

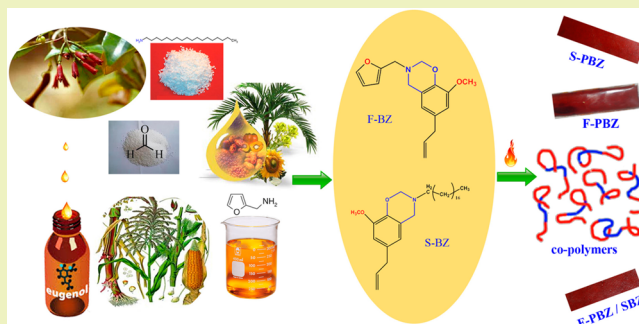
Synthesis and Copolymerization of Fully Biobased Benzoxazines from Renewable Resources

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ABSTRACT: A solventless method was adopted to synthesize two benzoxazine monomers from naturally occurring sources, i.e., eugenol (an extraction from clove), furfurylamine, stearylamine, and paraformaldehyde. The structure of the extracted eugenol and synthesized monomers were supported by FT-IR, ^1H NMR, ^{13}C NMR, and mass spectral analysis. The monomers were polymerized/copolymerized via ring-opening polymerization by heating as shown by FT-IR (disappearance of the peak due to oxazine ring at 920 cm^{-1}) and differential scanning calorimetry (DSC). The exothermic peak associated with curing was observed between $198\text{--}254\text{ }^\circ\text{C}$. DSC analysis shows that the onset of curing temperature for the copolymers decreased linearly from $207\text{--}202\text{ }^\circ\text{C}$ on increasing the content of F-Bz. The results from TGA analysis indicate that PF-Bz shows the maximum thermal stability when compared with PS-Bz and their copolymers. In the case of the copolymers, as the F-Bz content is increased, the thermal stability also increases. All the polymers also exhibit good flame retardant properties as shown by their LOI values (more than 26).

KEYWORDS: Eugenol, Biobased benzoxazines, Solventless method, Cross-link density, Flame retardancy



INTRODUCTION

Benzoxazine is a newly developed thermosetting phenolic resin, and it can be synthesized via Mannich condensation from phenol, amine, and formaldehyde.^{1,2} Benzoxazine has a single benzene ring fused to another six-membered heterocycle containing one oxygen atom and one nitrogen atom. There are a number of possible isomeric benzoxazines, depending on the relative position of the two hetero atoms of the oxazine ring system. Benzoxazine monomers can be polymerized by a thermally activated ring-opening polymerization reaction with no reaction by-products released and no catalyst required.^{3,4}

During the self-cross-linking polymerization reaction, the Mannich bridge structure $-\text{CH}_2-\text{NR}-\text{CH}_2$ was formed between benzoxazine molecules through the ring-opening reaction of the oxazine ring.⁵⁻⁷ So, as the polymerization proceeds, benzoxazine gradually gets converted into a three-dimensional network of polybenzoxazine. The benzoxazine-based materials possess excellent mechanical and thermal properties ($350\text{--}400\text{ }^\circ\text{C}$), high dimensional stability, low water absorption, high char yield ($28\text{--}66\%$), and near zero shrinkage upon curing, which make them a promising matrix candidate for high-performance composites especially in the microelectronics, aerospace, and packaging industries.⁸ The main strategies for tailoring the molecular structures of polybenzoxazine can be classified into three groups: (i) modification of benzoxazine monomers with additional functionalities, (ii) incorporation of benzoxazine moieties into polymer chains, and (iii) copolymerization of two or more benzoxazine monomers.⁹ Nowadays, the development of a biobased polymer (based on renewable organic raw materials)

using alternative sustainable processes deserves the increasing attention of both academic and industrial research.^{10,11}

In this study, eugenol, furfurylamine, stearylamine, and paraformaldehyde were chosen as raw materials (from natural source) to synthesize polybenzoxazines and its copolymers. Eugenol is a member of the phenyl propanoids class of chemical compounds. The name is derived from the scientific name for clove, *Eugenia aromaticum* or *Eugenia caryophyllate*. Clove is commercially cultivated in India, Madagascar, Sri Lanka, Indonesia, and South China. Eugenol is responsible for the aroma of cloves. It is the main component in the essential oil extracted from cloves comprising $72\text{--}90\%$ of the total. It is a clear to pale yellow oily liquid extracted from certain essential oils especially from clove, nutmeg, cinnamon, basil, and bay leaf. It is slightly soluble in water and soluble in organic solvents. It has a spicy clove-like aroma. Clove oil is widely used for flavoring pastry, special sauces, and condiments. It is also used in medicines, especially in preparations for the gums and teeth.¹²⁻¹⁴ Furfurylamine is a colorless to yellow liquid with an ammonia odor. It is an intermediate in the synthesis of many pharmaceutical, agricultural, and industrial chemicals. It is derived from corn cobs and wheat bran, which are agricultural byproducts. Stearylamine is obtained from vegetable oils. Paraformaldehyde is the smallest polyoxymethylene, which is the polymerization product of formaldehyde with a typical degree

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Scheme 1. Synthesis of Benzoxazine Monomers

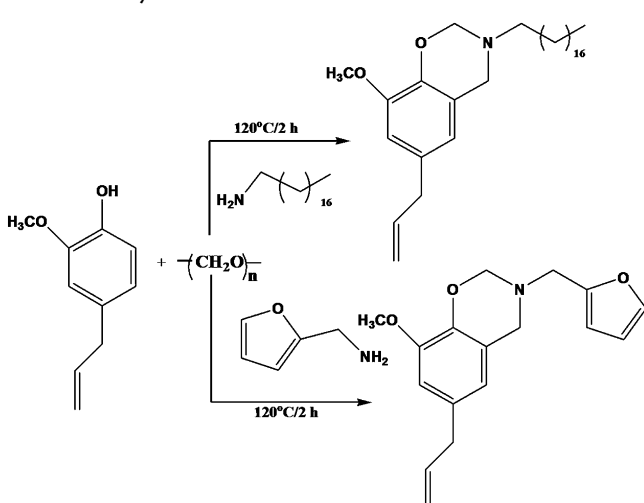


Table 1. DSC Data of F-Bz, S-Bz, and Their Copolymers

sample no.	sample	mole ratio S-Bz/F-Bz	T_m (°C)	T_{onset} (°C)	T_{max} (°C)	$T_{processing\ window}$ (°C)
1	a	1:0	49	218	231	169
2	b	3:1	49, 74	207	246	133
3	c	1:1	49, 74	204	243	130
4	d	1:3	49, 74	202	226	128
5	e	0:1	74	198	222	124

of polymerization of 8–100 units. Paraformaldehyde commonly has a slight odor of formaldehyde due to decomposition.

The extraction of eugenol, synthesis of benzoxazine monomers, and copolymerization, along with the characterization, thermal polymerization, and thermo-mechanical properties of these new benzoxazines are described. The curing behavior of the individual benzoxazine monomers (F-Bz and S-Bz) and their effect on copolymerization has been investigated.

EXPERIMENTAL SECTION

Materials. Stearylamine was purchased from Sisco Research Laboratories, Pvt. Ltd., India. Furfurylamine was purchased from Aldrich, India. Paraformaldehyde was purchased from Merck Limited, India. Dichloromethane (DCM) was purchased from Alfa Aesar (Johnson Mathew Company), India, Pvt. Ltd. Tetrahydrofuran (THF) was purchased from Fisher Scientific (a part of Thermo Fisher Scientific, India, Pvt. Ltd.). All other chemicals are of analytical grade and were purchased from Spectrochem Pvt. Ltd., India. All chemicals were used without further purification.

Instrumentation. Fourier transform infrared (FT-IR) spectra of the samples were obtained using an ABB Bomem (Model MB 3000) spectrometer. The samples were ground with spectroscopy-grade KBr and made into pellets. ^1H (500 MHz) and ^{13}C (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Joel spectrometer with tetramethylsilane (TMS) as the internal standard. Solutions were prepared in CDCl_3 . Differential scanning calorimetry (DSC) was performed in a TA Instruments Q₁₀ model using 5–10 mg of the sample at a heating rate of 10 °C/min in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out using a Netzsch 242 DMA at a heating rate of 10 °C/min from 30 to 250 °C. The glass transition temperature (T_g) values were obtained by second heating scans; the samples were heated from room temperature to 350 °C, cooled to room temperature, and heated again to 350 °C under a nitrogen atmosphere. The heating rate of the second scans was 10 °C/min. The halfway point between the two tangent lines above

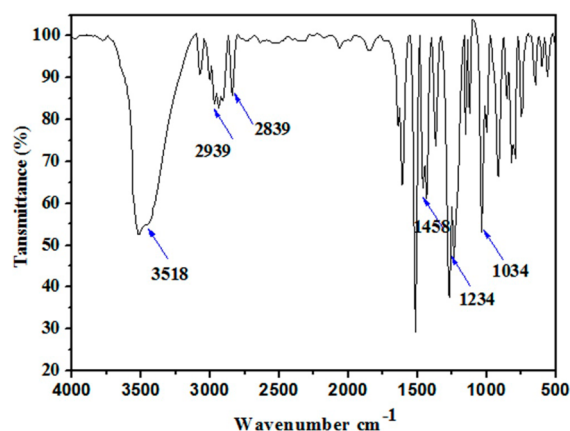


Figure 1. FT-IR spectrum of eugenol.

and below the transition region of the second scan curve is defined as T_g . Thermogravimetric analysis (TGA) was performed using a TA Q 600 thermal analyzer. Cured samples were analyzed in an open silicon pan at a heating rate of 20 °C/min in a nitrogen atmosphere, up to a maximum temperature of 800 °C.

Extraction of Eugenol. Fifteen grams of cloves was taken and crushed well. It was then transferred into a 250 mL round-bottomed flask and to it distilled water (150 mL) was added, and the contents were heated to 50 °C. When the solution begins to boil, the condensed vapor was collected as a milky white distillate in an Erlenmeyer flask. The distillation process was continued until no more oily material was seen in the condenser. The distillate was transferred into a 250 mL separatory funnel and to it 25 mL of dichloromethane was added. Two layers were formed, which were separated. To the organic layer, a 5% solution of KOH was added, and the aqueous layer was separated. The process was repeated twice, and the combined aqueous layer was acidified by using 5% HCl dropwise until the solution turned cloudy. To the cloudy solution, dichloromethane was added, from which the organic layer was separated. The organic layer (dichloromethane layer) was further washed with distilled water, and the separated organic layer was washed with 15 mL of saturated sodium chloride solution. The organic layer thus obtained was dried with anhydrous sodium sulfate. The dichloromethane solution was further distilled to get a pale yellow viscous liquid of eugenol.^{15,16} Yield: 65%. FT-IR (KBr, cm^{-1}): 3521, 3078, 3009, 2970, 2939, 2901, 2839, 1643, 1612, 1512, 1458, 1435, 1366, 1273, 1237, 1149, 1120, 1034, 995, 910, 849, 818, 749, 648, 549, 555. ^1H NMR (CDCl_3 , ppm): 3.31 (d, 2H), 3.82 (s, 3H), 5.08 (d, 2H), 5.66 (s, 1H), 5.95 (m, 1H), 6.5–7.0 (m, 3H). ^{13}C NMR (CDCl_3 , ppm): 40, 56, 110, 114, 115, 121, 132, 137, 144, 146; m/e value, 163.0

Synthesis of 6-Allyl-3-furfuryl-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine [F-Bz]. Eugenol (0.05 mol, 8.2 g), furfurylamine (0.05 mol, 4.85 g), and paraformaldehyde (0.1 mol, 3 g) were mixed and stirred at room temperature until the solid was dissolved. After which the mixture was heated to 100 °C for 2 h, cooled to room temperature, and concentrated under reduced pressure. The residual solid was crystallized from ethanol at 70 °C, filtered, and dried under vacuum to obtain F-Bz as a pale yellow powder. Yield: 91%, mp, 74 °C. FT-IR (KBr, cm^{-1}): 2908, 2839, 1589, 1497, 1458, 1296, 1227, 1149, 1011, 920, 833, 733. ^1H NMR (CDCl_3 , ppm): 3.21 (d, 2H), 3.80 (s, 3H), 3.85 (s, 2H), 3.97 (s, 2H), 4.88 (s, 2H), 5.03 (d, 2h), 5.87 (m, 1H), 6.25–6.84 (m, 4H), 7.29 (d, 1H). ^{13}C NMR (CDCl_3 , ppm): 39, 47, 48, 55, 81, 108, 109, 114, 115, 118, 120, 131, 136, 139, 141, 146, 152; m/e value, 285.80 (Scheme 1).

Synthesis of 6-Allyl-3-octadecyl-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine [S-Bz]. Eugenol (0.05 mol, 8.2 g), stearylamine (0.05 mol, 13.5 g), and paraformaldehyde (0.1 mol, 3 g) were mixed and stirred at room temperature until the solids were dissolved. The solution was then heated to 100 °C for 2 h, cooled to room temperature, and concentrated under reduced pressure. The residual solid was crystallized from ethanol at 70 °C, filtered, and dried under

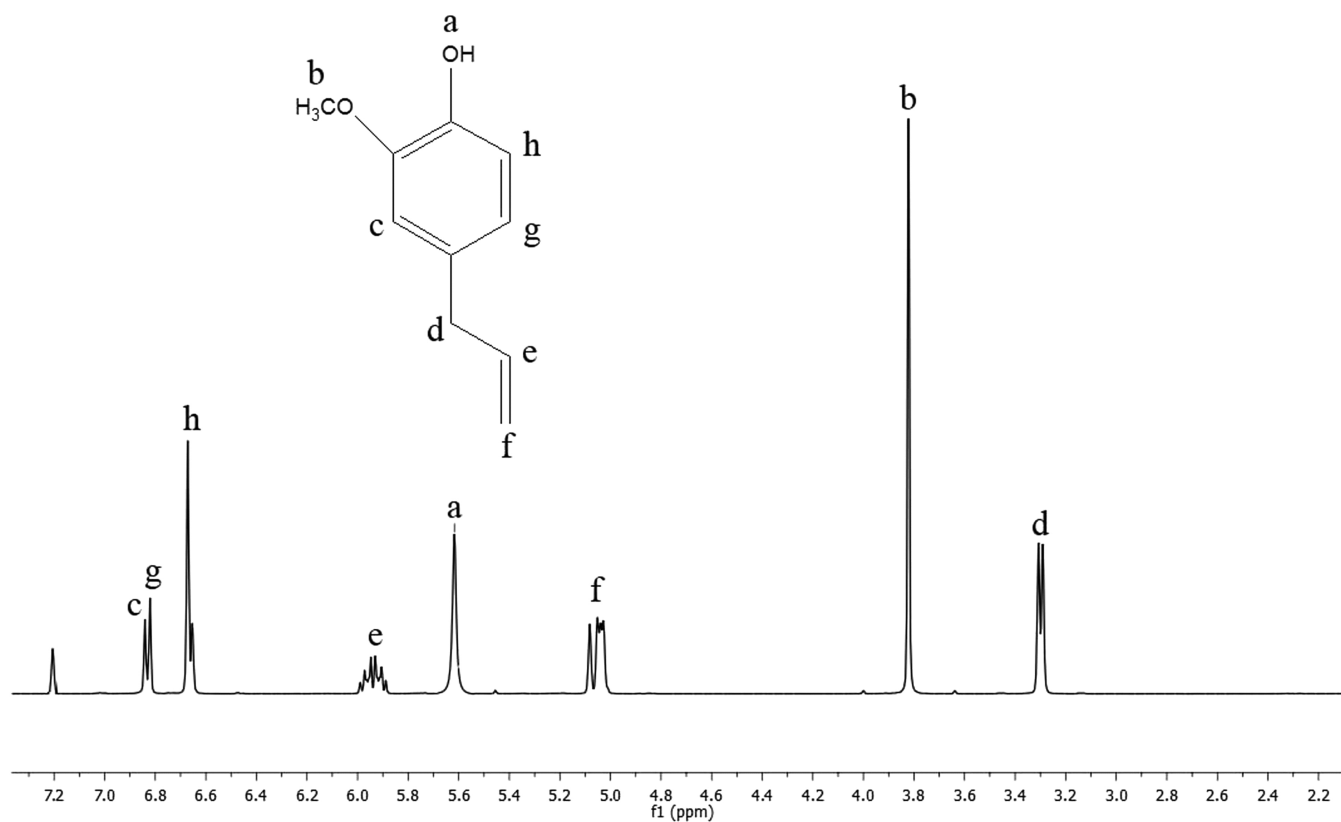


Figure 2. ¹H NMR spectrum of eugenol.

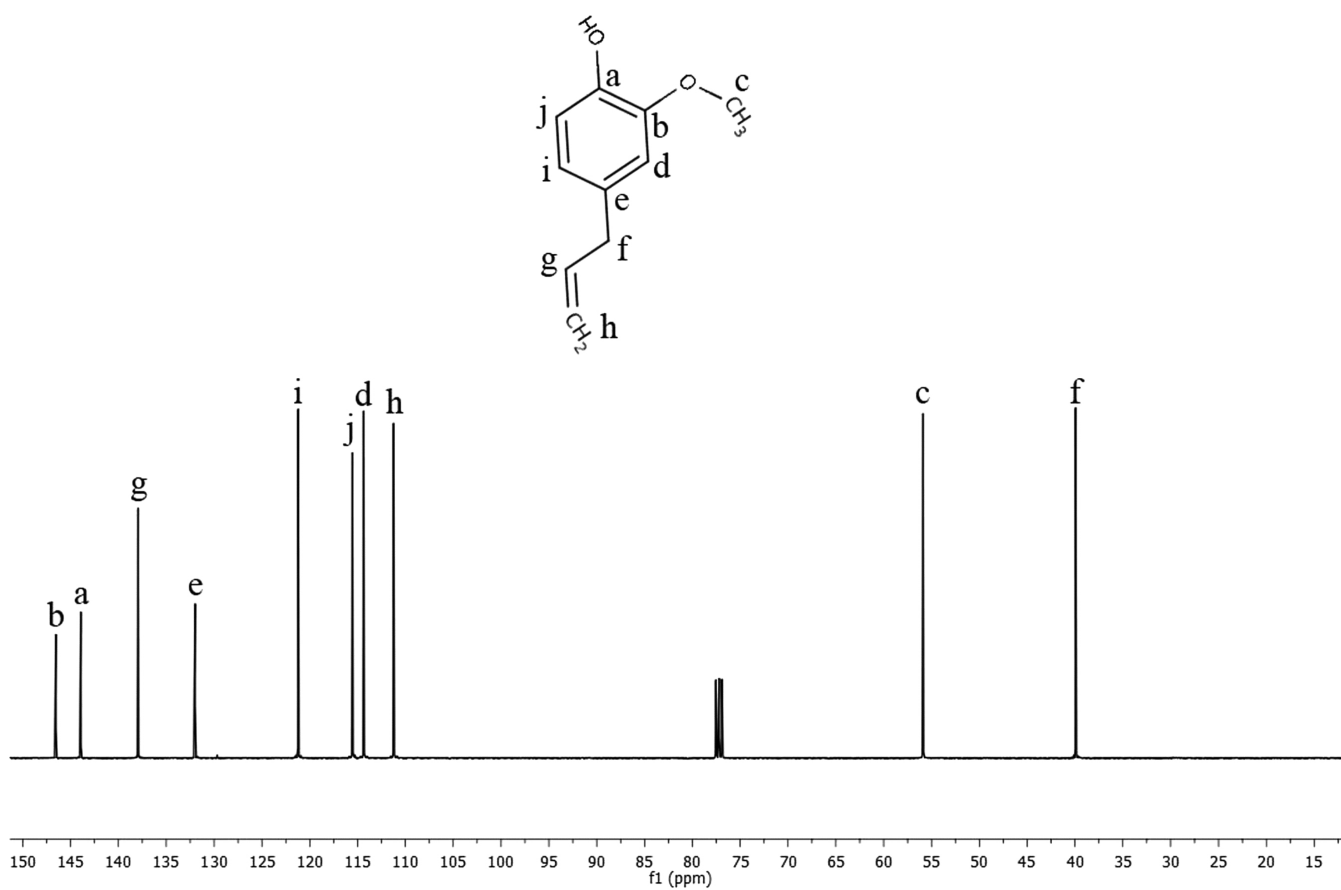


Figure 3. ¹³C NMR spectrum of eugenol.

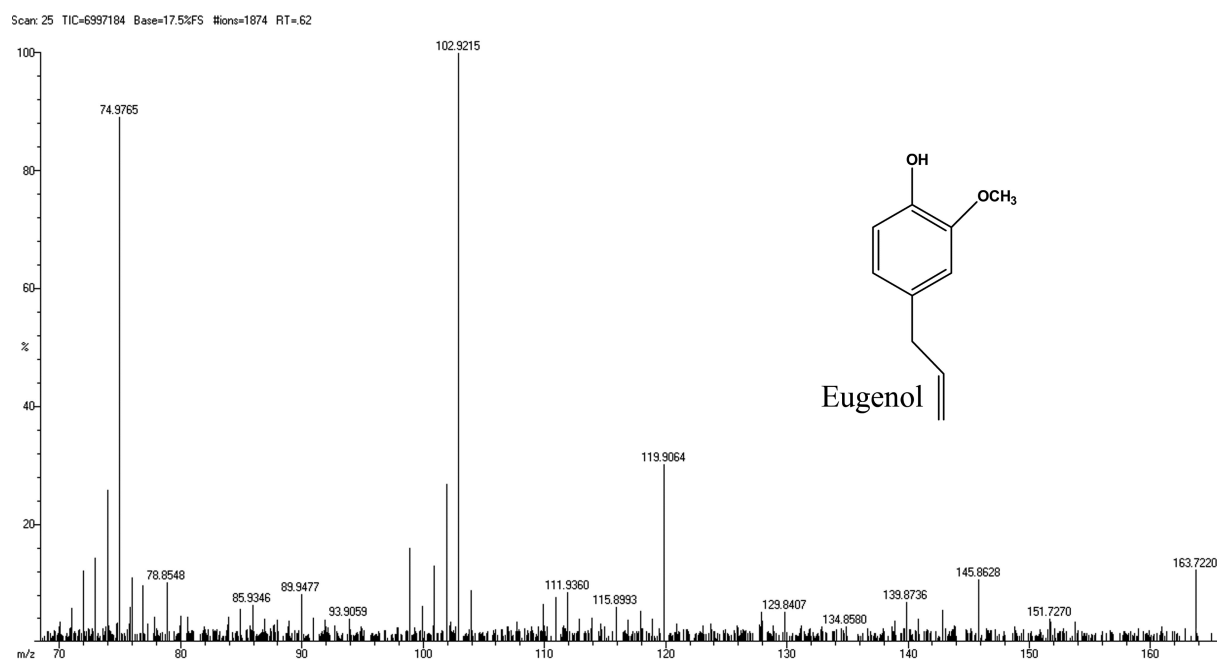


Figure 4. Mass spectrum of eugenol.

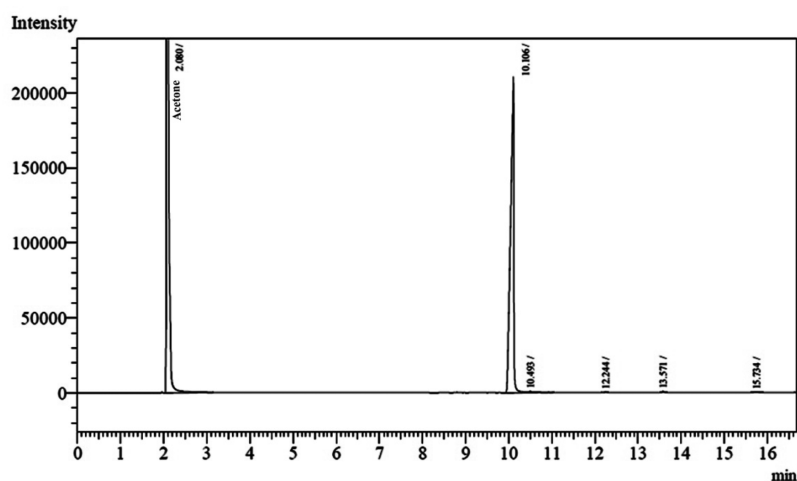


Figure 5. Gas chromatography of eugenol.

vacuum to obtain S-Bz as a pale yellow powder. Yield: 89%, mp 49 °C. FT-IR (KBr, cm^{-1}): 2924, 2854, 1589, 1497, 1466, 1381, 1281, 1227, 1149, 1095, 995, 918, 841, 717. ^1H NMR (CDCl_3 , ppm): 0.81 (t, 3H), 1.18 (m, 30H), 1.47 (m, 2H), 2.69 (d, 2H), 3.22 (d, 2H), 3.76 (s, 3H), 3.89 (s, 2H), 4.85 (s, 2H), 5.03 (d, 2H), 5.9 (m, 1H), 6.25–7.0 (m, 2H). ^{13}C NMR (CDCl_3 , ppm): 15–35, 40, 50, 52, 56, 83, 110, 115, 118, 120, 131, 138, 142, 147; m/e value, 456.77 (Scheme 1).

Copolymerization of F-Bz and S-Bz. For the preparations of the F-Bz and S-Bz copolymers in a 1:3 mol ratio, 1 mol of the F-Bz monomer and 3 mol of the S-Bz monomer were taken and dissolved in 10 mL of THF and stirred at room temperature until a homogeneous solution forms. The solution was then transformed into a mold and cured in a heating oven at 100, 150, 200, and 230 °C each at 1 h to obtain the copolymer. In a similar way, the other copolymers were prepared by adding different mole ratios of the F-Bz and S-Bz monomers. The copolymer mole ratios are given in Table 1.

Preparation of Samples for DMA Analysis. A synthesized benzoxazine monomer (F-Bz) (5 g) was dissolved in THF (10 mL) and stirred for 30 min at room temperature and further stirred for 5 h in open air to evaporate most of the THF. The solution was then poured into the mold and cured at 100 °C/1 h, 150 °C/1 h, and 200 °C/1 h,

and then post cured at 230 °C for 1 h. The cured samples were brown colored with 3 mm thickness. A similar procedure was adopted for the other benzoxazine monomer (S-Bz) and their copolymers. The mole ratios of the copolymers are given in Table 1.

RESULTS AND DISCUSSION

Characterization of Extracted Eugenol. The chemical structure of the extracted eugenol was confirmed by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy. Figure 1 shows the FT-IR spectrum of eugenol. The spectrum shows absorption bands at 1034 and 1234 cm^{-1} due to symmetric and asymmetric stretching modes of C–O–C of the $-\text{OCH}_3$ group attached to the benzene ring. A broad absorption at 3526 cm^{-1} shows the presence of the $-\text{OH}$ group, whereas the alkyl group present in eugenol gave symmetric and asymmetric stretching vibrations at 2839 and 2939 cm^{-1} . The bands at 1458 and 849 cm^{-1} correspond to the $-\text{CH}$ in-plane and out-of-plane bending modes of the trisubstituted benzene ring, respectively.^{17–19}

Figure 2 displays the ^1H NMR spectrum of eugenol. The singlet at 3.82 ppm is due to the $-\text{OCH}_3$ protons. The doublets at 3.21 and 5.05 ppm and the multiplet at 5.95 ppm are assigned to the allyl protons $[-\text{CH}_2-\text{CH}=\text{CH}_2-]$. $-\text{OH}$ protons appear at 5.66 ppm, and aromatic protons appear in the

range of 6.5–7.0 ppm. The peak at 7.2 ppm is due to the solvent peak (CDCl_3). Figure 3 shows the ^{13}C NMR spectrum of eugenol. The methoxy carbons ($-\text{OCH}_3$) gave peaks at 56 ppm. The alkyl carbons $[-\text{CH}_2-\text{CH}=\text{CH}_2]$ gave peaks at 115, 137, and 40 ppm, and the aromatic carbons gave peaks around 120–150 ppm.^{14,20,21}

The mass spectrum of eugenol is shown in Figure 4, which shows the molecular ion peak at 163 for eugenol, and the purity of eugenol is confirmed by GC analysis as shown in Figure 5 showing 98.7% of eugenol.

Characterization of Synthesized Benzoxazine Monomers. The structures of the benzoxazine monomers are supported by the FT-IR spectra as shown in Figure 6. The characteristic absorptions of the benzoxazine ring structure of both F-Bz and S-Bz appeared at 1233 and 1029 cm^{-1} (due to the asymmetric and symmetric stretching modes of $\text{C}-\text{O}-\text{C}$, respectively), while the peak at 920 cm^{-1} confirms the presence of a benzene ring with an oxazine ring attached to it.²² Moreover, the spectrum shows a peak at 1150 cm^{-1} for both of the benzoxazines (F-Bz and S-Bz) due to the $\text{C}-\text{N}-\text{C}$ symmetric stretching vibrations. The asymmetric and symmetric stretching vibration of methoxy carbonyl attached to the benzene ring was found at 1227 and 1011 cm^{-1} . Whereas both of the methylene groups ($-\text{CH}_2-$), one in the benzoxazine ring and the other

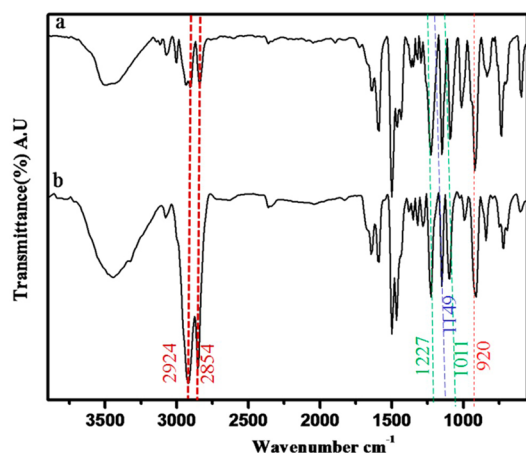


Figure 6. FT-IR spectra of (a) F-Bz and (b) S-Bz benzoxazine monomers.

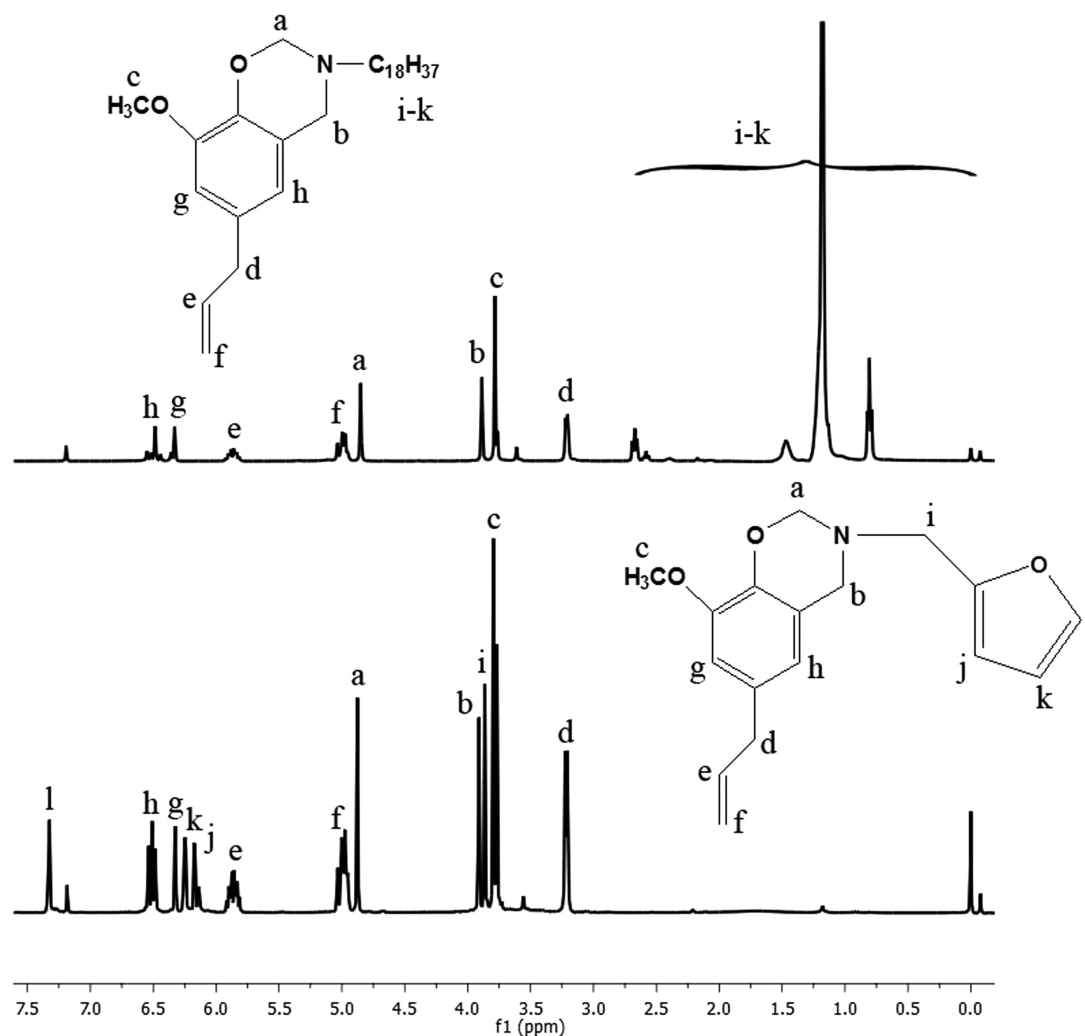


Figure 7. ^1H NMR spectra of (a) F-Bz and (b) S-Bz benzoxazine monomers.

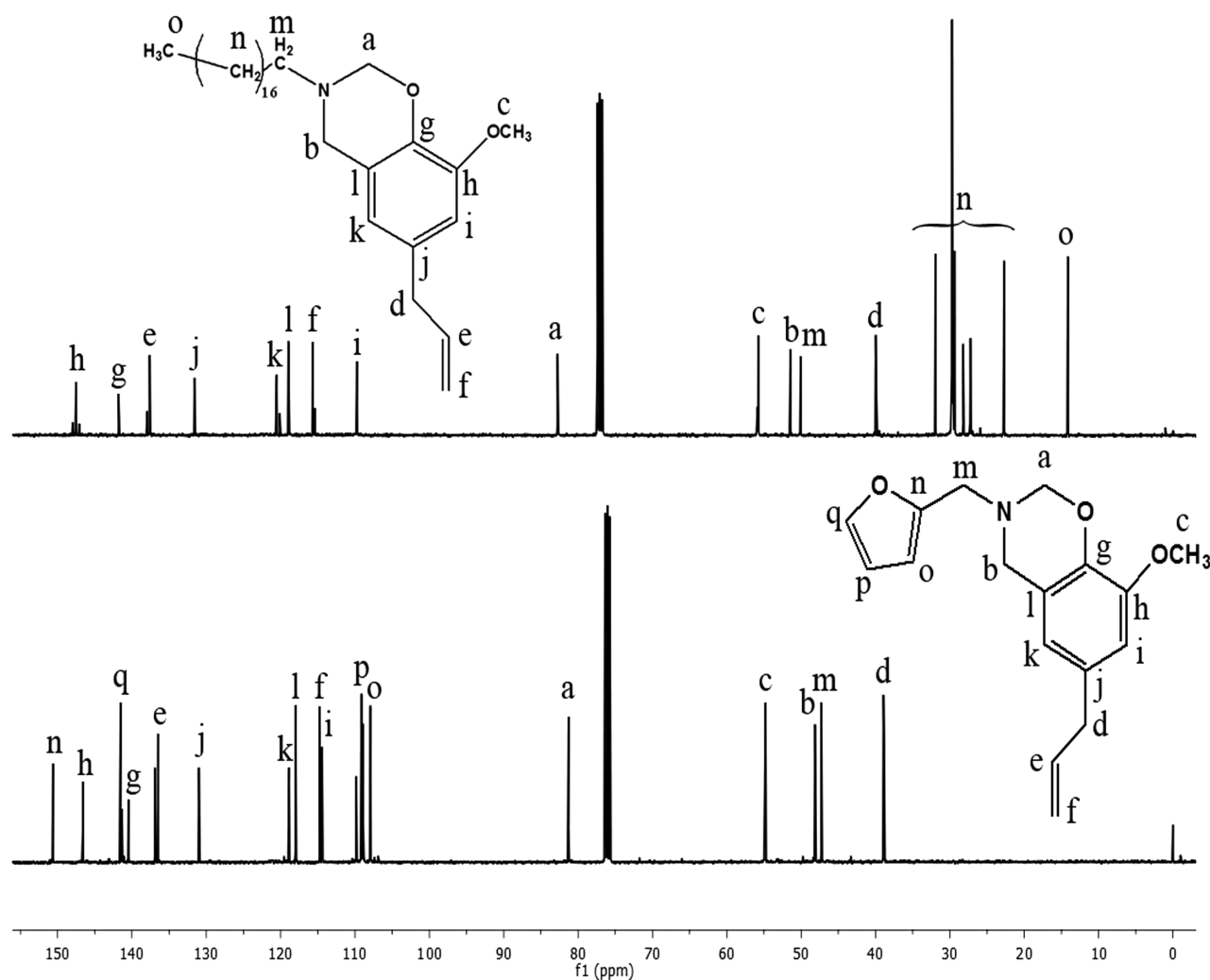


Figure 8. ^{13}C NMR spectra of (a) F-Bz and (b) S-Bz benzoxazine monomers.

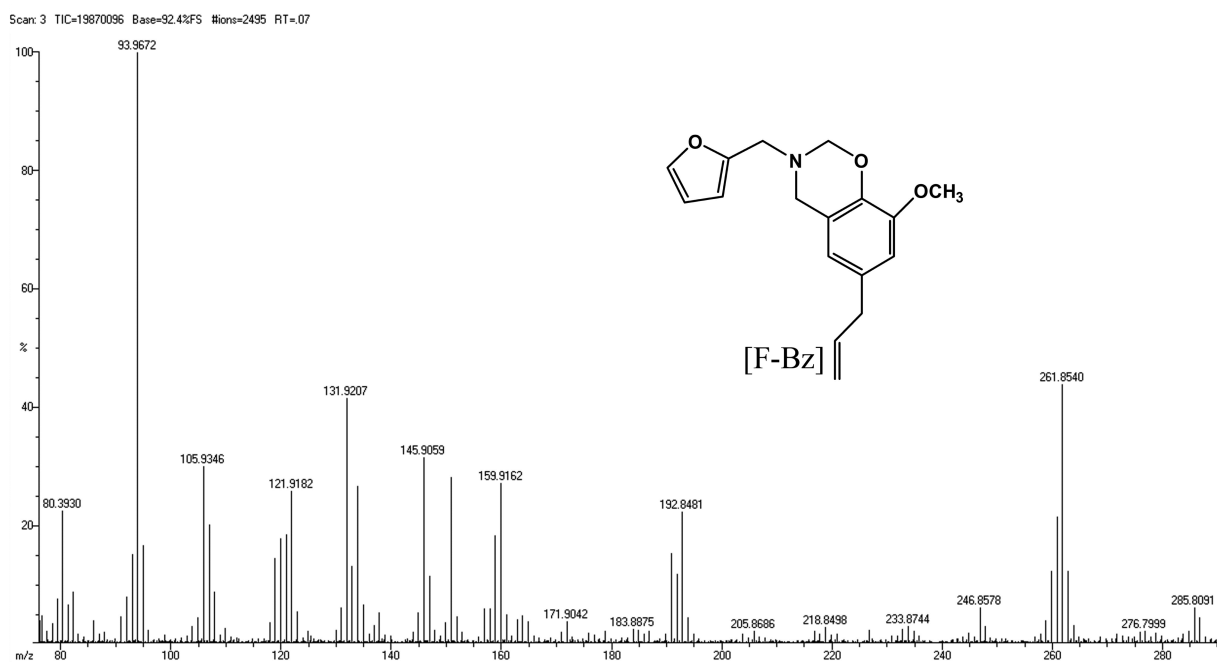


Figure 9. Mass spectrum of benzoxazine monomers (F-Bz).

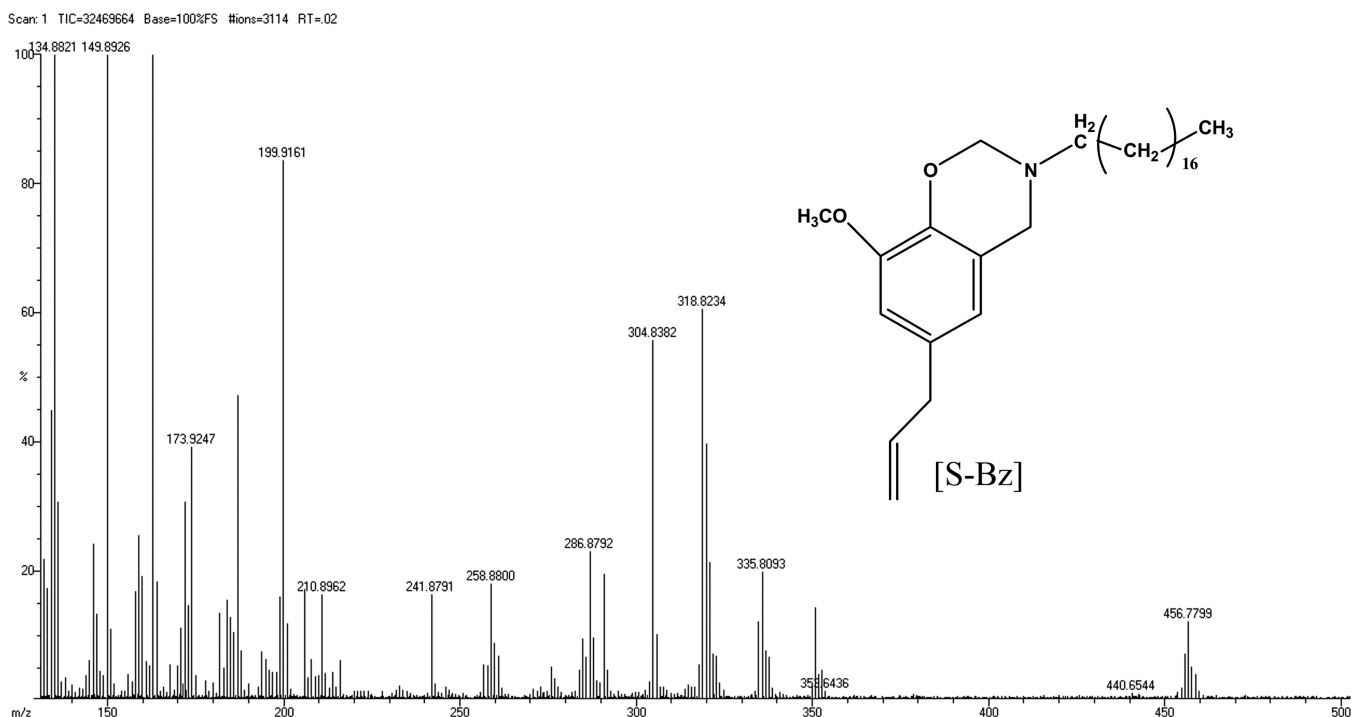


Figure 10. Mass spectrum of of benzoxazine monomers (S-Bz).

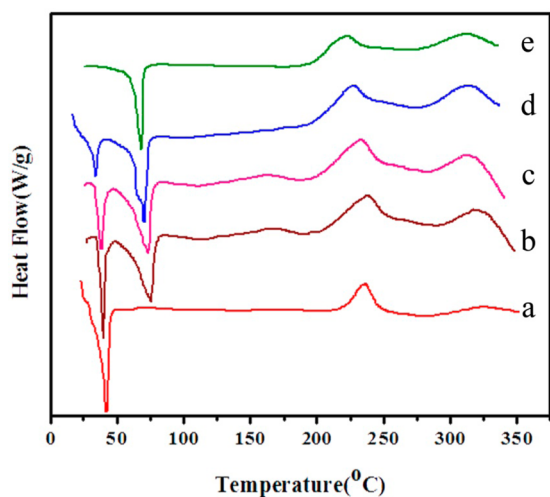


Figure 11. DSC curves of the F-Bz/S-Bz mixtures with various F-Bz contents in molar ratios (a) 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.

attached with the eugenol group, gave bands for its stretching vibrations between 2924 and 2854 cm^{-1} , respectively.^{3,19,23} The intensity of the C–H peaks (both symmetric and asymmetric) in S-Bz is more when compared with F-Bz, indicating the presence of an alkyl side chain of stearylamine. The peaks observed at 1589 , 995 , and 733 cm^{-1} may be attributed to the vibrations of the furan ring.

The ^1H NMR spectra shown in Figure 7 further confirms the structures of F-Bz and S-Bz. The resonance peaks at 3.97 and 4.88 ppm are assigned to $\text{Ph}-\text{CH}_2-\text{N}$ and $-\text{O}-\text{CH}_2-\text{N}$ of the oxazine ring, respectively. The singlet at 3.8 ppm is due to the $-\text{OCH}_3$ protons. The doublets at 3.21 , 5.87 , and 5.03 ppm are assigned to $[-\text{CH}_2-\text{CH}=\text{CH}_2-]$ allyl protons. The furan ring protons resonate at 6.25 , 6.84 , and 7.29 ppm , and the

methylene protons ($-\text{CH}_2$) connecting the furan and oxazine ring resonate at 3.85 ppm . Similarly, the ^1H NMR spectrum (Figure 5) of S-Bz displayed two resonances centered at 3.89 and 4.85 ppm , which are consistent with the formation of the oxazine ring, whereas the long aliphatic chain of the oxazine gave multiplets at 2.69 , 1.18 , and 0.81 ppm .^{14,24} The peak at 7.2 ppm is due to the solvent peak (CDCl_3).

The ^{13}C NMR spectra shown in Figure 8 also confirm the structures of F-Bz and S-Bz. The characteristic carbon resonance of the oxazine ring is found at 48 and 81 ppm for $\text{Ph}-\text{CH}_2-\text{N}$ and $\text{O}-\text{CH}_2-\text{N}$, respectively. The peak at 55 ppm is attributed to the $-\text{OCH}_3$ carbon, and the peaks at 114 , 136 , and 39 ppm are assigned to $-\text{CH}_2-\text{CH}=\text{CH}-$ allyl carbons. The furan ring carbons of F-Bz gave peaks between 100 and 150 ppm . The peak corresponding to the $-\text{CH}_2-\text{N}$ of the furan ring appeared at 47 ppm , whereas the aliphatic moiety attached to the oxazine ring of S-Bz gave characteristic peaks in between 15 and 35 ppm .¹⁴ The mass spectrum of F-Bz and S-Bz is shown in Figures 9 and 10, which shows the molecular ion peak at $m/e = 285.80$ for F-Bz and at $m/e = 456.77$ for S-Bz.

Thermal Behavior of Monomers and Polymers and Their Copolymers. The polymerization behaviors of the individual monomers (F-Bz and S-Bz) and their copolymers were studied using DSC at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere from 30 to $350\text{ }^\circ\text{C}$. Figure 11 shows the DSC thermograms of the monomers and their copolymers. The data are summarized in Table 1. The two benzoxazine monomers (S-Bz and F-Bz) melt at 49 and $74\text{ }^\circ\text{C}$, which is shown by sharp endotherms at this point. Similarly, when the two monomers are copolymerized, each copolymer displays two endotherms corresponding to their individual melting points. The onset of curing is around $218\text{ }^\circ\text{C}$ for S-Bz and $198\text{ }^\circ\text{C}$ for F-Bz. But for the copolymer mixtures, the onset of curing temperature decreased linearly with increasing F-Bz content (from 207 to $202\text{ }^\circ\text{C}$). The presence of an electronegative atom

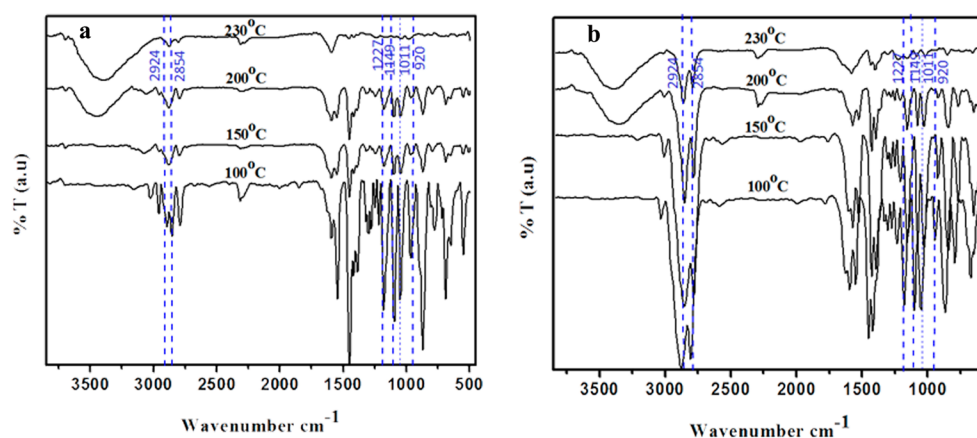


Figure 12. FT-IR spectra of (a) F-Bz and (b) S-Bz at different curing temperatures.

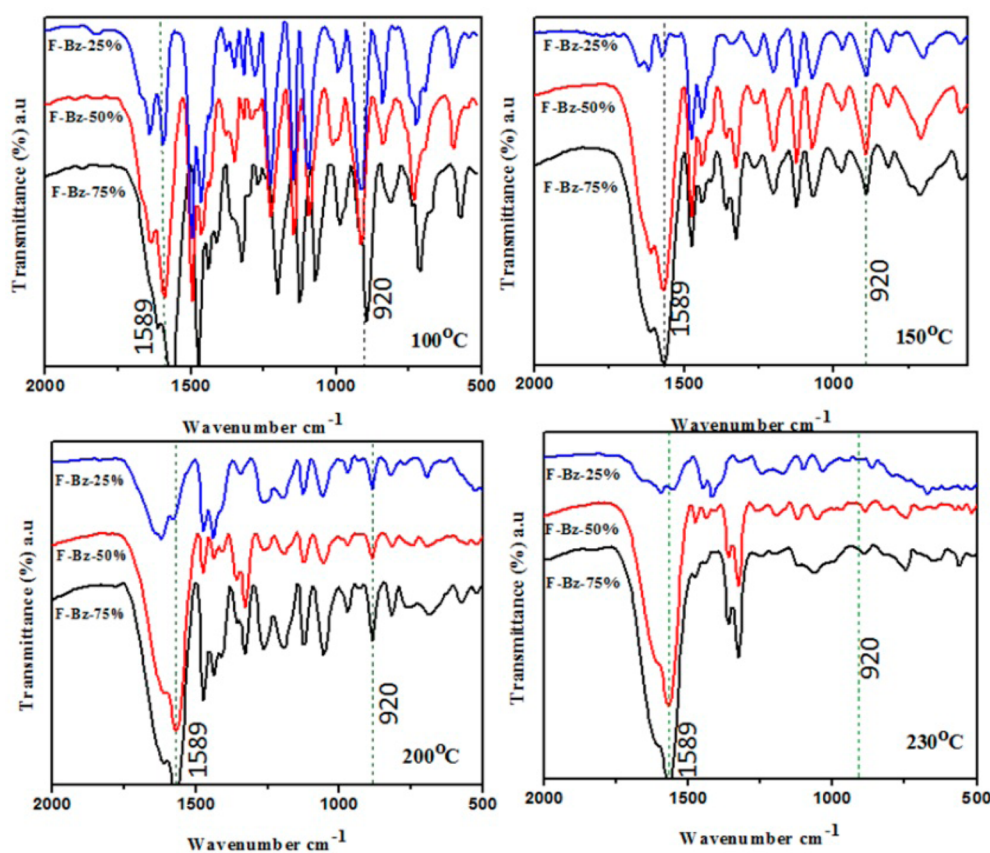
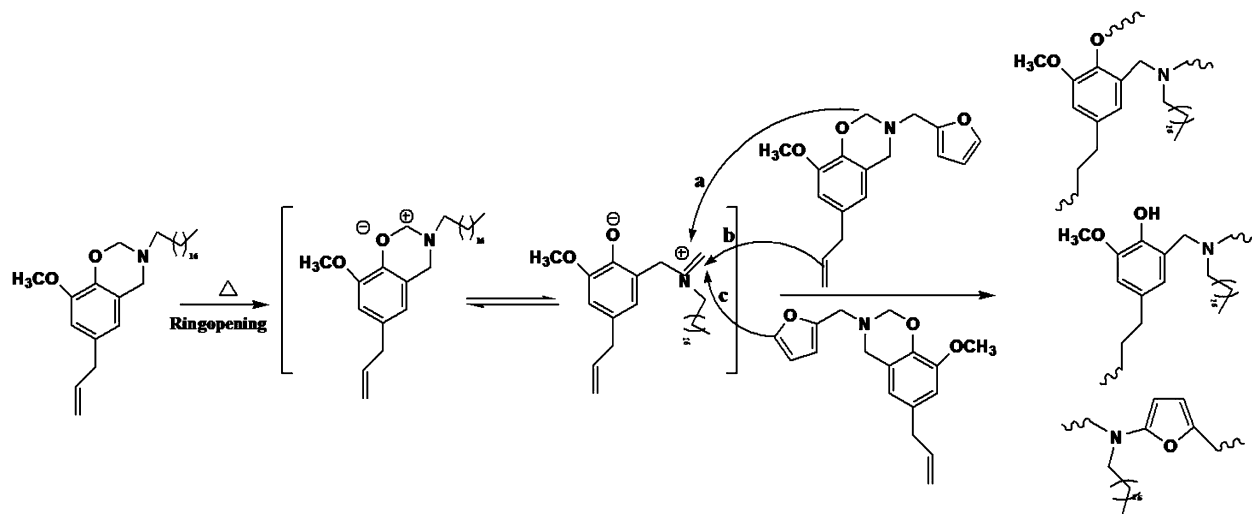


Figure 13. FT-IR spectra of copolymers cured at different temperatures.

(i.e., oxygen) in the furan ring makes the attack of the furan ring to the phenolic moiety of benzoxazine viable, thereby promoting the curing reaction, thus confirming that copolymerization of F-Bz and S-Bz has occurred. The exothermic final for the individual monomers was observed at 234 and 249 °C, and for the copolymers, it was observed between 237 and 257 °C. It is well known that ring-opening polymerization of benzoxazine will exhibit an exothermic peak around 200–250 °C. The biobased benzoxazines (S-Bz and F-Bz) also display a similar exothermic behavior in the high-temperature range. The processing window is defined as the temperature difference between the melting point and onset of polymerization. The S-Bz monomer shows a processing window of 169 °C, and the F-Bz monomer shows a processing window of

124 °C. Whereas for the copolymers, it is between 128 and 133 °C, showing a wide range of processability for both the monomers and their copolymers.²⁴ In addition, the neat polymers and their copolymers showed another exothermic peak centered at 335 °C, which appears due to the degradation of the aliphatic chains present in it.²⁵

The curing reaction of the monomers and copolymers were further confirmed by FT-IR analysis. Figures 12 and 13 show the FT-IR spectra of the monomers and copolymers after heating at 100, 150, 200, and 230 °C for 1 h at each temperature. The curing process proceeds via the cleavage of C–O–C bond of the oxazine ring. As a result, there is a decrease in the intensity of peaks around 920, 1029, 1233, and 1350 cm^{-1} , which is due to the stretching vibrations of the oxazine ring,

Scheme 2. Copolymerization Mechanism of F-Bz/S-Bz Mixtures^a

^aIllustration according to Wang et al.¹⁹

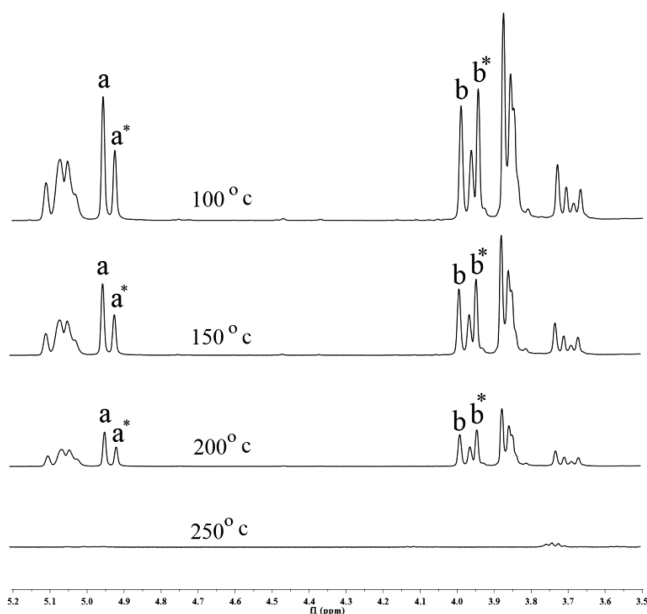


Figure 14. ¹H NMR spectra of copolybenzoxazines (F-Bz/SBz molar ratio 1:1) cured at different temperatures.

C–O–C of the oxazine ring, and –CH₂ of the benzene ring. At still higher temperatures (say 200 °C), the allyl group present in the eugenol part also involves in curing. This is supported by the disappearance of the stretching vibrations of the allylic moiety at 1636 cm⁻¹ (Scheme 2). Moreover, the furan ring also involves the curing process resulting in the formation of a substituted furan ring in the polymer network. This is shown by the broadening of vibrations of the furan ring at 1589 cm⁻¹. On the other hand, there are close similarities in the FT-IR spectra of the cured F-Bz and S-Bz mixture upon variation of the molar ratio. These further imply that homogeneous copolymerization occurred during the curing process.^{19,26,27}

Figure 14 shows the ¹H NMR spectra of the benzoxazine copolymer in an equimolar ratio [F-Bz/S-Bz (1:1)], which are cured at 100, 150, 200, and 250 °C for 1 h. The spectrum at 100 °C shows the characteristic peaks of the oxazine ring protons at 4.95 and 4.92 ppm for the methylene protons of

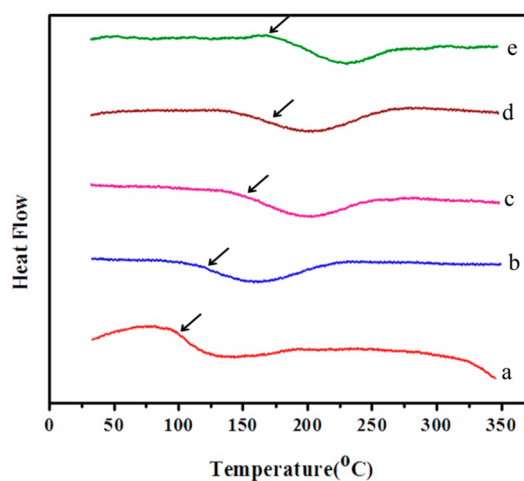


Figure 15. DSC curves (second scan) of F-Bz/S-Bz mixtures with various F-Bz contents in molar ratios (a) 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.

O–CH₂–N and at 4.0 and 3.95 ppm for the methylene protons of Ar–CH₂–N. As shown in the figure, the oxazine ring protons decreased on further curing at 150 and 200 °C. Finally, at 250 °C, a copolymer was formed that does not dissolve in the solvent and is shown by the absence of peaks. All these results confirm that copolymerization of the two benzoxazine monomers, F-Bz and S-Bz, has occurred.

Benzoxazine copolymers were prepared by curing F-Bz and S-Bz mixtures as shown in the Experimental Section. Figure 15 displays the DSC thermograms, and Table 2 shows the *T_g* values of the individual polymers and their copolymers. The glass transition temperature (*T_g*) is the temperature region where the polymer transitions form a hard glassy material to a soft rubbery material. As benzoxazines are thermosetting materials and chemically cross-link during the curing process, the final cured material does not melt or reflow when heated (unlike thermoplastic materials) but undergoes a slight softening (phase change) at elevated temperatures. As shown in the thermograms, furfurylamine-based polybenzoxazine (PF-Bz) shows a *T_g* value of 148 °C when compared with stearylamine-based polybenzoxazine

Table 2. DMA Data and Cross-Linking Density of PF-Bz, PS-Bz, and Their Copolymers

sample no.	sample	mole ratio PS-Bz/PF-Bz	ϵ' (GPa)		T_g ($^{\circ}\text{C}$)	$V_e \times 10^5$ (mol m $^{-3}$)	
			initial	at 50 $^{\circ}\text{C}$		initial	at 50 $^{\circ}\text{C}$
1	a	1:0	2.82	2.53	101	3.7	3.5
2	b	3:1	2.94	2.71	106	4.0	3.6
3	c	1:1	3.12	2.98	125	4.1	3.9
4	d	1:3	3.29	3.13	154	4.4	4.1
5	e	0:1	3.33	3.15	148	4.4	4.1

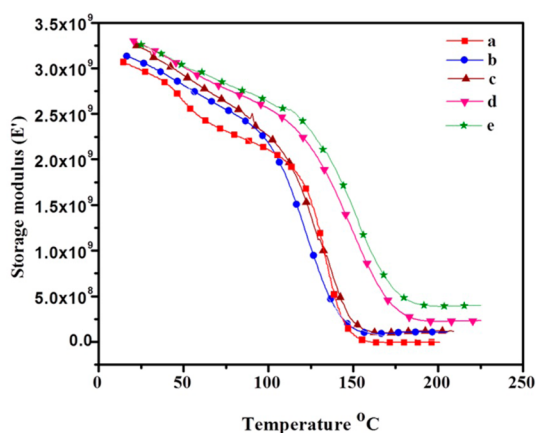


Figure 16. DMA curves showing storage modulus of PF-Bz/PS-Bz mixtures with various F-Bz contents in molar ratios (a) 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.

(T_g of PS-Bz = 101 $^{\circ}\text{C}$). Whereas for the copolymer mixtures, the one that contains the highest ratio of F-Bz (i.e., F75:S25) displays a high T_g value of 154 $^{\circ}\text{C}$. These results may be attributed to the fact that the polybenzoxazine with a furan ring and the copolymer with an increased furan ring content increases the cross-linking density by means of its rigid backbone structure.^{19,28}

There are a number of important material parameters that can be derived from the DMA data. The initial storage modulus ϵ' of a solid sample at room temperature provides a measure of the stiffness of the material under shear deformation. As shown in Figure 16, the initial storage modulus of the PF-Bz is 3.33 and that of PS-Bz is 2.82 GPa. The values are given in Table 2, which indicate that the storage moduli of the copolymers were increased with increasing F-Bz content. The storage modulus of PF-Bz is superior when compared with PS-Bz because the furan ring structure improved the cross-linking densities of polymers. In addition, according to the $\tan \delta$ plots of the polybenzoxazines in Figure 17, it can be found that the T_g values are 148 $^{\circ}\text{C}$ for PF-Bz and 101 $^{\circ}\text{C}$ for PS-Bz, and for the copolymers, they increased from 106 to 154 $^{\circ}\text{C}$. These values are close to those obtained from the second scan of DSC (T_g values).

The cross-linking density of the polymers was calculated from the value of the storage modulus at room temperature and at 50 $^{\circ}\text{C}$. Cross-link density is defined as the number of cross-link points per unit volume. The value of the cross-link density may be on the order of 10^{-3} to 10^{-5} mol/cm 3 for a typical rubber material, corresponding to 15 to 1500 monomer units between the cross-links. The cross-link density of the highly cross-linked thermoset can be determined by a modulus measurement using the following equation

$$V_e = \epsilon' / 3RT$$

where ϵ' = tensile storage modulus; T = temperature in K corresponding to storage modulus; and R = gas constant. Table 2

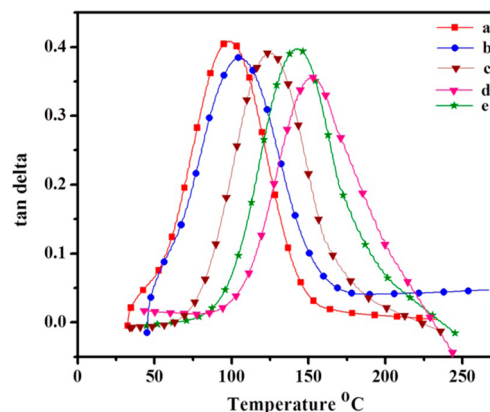


Figure 17. DMA curves showing loss modulus of PF-Bz/PS-Bz mixtures with various F-Bz contents in molar ratios (a) 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.

shows the cross-linking density of the polymers. It is shown that cross-link density obviously increased with increasing F-Bz content.

Thermogravimetric analysis was used to study the thermal stability of the polymers and its copolymers. The thermogram in Figure 18 displays the initial degradation temperature (T_i), 5% weight loss temperature (T_5), 10% weight loss temperature (T_{10}), and char yield (CY) at 800 $^{\circ}\text{C}$ for the polymers and their copolymers. Among them, the furfurylamine-based polymer (PF-Bz) shows the highest thermal stability [T_i , 349 $^{\circ}\text{C}$; T_5 , 361 $^{\circ}\text{C}$; and T_{10} , 394 $^{\circ}\text{C}$]. Whereas for the copolymers, the one that contains the high ratio of furfurylamine [F75:S25] has the highest thermal stability [T_i , 328 $^{\circ}\text{C}$; T_5 , 342 $^{\circ}\text{C}$; and T_{10} , 376 $^{\circ}\text{C}$].^{19,28} The presence of a furan ring structure had an enhancing effect on the degradation temperature of the copolybenzoxazine of F-Bz and S-Bz by means of increasing the cross-linking density of the cured resin. The char yield of neat polybenzoxazine derived from F-Bz was 53.8%, which is much higher than that of the polymer from S-Bz (about 23.9%).

The limiting oxygen index (LOI) value, which is taken as an indicator to evaluate the polymer's flame retardancy,⁴ was measured as shown in Table 3. The char yield of a material can be used to estimate the LOI according to the Van Krevelen and Hofytzer equation. LOI is defined as the minimum fraction of oxygen in a mixture of O $_2$ and N $_2$ that will support flaming combustion.²⁹ The LOI values calculated from the char yield resulted from TGA analysis by using the following Van Krevelen and Hofytzer equation³⁰

$$\text{LOI} = 17.5 + 0.4(\text{CY})$$

where LOI = limiting oxygen index, and CY = char yield (from TGA data).

The char yields of PF-Bz and S-Bz and their copolymers were found to be high, in the range of 27–39%, indicating high flame

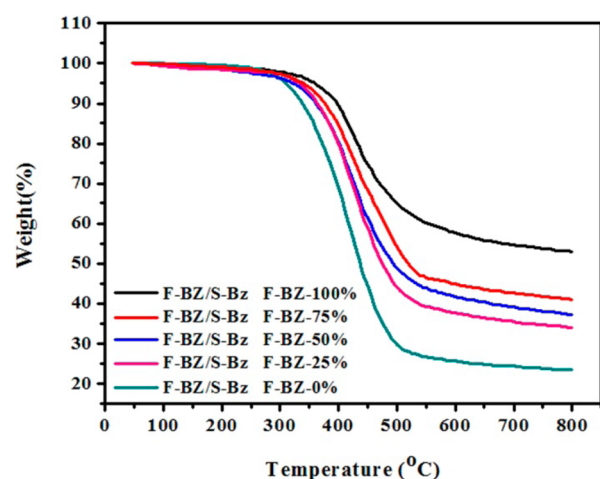


Figure 18. TGA curves of PF-Bz/PS-Bz mixtures with various F-Bz contents in molar ratios (a) 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.

Table 3. TGA Data of PF-Bz, PS-Bz, and Their Copolymers

sample no.	sample	mole ratio S-PBz/F-PBz	$T_{10\%}$	$T_{5\%}$	$T_{10\%}$	char yield (%)	LOI values
1	a	1:0	305	313	341	23.9	27.1
2	b	3:1	312	324	353	34.6	31.3
3	c	1:1	325	336	362	38.0	32.7
4	d	1:3	328	342	376	41.8	34.2
5	e	0:1	349	361	394	53.8	39.0

retardancy, which is expressed in terms of their LOI value. In general, the LOI value of the polymer should be above the threshold value of 26 to render a self-extinguishing property and to qualify their requirement in many applications requiring good flame resistance. It was found that in the prepared polymers (PF-Bz and PS-Bz) and their copolymers the LOI value increases with an increase in char yield showing values greater than 26 as expected, thus confirming their good flame retardant properties.^{4,30,31}

CONCLUSIONS

Biobased benzoxazine monomers (F-Bz and S-Bz) have been successfully synthesized by a solventless method from well-known renewable organic resources (eugenol, stearylamine, and furfurylamine). The structures of the monomers were supported by FT-IR, ¹H NMR, ¹³C NMR, and HR-MS spectra, which showed the existence of a reactive benzoxazine ring. Both of the monomers (F-Bz and S-Bz) and their copolymers are processable to a greater extent as they possess a wide range processing window. Moreover, both the thermal and mechanical properties of the polymer [PF-Bz] and its copolymer [F75:S25] are enhanced as the furan ring increased the cross-link density. From the aforementioned results, we conclude that the synthesized polybenzoxazines from renewable sources can be used in ecofriendly processes with desirable properties.

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Notes

The authors declare no competing financial interest.

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