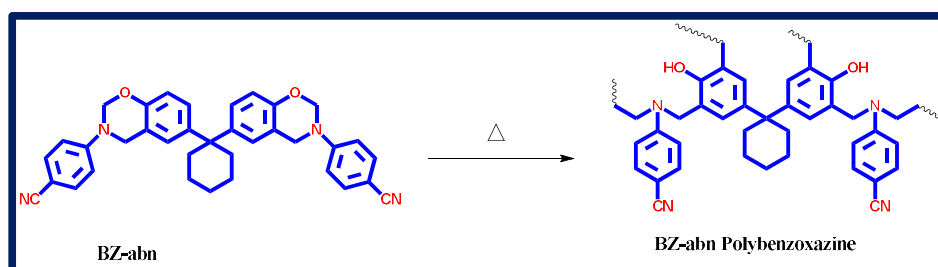
Scheme 1. Synthesis of bisphenol-F /4-aminobenzonitrile benzoxazine (BF-abn)



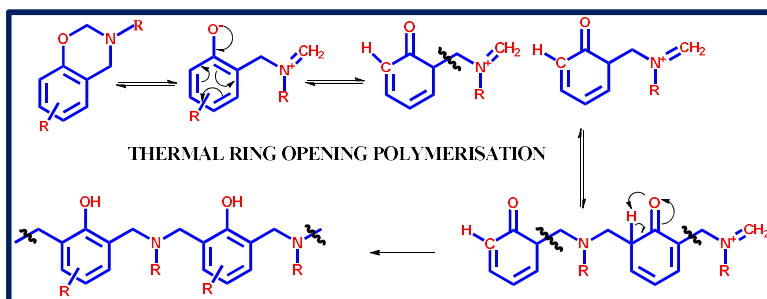
Scheme 2. Synthesis of bisphenol-Z/4-aminobenzonitrile benzoxazine (BZ-abn)



Scheme 3. Synthesis of poly(BF-abn)



Scheme 4. Synthesis of poly(BZ-abn)



Scheme 5. The general curing mechanism of benzoxazines

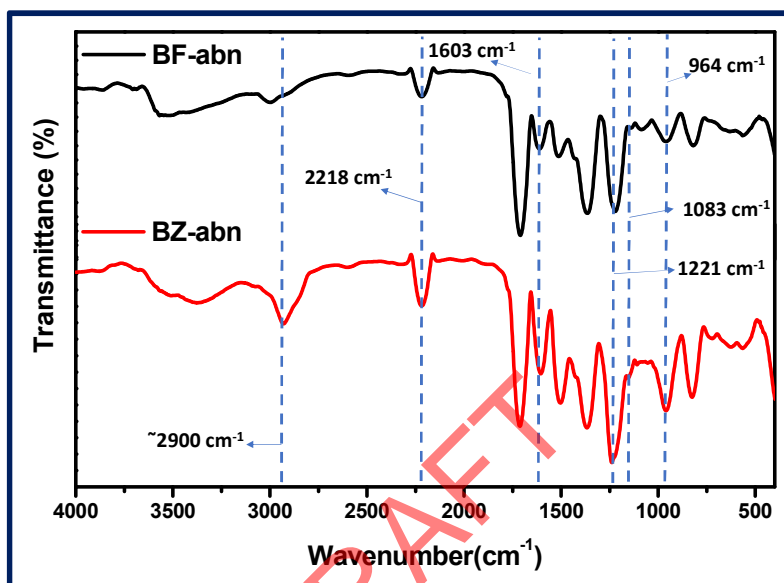


Figure 1. FTIR spectra of benzoxazine monomers

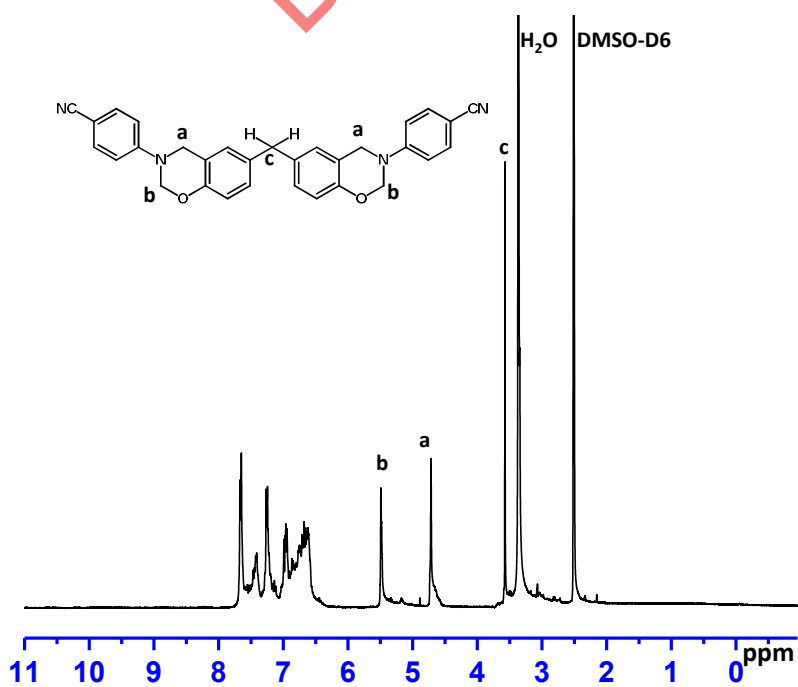


Figure 2. ¹H-NMR spectrum of BF-abn benzoxazine

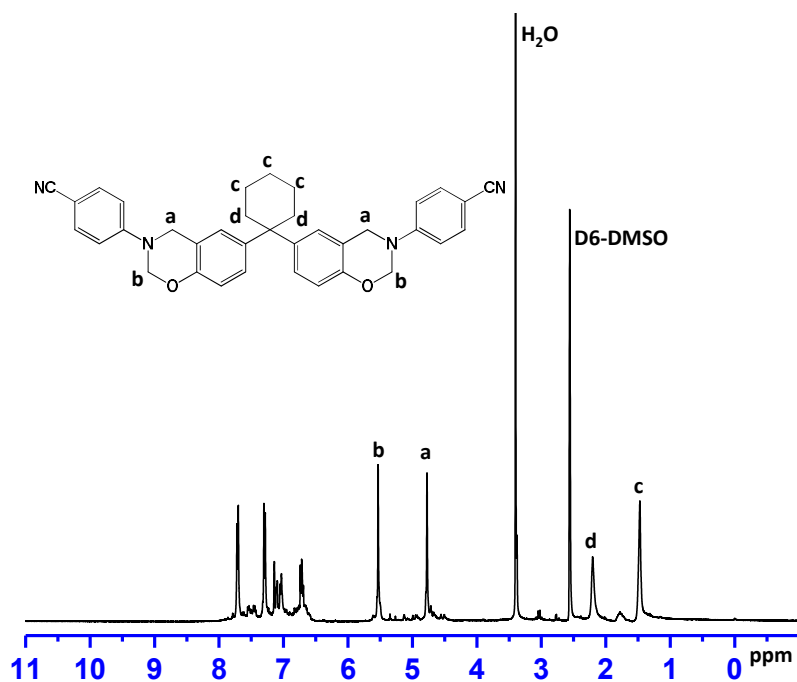


Figure 3. $^1\text{H-NMR}$ spectrum of BZ-abn benzoxazine

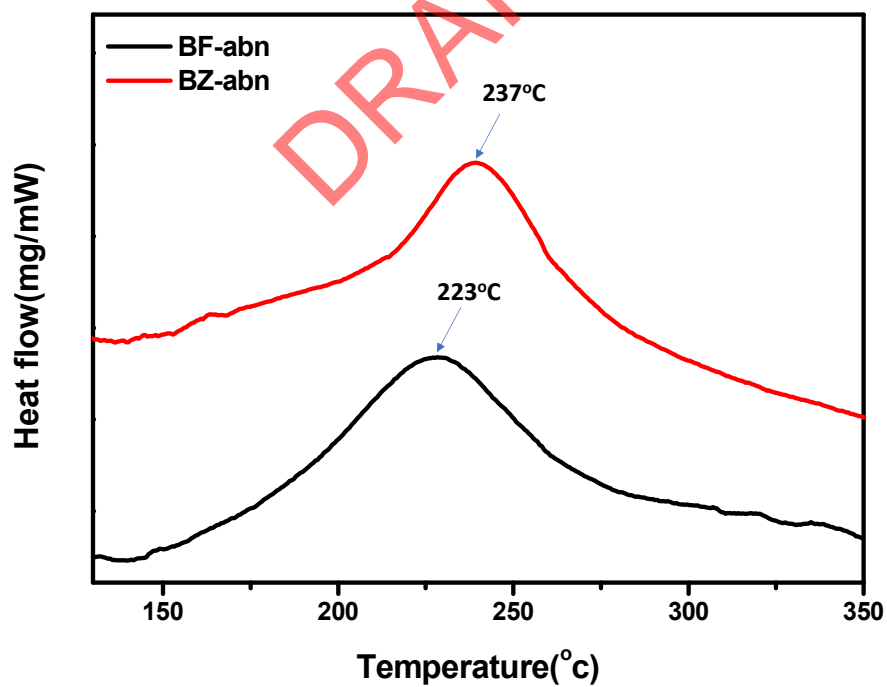


Figure 4. DSC traces of benzoxazines at the heating rate of $10^\circ\text{C}/\text{min}$

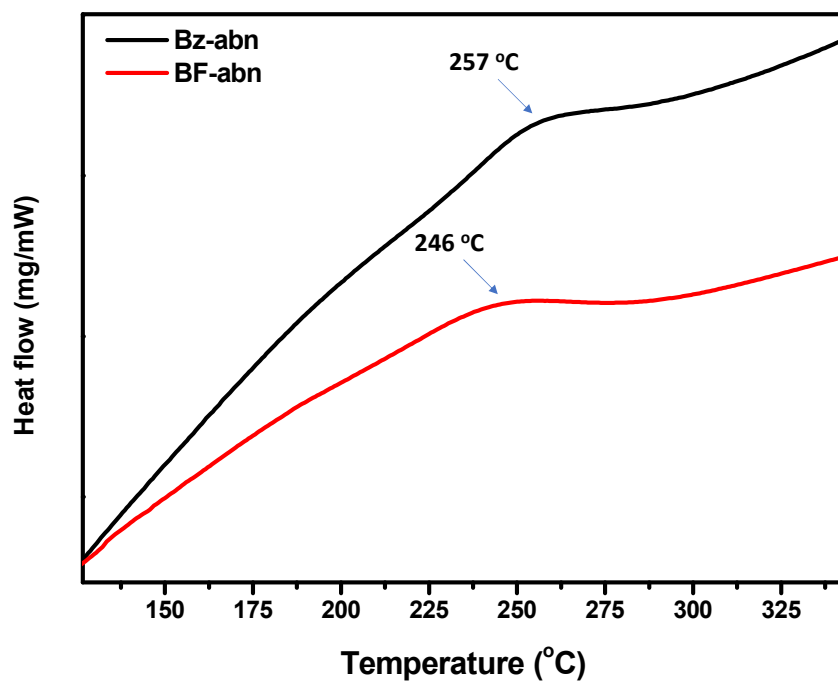


Figure 5. DSC traces of benzoxazines at the heating rate of 20°C/min

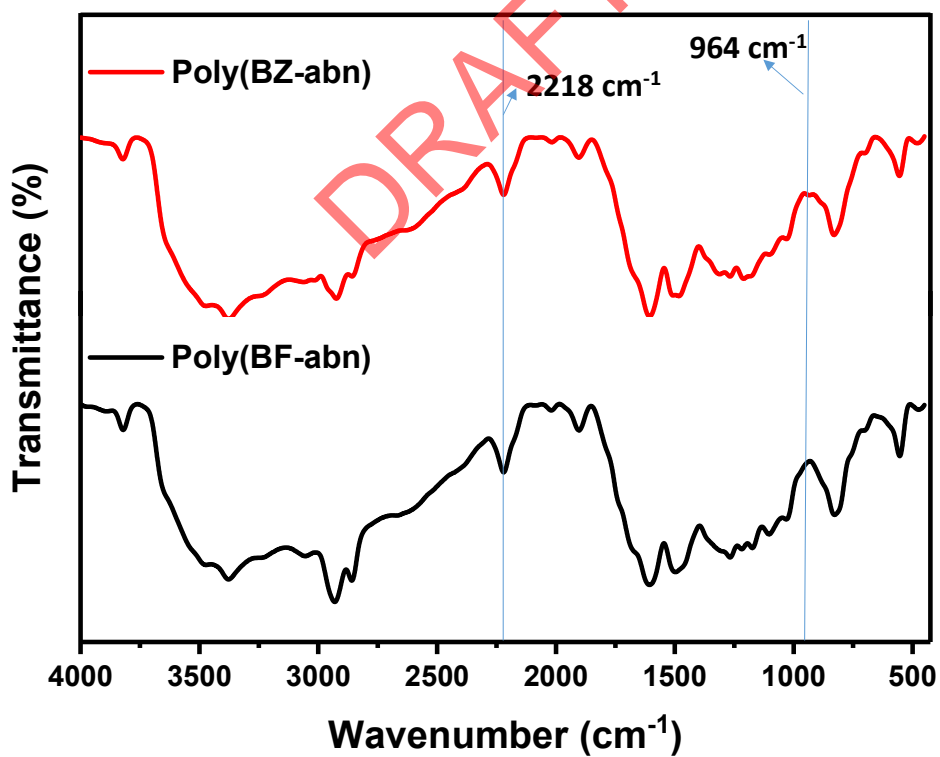


Figure 6. FTIR spectra of polybenzoxazines

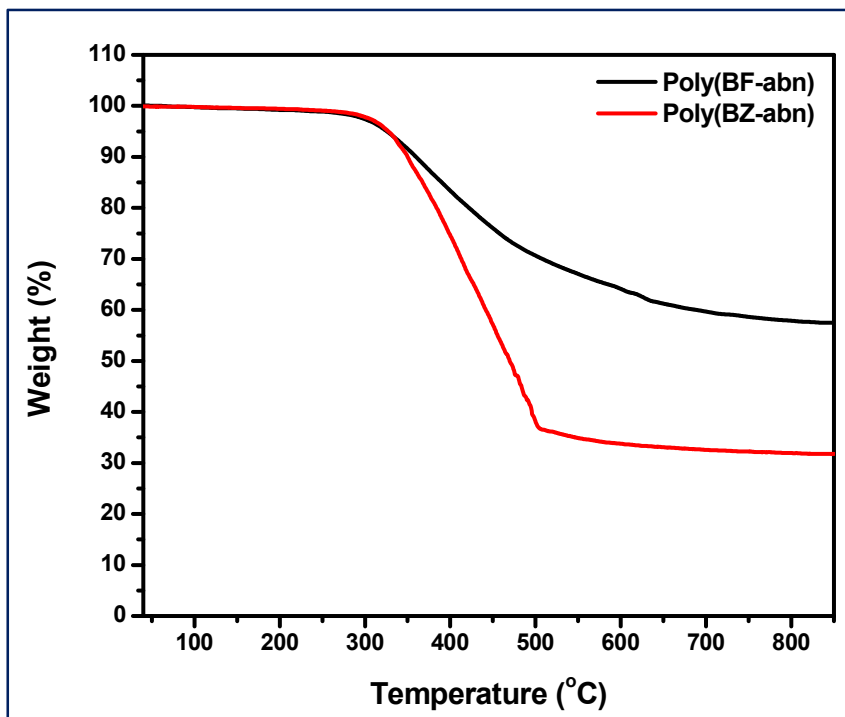


Figure 7. TGA traces of polybenzoxazines

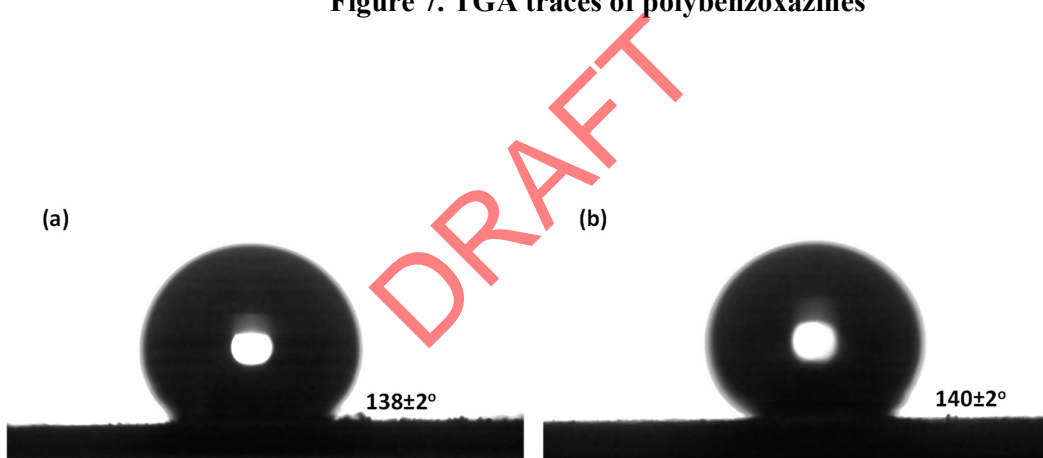


Figure 8. The water contact angle of (a) poly(BF-abn) (b) poly(BZ-abn)