Supporting Information

Design and Preparation of Benzoxazine Resin with High-frequency Low Dielectric Constants and Ultra-low Dielectric Losses

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1. EXPERIMENTAL SECTION

1. Materials

P-tert-butylphenol was purchased from Shanghai Macklin Biochemical Reagent Co., Ltd. DAM (99%) and DAH (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Bisphenol A was purchased from Chengdu Chemical Reagent Co., Ltd. Paraformaldehyde (96%) was obtained from Tianjin Fuchen Chemical Reagent Factory. Toluene, ethanol, and methanol were purchased from Tianjin Tianli Chemical Reagent Co., Ltd. All other chemicals were used as received.

2. Preparation of Main-chain Benzoxazine Copolymer Prepolymers

Main-chain benzoxazine copolymer prepolymers were typically synthesized using bisphenol A, p-tert-butylphenol, diamine, and paraformaldehyde as starting materials by employing solution methods (Scheme 1(a)). The molar ratio of phenolic hydroxyl groups, amine groups, and aldehyde groups was theoretically predetermined as 1: 1: 2. In addition, the molar ratio of bisphenol A to p-tert-butylphenol was 1: 2. A mixture of bisphenol A, p-tert-butylphenol, diamine, and paraformaldehyde was dissolved in toluene/ethanol (2:1 v/v), and then refluxed in a flask equipped with a condenser. The reaction mixture was stirred at 80 ^{o}C for 8 h. In order to remove the initial reactants and soluble part, the resulting yellow transparent liquid was precipitated by methanol, and then dried in a vacuum oven at 55 ^{o}C overnight. Two types of main-chain benzoxazine copolymer prepolymers were prepared based on DAH and DAM, and coded as TAH and TAM, respectively.

For comparison, main-chain benzoxazines (Scheme 1(b)) and p-tert-butylphenol based benzoxazines (Scheme 1(c)) were also prepared in the same method. Two types of main-chain benzoxazine prepolymers were prepared based on DAH and DAM, and coded as AH and AM, respectively. In addition, two kinds of difunctional benzoxazine monomers were also obtained by DAH and DAM as diamines, respectively, and coded as TH and TM.

3. **Preparation of Cured Benzoxazine Films**

The solvent of all precursors was removed from the vacuum oven at 60–80 °C for 2 h and then cured in an ordinary oven at 100 °C for 2 h, 120 °C for 2 h, 160 °C for 2 h, 180 °C for 2 h, and 200 °C for 1 h, separately. Finally, the cured films (diameter: 42 mm, thickness: approximately 0.8 mm) were obtained after cooling down the samples naturally.

4. **Characterizations**

Proton Nuclear Magnetic Resonance (^{1}H-NMR)

^{1}H-NMR spectra were taken on a Bruker NMR spectrometer (AVANCE III HD, 400 MHz). All samples were dissolved in deuterated chloroform and tetramethylsilane (TMS) was used as an internal standard.

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy was carried out on a spectrometer (Nicolet 6700, Thermo scientific, USA). Spectra in the wavenumber range of 4000-400 cm^{-1} were collected over 40 scans with a resolution of 2 cm^{-1}. The test specimens were vacuum-dried and then prepared by the KBr-disk method.

Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimeter (DSC 3, Mettler Toledo, Switzerland) was used to study the curing behaviors of the copolymer precursors. The powder samples were analyzed directly, approximately 4 mg each time. Indium was used for temperature calibration and nitrogen as the flushing gas. Non-isothermal experiments of samples were carried out at 10 °C min^{-1} from 30 up to 300 °C. Experiments were always performed below 320 °C to prevent any possible degradation reactions inside the chamber. The same measurement method was used to check for complete cure and the glass transition temperature of the cured resin. Sample weights were taken after each non-isothermal test. The weight losses, if there were any, were negligible.

Dynamic Thermal Mechanical Analysis (DMA)

The thermo-mechanical properties of the cured samples were conducted using a dynamic mechanical analyzer (DMA/SDTA861e, Mettler Toledo, Switzerland) with the shear mode. The samples (length: 8 mm, width: 7 mm, thickness: ca. 1.5 mm) were measured with a vibration frequency of 1 Hz, maximum force amplitude of 5 N, maximum displacement amplitude of 10 μm, and a heating rate of 5 °C min^{-1} from 30 to 300 °C under air atmosphere.

Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC, Waters 2695, USA) was measured with Waters station equipped with a Waters 440 ultraviolet (UV) detector fixed at 254 nm and a Waters 410 refractive index (RI) detector. THF was used as a carrier solvent at a flow rate of 1.0 mL min^{-1}.

Dielectric property measurement

The dielectric properties of the films were tested using a microwave vector network analyzer (Keysight N5232A, Agilent) with a split post dielectric resonator (SPDR) method at the microwave frequencies of 5 GHz and 10 GHz. The films were dried before measurements, and then tested at room temperature.

Thermogravimetric Analysis (TGA)

TGA and corresponding differential thermo-gravimetric analysis (DTG) was performed using the SDT Q600 thermogravimetric analyzer (TA, USA). The samples were examined under a nitrogen atmosphere from 25 to 800 °C at a heating rate of 10 °C min^{-1}.

Field Emission Scanning Electron Microscope (FESEM)

The cured films were fractured after immersing them in liquid nitrogen for the purpose of analyzing the cross-section morphologies of the films. Afterward, the fractured surfaces of the films were gold-coated in a JUC-500 Magnetron Sputtering Device (JEOL, Tokyo, Japan), and a field emission scanning electron microscope (FESEM, INSPECT F, FEI, Netherlands) was used for observing the cross-section of the samples. The surface morphologies of cured films were also observed by FESEM.

Thermal Mechanical Analyzer (TMA)

TMA was performed using the Q400 thermal mechanical analyzer (TA, USA). Cured films were measured in standard mode with an expansion probe, the applied force being 0.05 N. The expansion of the films was measured over a temperature range of 40 to a maximum temperature of 240 °C under air atmosphere.

Breakdown Strength Measurements

Dielectric breakdown strength measurements were performed on a voltage breakdown tester

DDJ-50KV (Beijing Guance Testing Instrument Co. Ltd., China) under a direct-current voltage ramp of 500V s^{-1}. Each cured film was subjected to 12 breakdown measurements, and an average of these values was given as the breakdown strength of the film.

Leakage Current Level

Conduction currents were obtained by the DMM4020 5-1/2 digit multimeter (Tektronix, USA) under the electric field provided by a Z-VI DC high voltage generator (Suzhou Industrial Park Haiwo Science and Technology Co. Ltd.).

2. Figures and figure captions:

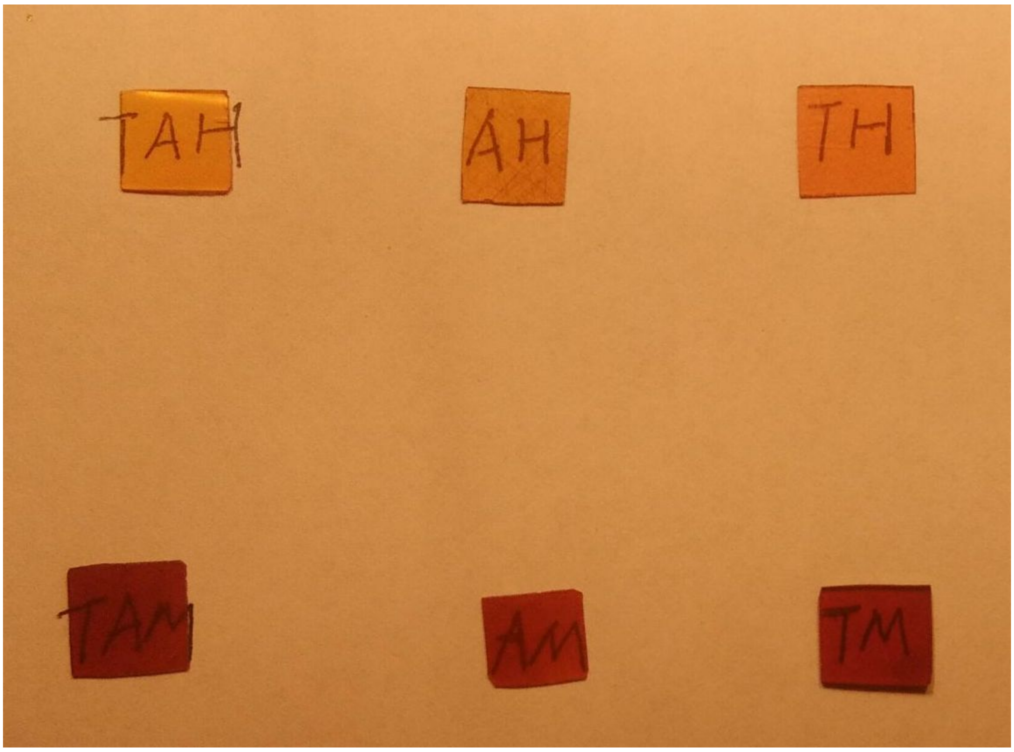


Figure S1. Digital photos of cured films.

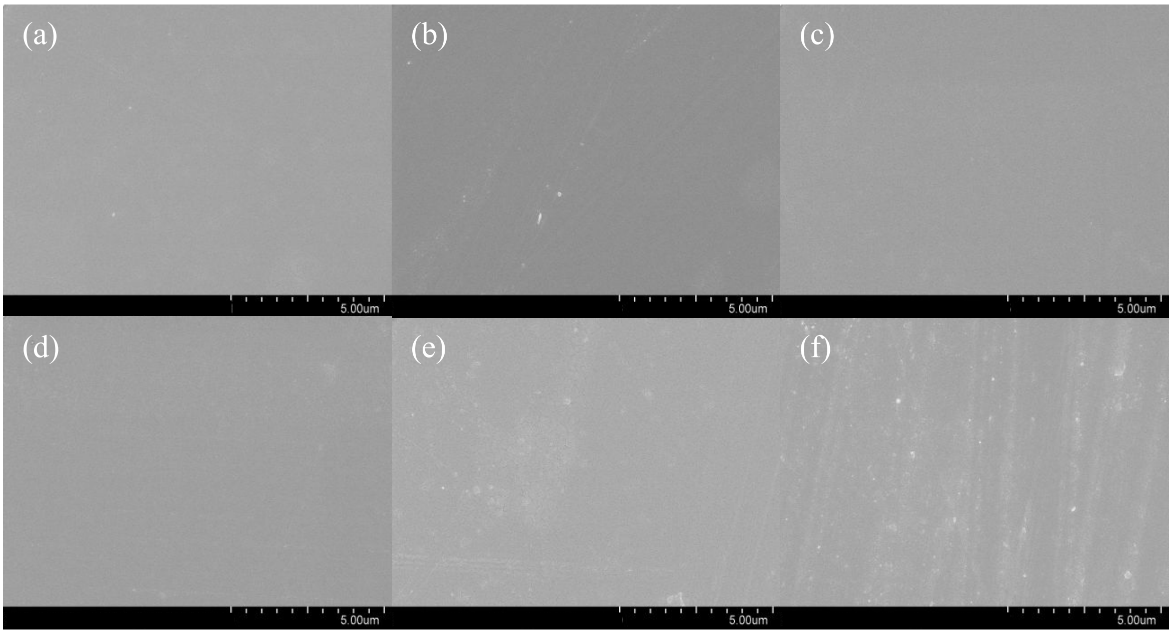


Figure S2. FESEM photographs of surfaces of TAH (a), AH (b), TH (c), TAM (d), AM (e), and TM (f) cured films (magnification scale: ×10000).

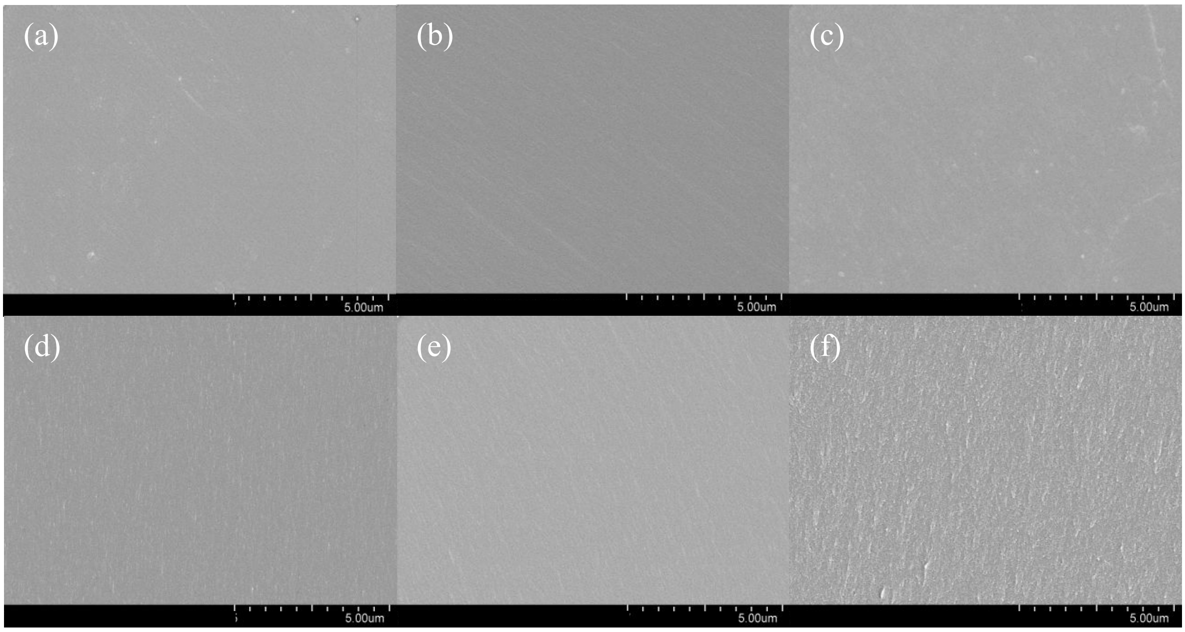


Figure S3. FESEM photographs of fracture surfaces of TAH (a), AH (b), TH (c), TAM (d), AM (e), and TM (f) cured films (magnification scale: ×10000).

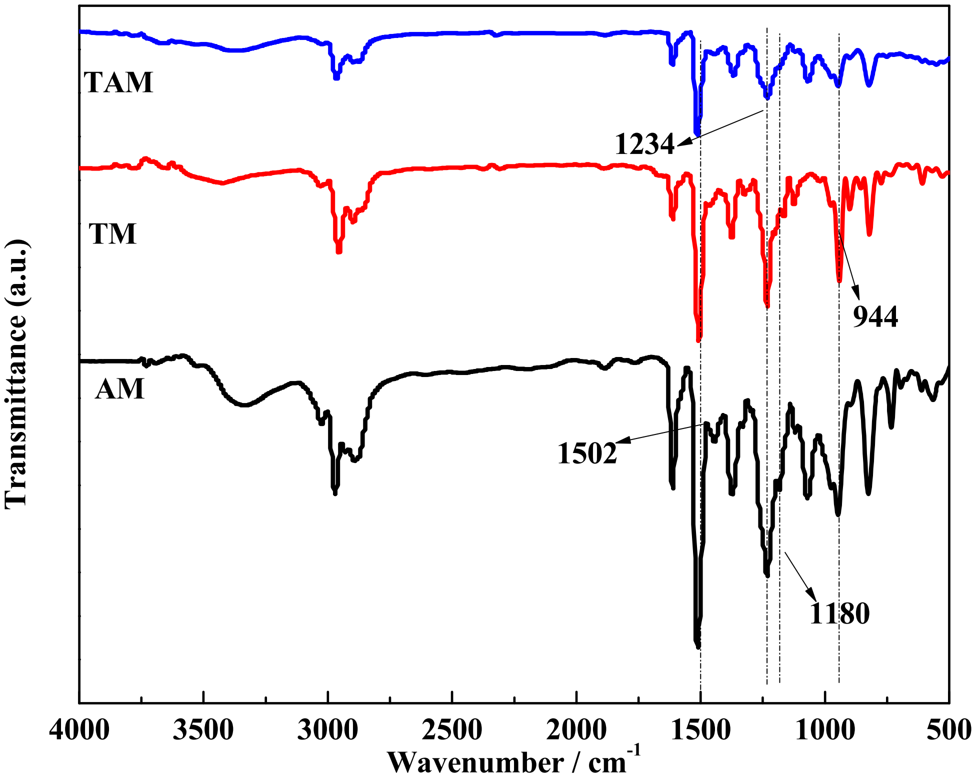


Figure S4. FTIR spectra of TAM, TM, and AM benzoxazine prepolymers.

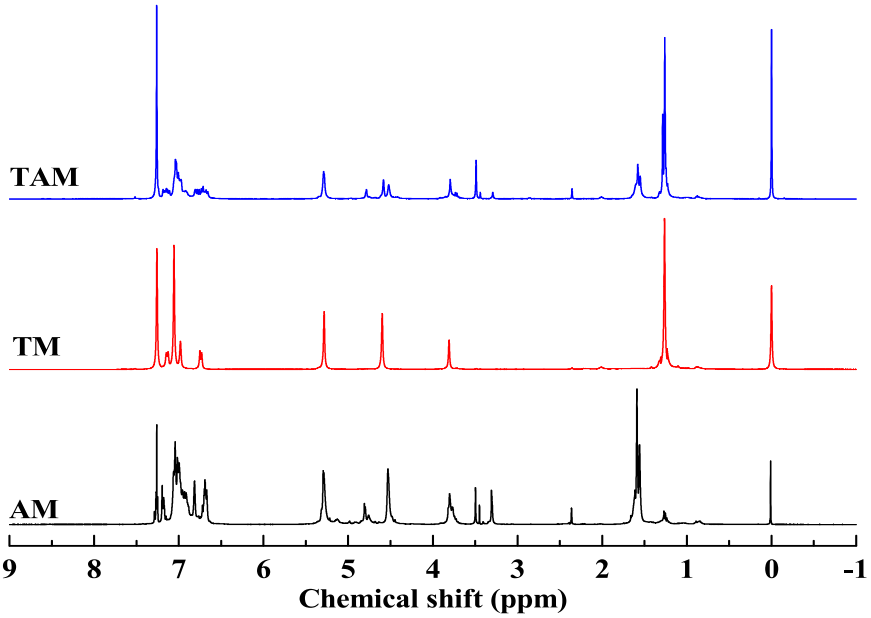
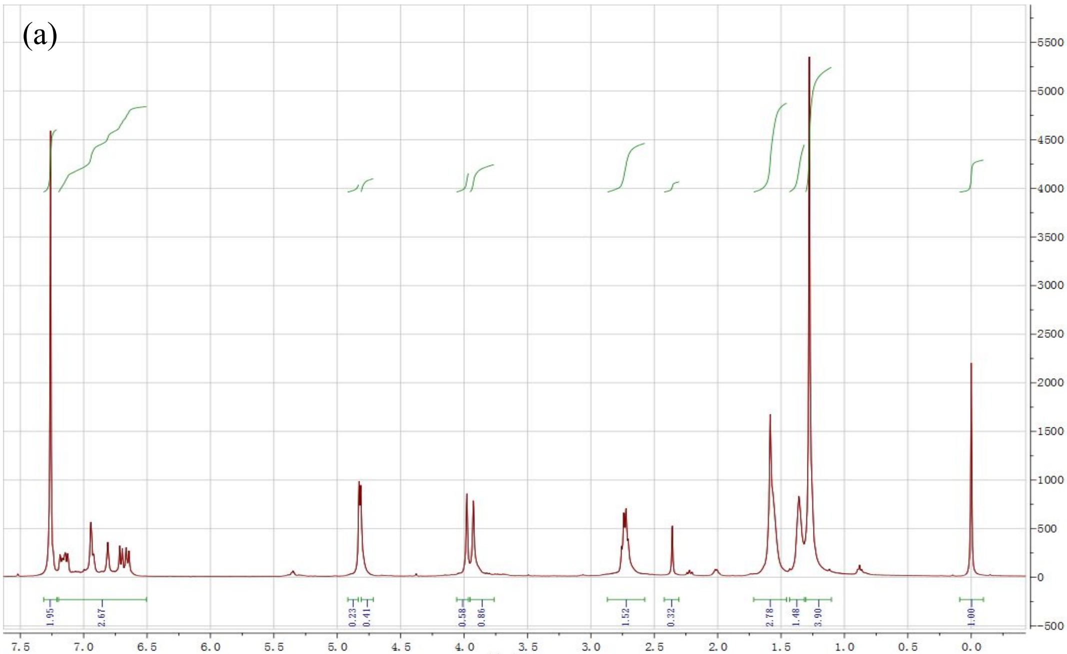
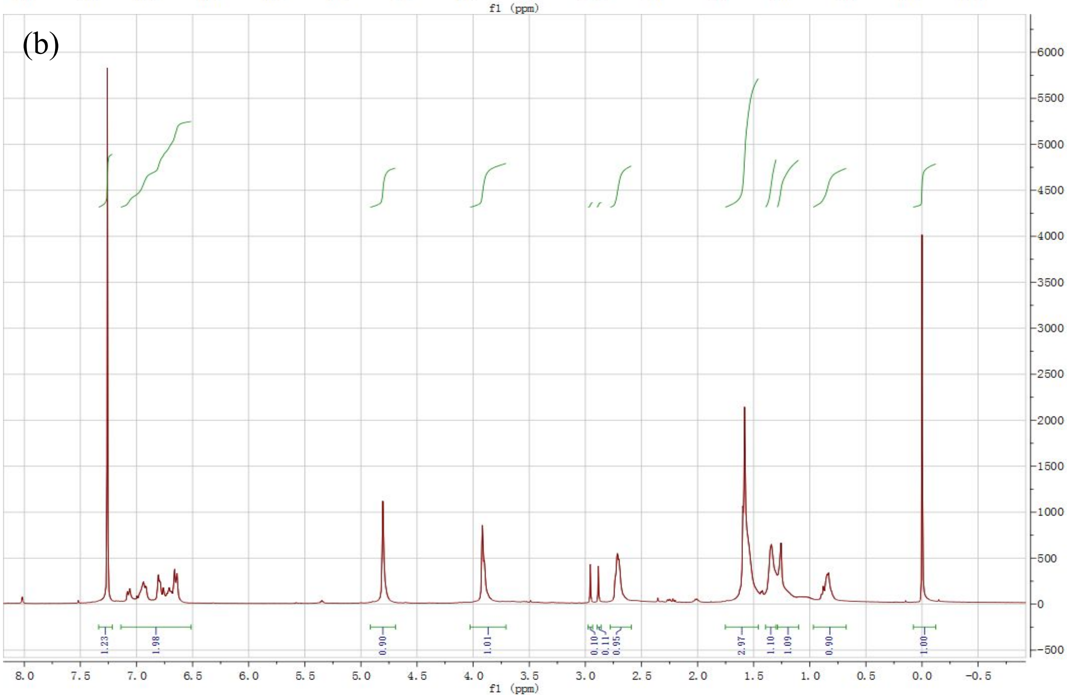


Figure S5. ^{1}H-NMR spectra of TAM, TM, and AM benzoxazine prepolymers.


(a)
1.95
2.67
0.23
0.41
0.58
0.86
1.52
0.32
2.78
1.48
3.90
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


(b)
1.23
1.98
0.90
1.01
0.10
0.11
0.95
2.97
1.10
1.09
0.90
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
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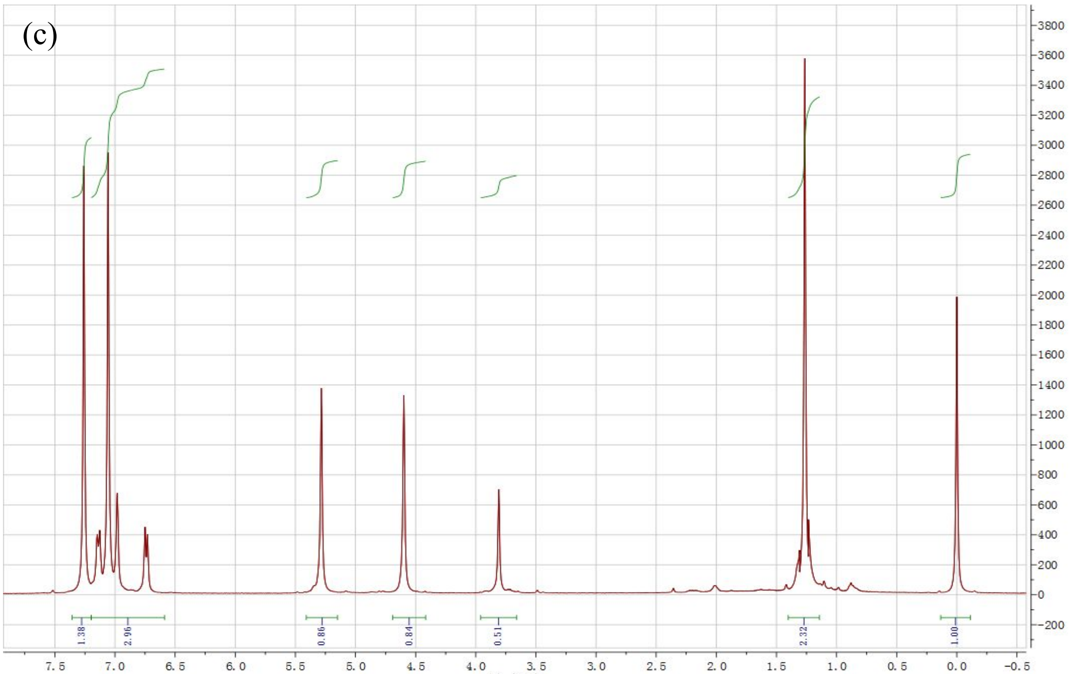
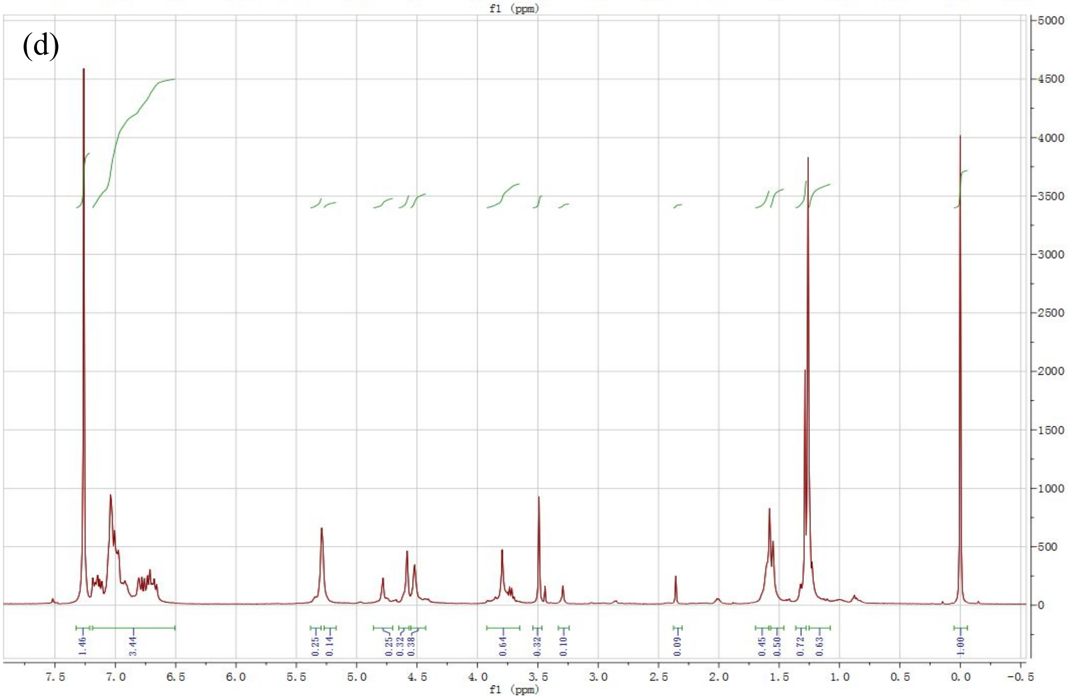
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


(c)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
1.38
2.96
0.86
0.84
0.51
2.32
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


(d)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.46
3.44
0.25
0.14
0.25
0.32
0.38
0.64
0.32
0.10
0.09
0.45
0.50
0.72
0.63
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

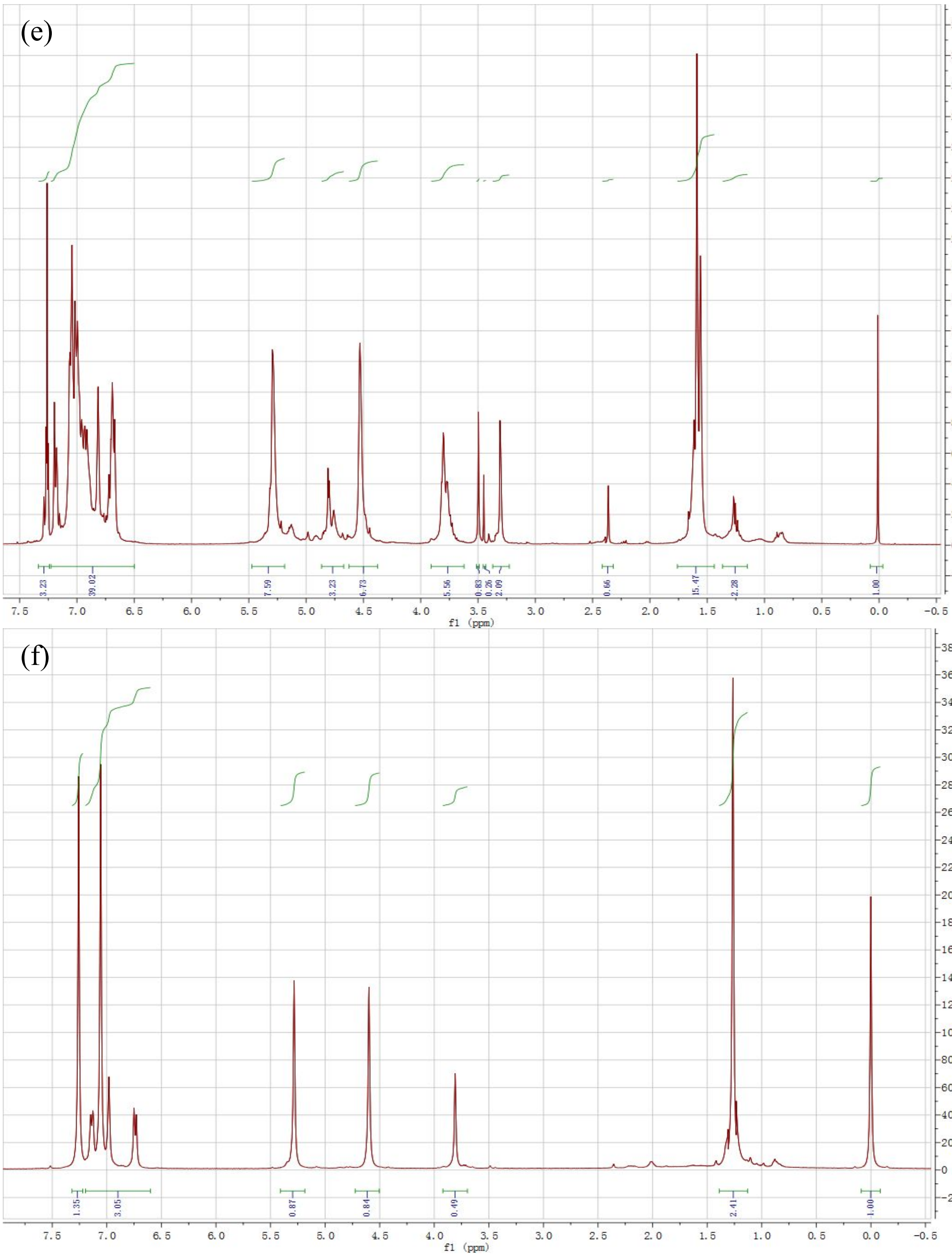


Figure S6. Original ^{1}H-NMR spectra of TAH (a), AH (b), TH (c), TAM (d), AM (e), and TM (f) benzoxazines.

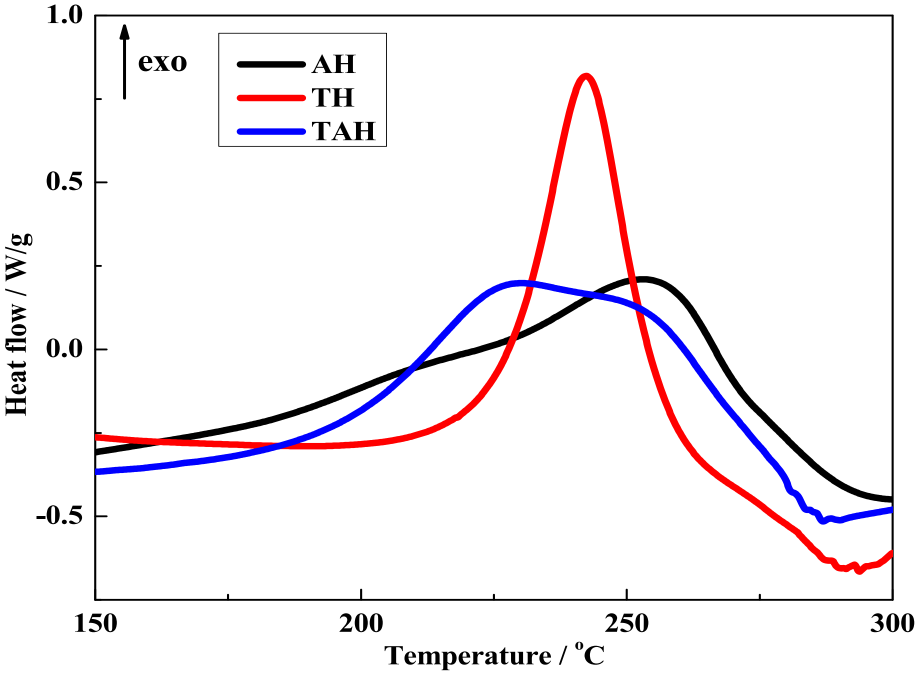


Figure S7. DSC thermograms of TAH, TH, and AH benzoxazine prepolymers.

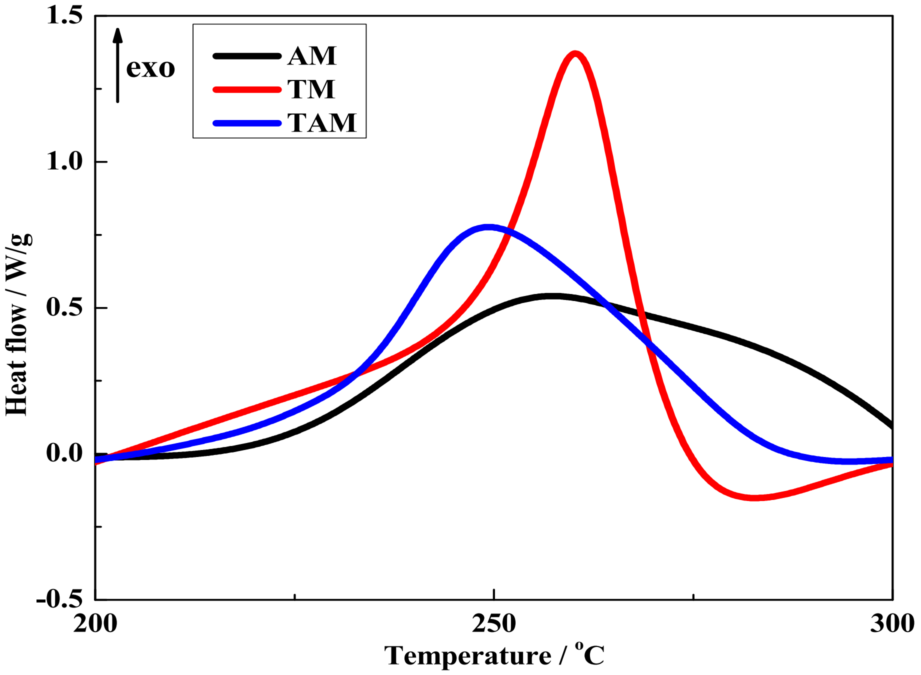


Figure S8. DSC thermograms of TAM, TM, and AM benzoxazine prepolymers.

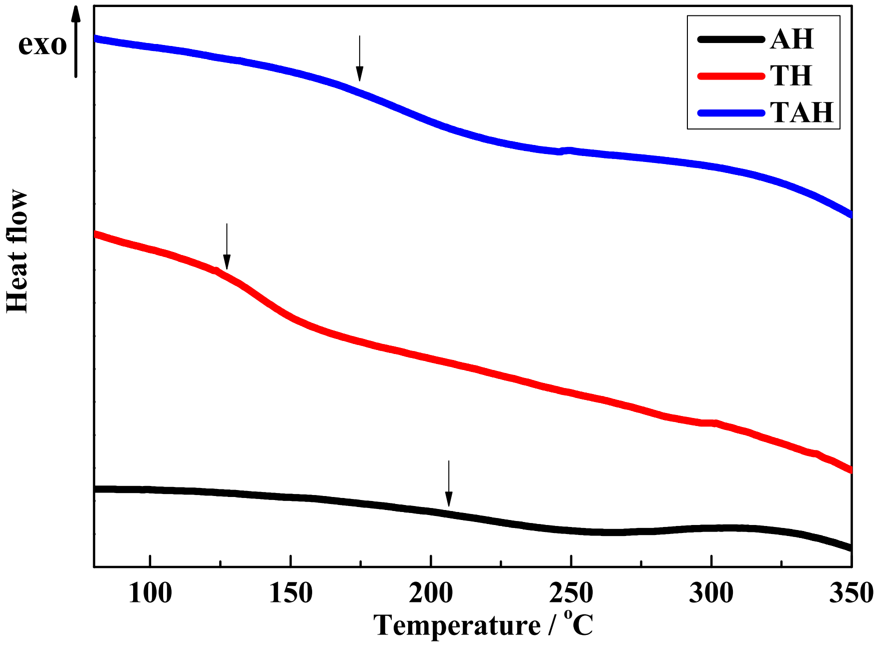


Figure S9. DSC thermograms of cured TAH, TH, and AH benzoxazine films.

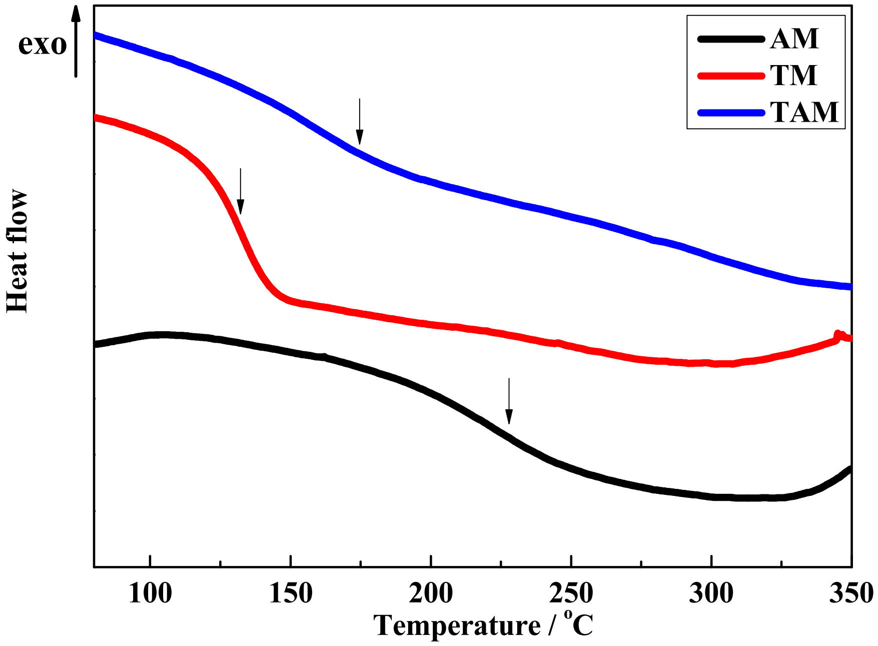


Figure S10. DSC thermograms of cured TAM, TM, and AM benzoxazine films.

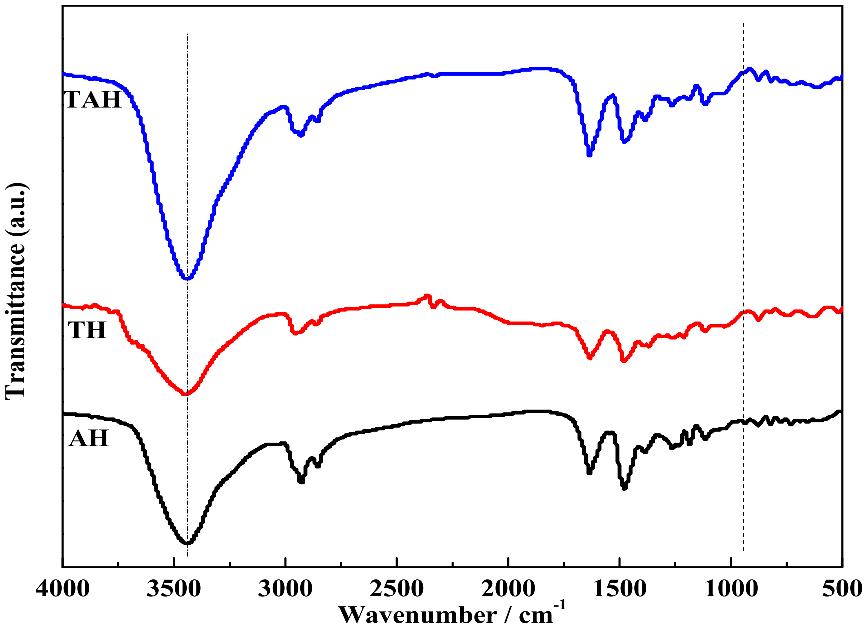


Figure S11. FTIR spectra of cured TAH, TH, and AH benzoxazine polymers.

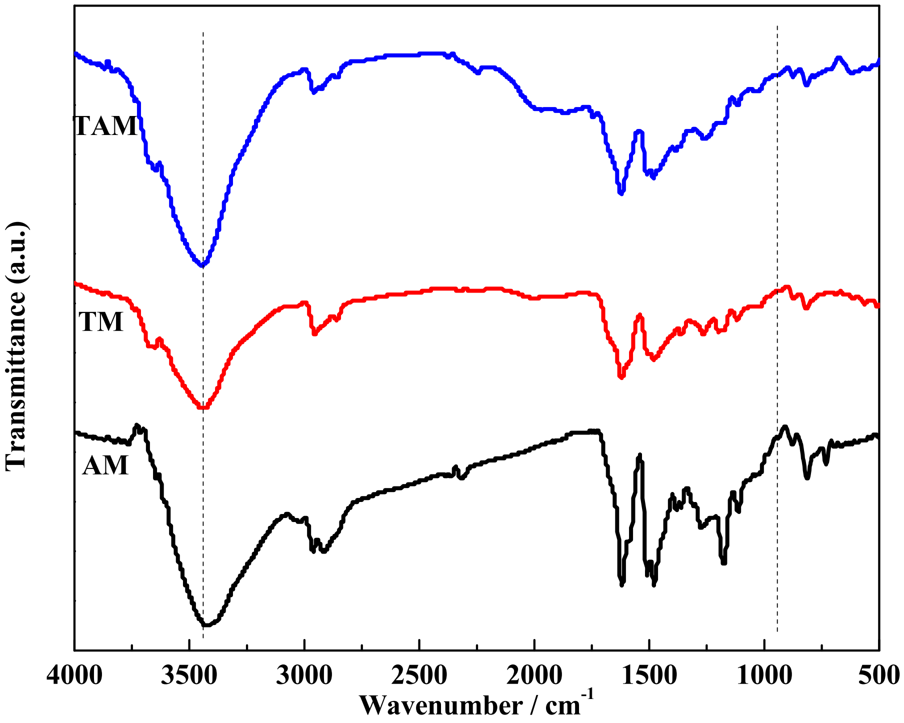


Figure S12. FTIR spectra of cured TAM, TM, and AM benzoxazine polymers.

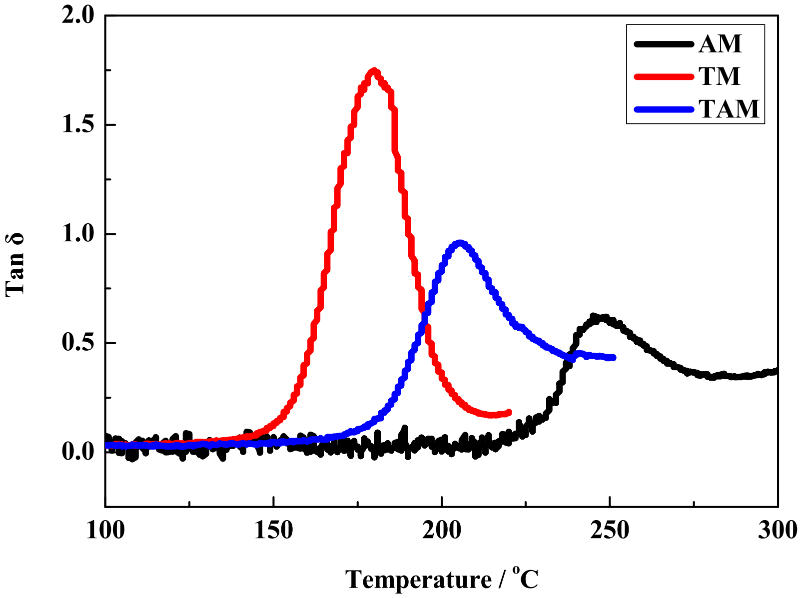


Figure S13 Temperature dependence of the loss factor (tan δ) results for TAM, TM, and AM ploybenzoxazines.

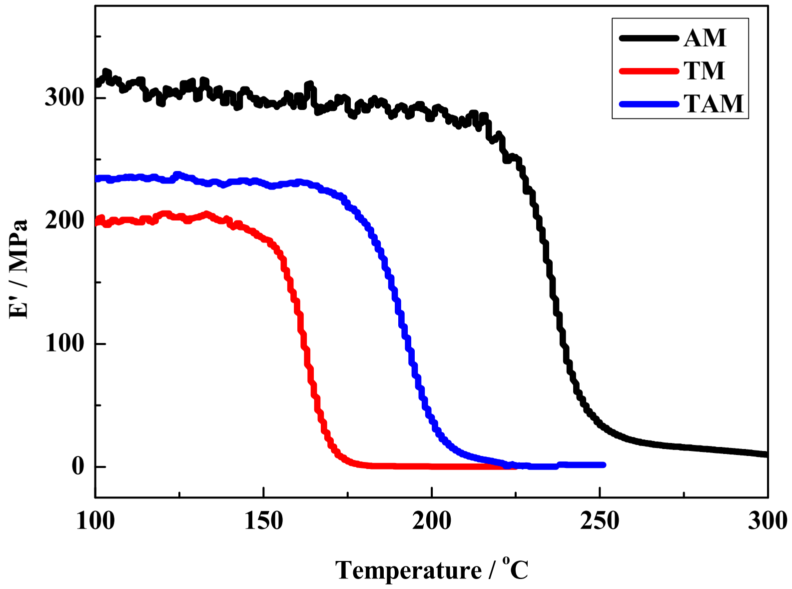


Figure S14 Temperature dependence of the storage modulus (E') results for TAM, TM, and AM ploybenzoxazines.

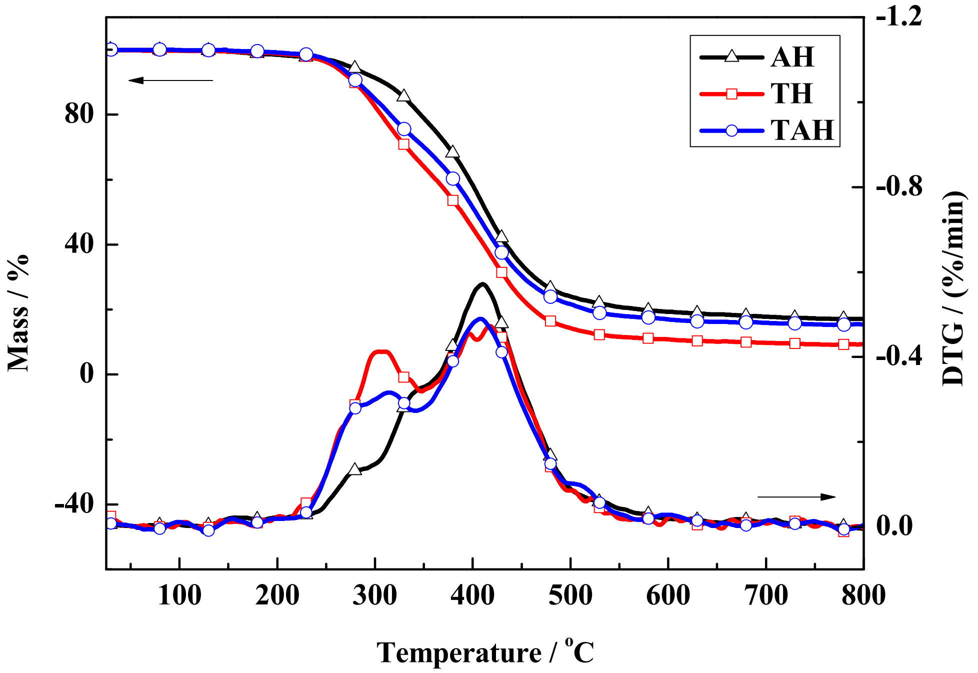


Figure S15 TGA and DTG thermograms of TAH, TH, and AH ploybenzoxazines.

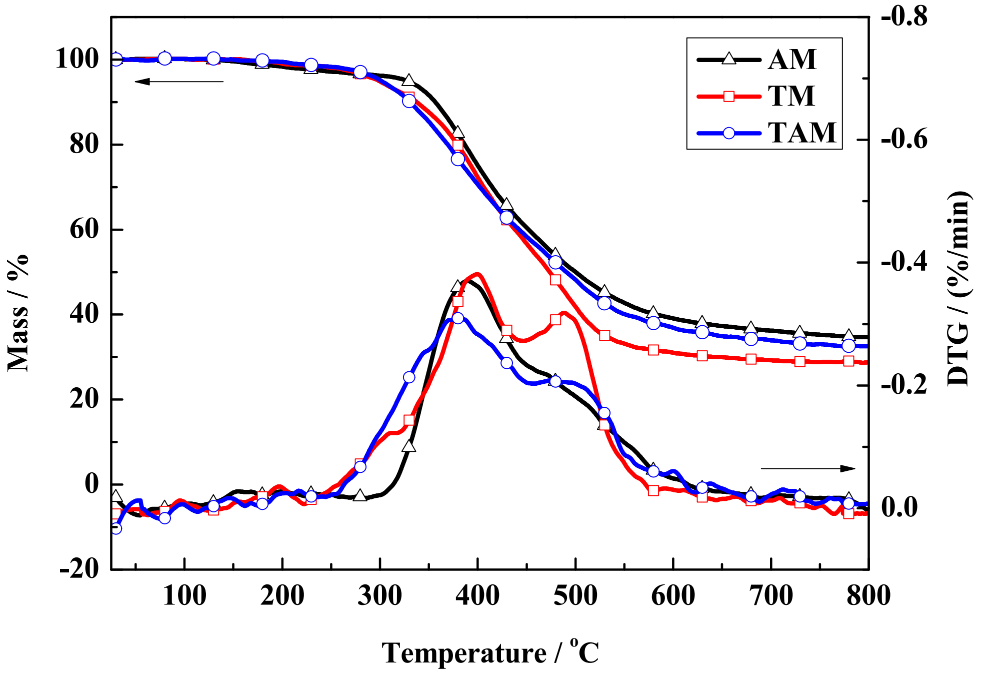


Figure S16 TGA and DTG thermograms of TAM, TM, and AM ploybenzoxazines.

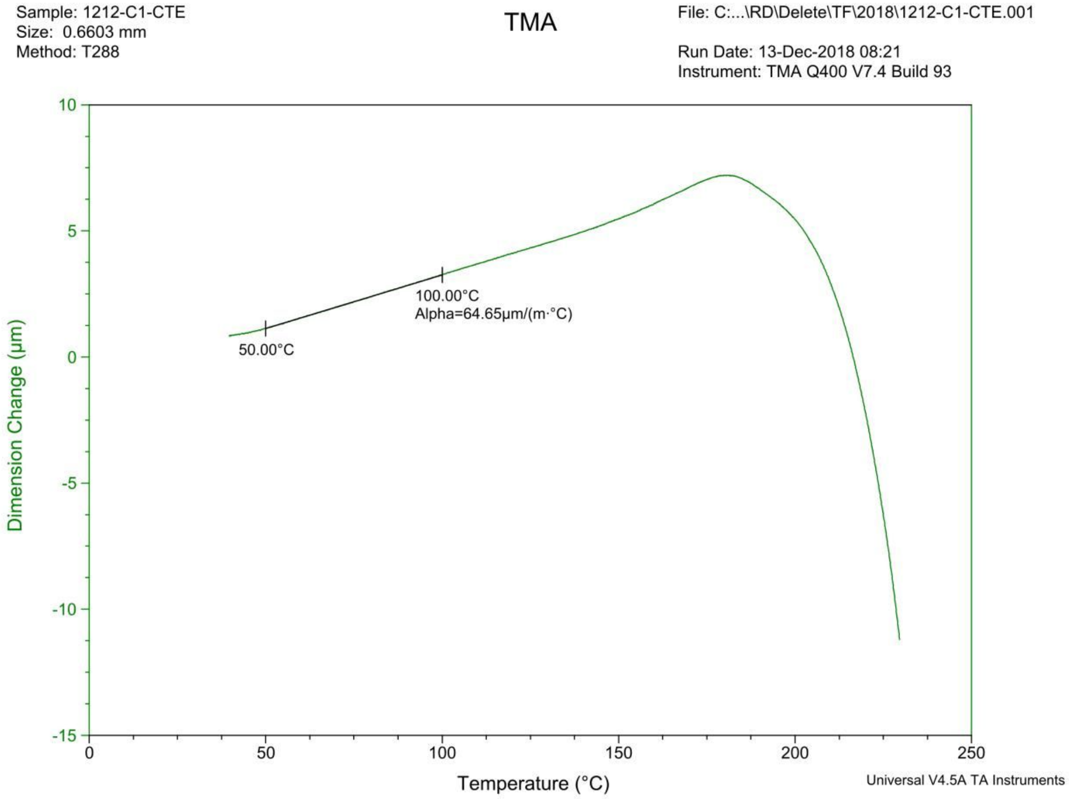


Figure S17 Thermomechanical analysis of cured TAH film.

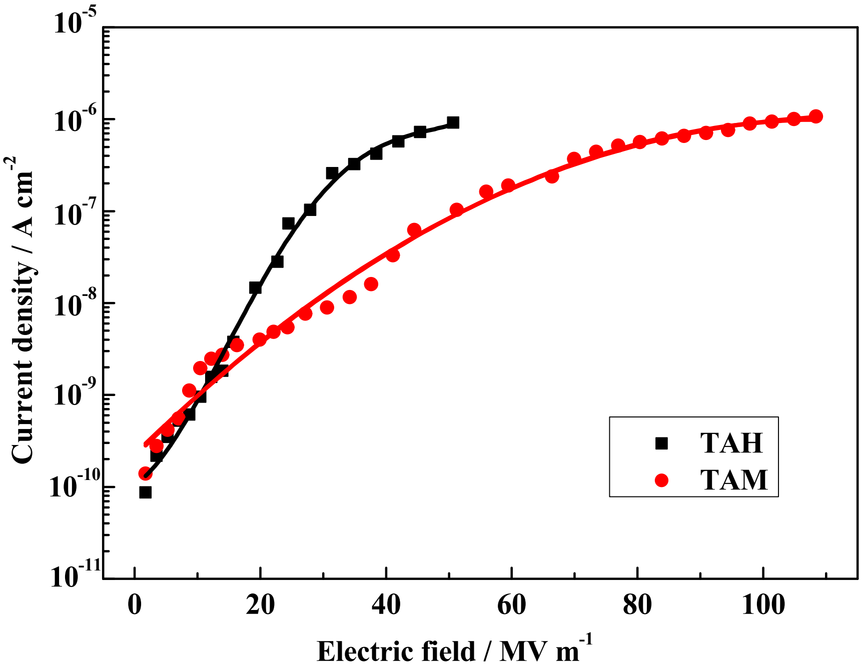


Figure S18 Conduction current density of copolymer films as a function of electric fields.

Table S1 Rough comparison of dielectric properties of benzoxazine resins.

Name	Raw materials (amines+phenols)	Dielectric constant	Dielectric loss	Ref.
B-a	bisphenol A+aniline	3.56±0.01 (100kHz)	0.00206 (100kHz)	1
F-1/B-a (1: 1)	F-1(4-(trifluoromethyl)aniline +hexafluorobisphenol A)	2.36±0.01 (100kHz)	0.00440 (100kHz)	
BOZ-1	4,4'-[(2,3,5,6-tetrafluoro-1,4-phenylene)-bis-(oxy)]dianiline +2-hydroxybenzaldehyde	2.35(100kHz)	0.0221 (100kHz)	2
BOZ-2	3,3'-[(2,3,5,6-tetrafluoro-1,4-phenylene)-bis-(oxy)]dianiline+ 2-hydroxybenzaldehyde	2.61(100kHz)	0.0248 (100kHz)	
BOZ-3	4,4'-[(2,2',3,3',5,5',6,6'-octafluoro-biphenyl-4,4'-diyl)bis(oxy)]dianiline+2-hydroxybenzaldehyde	2.39(100kHz)	0.0071 (100kHz)	
BOZ-4	3,3'-[(2,2',3,3',5,5',6,6'-octafluoro-biphenyl-4,4'-diyl)bis(oxy)]dianiline+2-hydroxybenzaldehyde	2.40(100kHz)	0.0230 (100kHz)	
BOZ-13	2-hydroxybenzaldehy + 2,2-bis(4-(4-aminophenoxy) -phenyl)propane	around 3.37 (1 MHz)		3
BOZ-14	2-hydroxybenzaldehy +2,2-bis(4-(4-aminophenoxy)-phenyl)hexafluoropropane	around 2.40 (1 MHz)		
BOZ-15	2-hydroxybenzaldehy +2,2 -bis(4-(4-amino-2-trifluoromethylphenoxy) phenyl)propane	around 2.42 (1 MHz)		
BOZ-16	2-hydroxybenzaldehy +2,2-bis(4-(4-amino-2-trifluoromethylphenoxy)phenyl)hexafluoropropane	around 2.42 (1 MHz)		
PBz	BZ-Cy-OH(trans-4-aminocyclohexanol hydrochloride +1,1-bis (3-methyl-4-hydroxy phenyl) cyclohexane)	3.34(1 MHz)		4

Name	Raw materials (amines+phenols)	Dielectric constant	Dielectric loss	Ref.
BPA-FBz	bisphenol A+furan anime	3.5(1 MHz)		5
MA-F /BPA-FBz (1: 1)	5-furfuryl-2,2-dimethyl-[1,3]dioxane-4,6-dione (MA-F)+BPA-FBz	3.0(1 MHz)		
DM	dehydroabietylamine+ 4-methylumbelliferone	about 3.01 (1 MHz,)		6
DG	dehydroabietylamine+guaiacol	about 3.15 (1 MHz,)		
M1	Octafluorocyclopentene(OFCP) + monofunctional benzoxazines (4-aminophenol+phenol)	3.19(1MHz)		7
M2	diamine (OFCP+4-aminophenol) +p-fluorophenol	2.61(1MHz)		
ploy(oTFA-ddm)	2,2,2-Trifluoro-N-(2-hydroxyphenyl)acetamide+ 4,4′-diaminodiphenylmethane	2.84(1 MHz)	0.022 (1 MHz)	8
cFPBO (further treated 260 °C/1 h)		2.19(1 MHz)	0.010 (1 MHz)	
OPS−Bz	OPS−OH($[PhSiO_{1.5}]_8$+3-hydroxy -4-nitrobenzoic acid+phydroxybenzoic acid)+aniline	1.79 (1 MHz.)	about 0.0097 (1 MHz)	9
HOH-a	HOH(2,2-bis(3-amino-4-hydroxy -lphenyl) propane (BAP) +p-hydroxybenzoic acid)+aniline	2.55 (1MHz)	0.030 (1MHz)	10
FOH-a	FOH(2,2-bis(3-amino-4-hydroxy-lphenyl) hexafluoropane+ p-hydroxybenzoic acid)+aniline	2.21(1MHz)	0.006 (1MHz)	
DDM–PBz	4,4'-diaminodiphenylmethane (DDM)+2-allyl phenol	3.44±0.01 (1 MHz)	0.0112± 0.001 (1 MHz)	11
PDMS–DDM–PBz	hydride terminated polydimethylsiloxane(PDMS)+ DDM–PBz	2.96±0.01 (1 MHz)	0.0074± 0.001 (1 MHz)	

Name	Raw materials (amines+phenols)	Dielectric constant	Dielectric loss	Ref.
DAH–PBz	diaminohexane (DAH)+ 2-allyl phenol	3.08±0.01 (1 MHz)	0.0070± 0.001(1 MHz)	
PDMS–DAH–PBz	hydride terminated polydimethylsiloxane(PDMS)+ DAH–PBz	2.42±0.01 (1 MHz)	0.0022± 0.001(1 MHz)	
DAROH-a	DAROH+aniline	2.3 (5 MHz)	0.010(5 MHz)	12
ALF8-BF	aliphatic diamine containing 8F+bisphenol AF	2.2(1GHz)	0.008 (1GHz)	13
ALH12-BA	1,6- hexamethylene diamine+bisphenol A	3.0(1GHz)	0.010 (1GHz)	
ARF12-BF	bisphenol AF+ 4,4′-(perfluorohexane-1,6-diyl) dibenzeneamine(ARF12)	2.4(1GHz)	0.024 (1GHz)	
ARH12-BA	4,4′-diamino-1,6-diphenylhexane (ARH12)+bisphenol A	2.9(1GHz)	0.010 (1GHz)	
ALF8-BA	aliphatic diamine containing 8F+bisphenol A	2.6(1GHz)	0.014 (1GHz)	
BPABZ	Bisphenol-A+aniline	3.31(1GHz)	0.0145 (1GHz)	14
BIPBZ	1,4-bisphenol+aniline	3.45(1GHz)	0.0181 (1GHz)	
DCPDBZ	dicyclopentadiene phenol novolac (DCPDNO)+aniline	2.95(1GHz)	0.0095 (1GHz)	
BA-a	bisphenol A+aniline	3.55(1 GHz)	0.0176(1 GHz)	15、16
BP-a	1,4-bisphenol+aniline	3.88(1 GHz)	0.0215(1 GHz)	
BE-a	4,4'-oxydiphenol+aniline	3.9(1 GHz)	0.0199(1 GHz)	16
P(P-oda)	4,4’-oxydianiline+phenol	3.48U(1 GHz)	7.9mU(1 GHz)	17
P-APPO-2	Amine end-capped Oligo (2,6-dimethyl phenylene oxide) (APPO)+2-hydroxybenzaldehyde	2.9 ± 0.01 (1 GHz)	0.0040 ± 0.00002 (1GHz)	18
P-APPO-1	APPO+phenol	2.9 ± 0.02 (1 GHz)	0.0043 ± 0.00006 (1GHz)	
BPA-APPO	APPO+biphenol A	2.9 ± 0.05 (1 GHz)	0.0040 ± 0.00005 (1GHz)	

Name	Raw materials (amines+phenols)	Dielectric constant	Dielectric loss	Ref.
BOZ	4-hydroxybenzyl alcohol+ diaminodiphenylmethane	3.57±0.01 (10 GHz)	0.024±0.001 (10 GHz)	19
BM	BOZ+4,4′-methylenediphenyl diisocyanate (MDI)	3.56±0.01 (10 GHz)	0.025±0.001 (10 GHz)	
BH	BOZ+ hexamethylene diisocyanate (HDI)	3.15±0.01 (10 GHz)	0.016±0.001 (10 GHz)	
BCM	BOZ+castor oil+MDI	3.22±0.01 (10 GHz)	0.023±0.001 (10 GHz)	
BCH	BOZ+Castor oil+HDI	2.96±0.01 (10 GHz)	0.023±0.001 (10 GHz)	
BAM-8	Bisphenol A+amine+ 4,4′-diaminodiphenylmethane	2.75 ± 0.01 (10 GHz)	0.023 ± 0.001 (10 GHz)	20
BAH-15	bisphenol A+amine+ 1,6-diaminohexane	2.54 ± 0.01 (10 GHz)	0.016 ± 0.001 (10 GHz)	21
TAH	bisphenol A+ p-tert-butylphenol +1,6-diaminohexane	2.26±0.01 (10 GHz)	0.0047±0.0001 (10 GHz)	This work
TH	bisphenol A+ p-tert-butylphenol	2.54±0.01 (10 GHz)	0.0045±0.0001 (10 GHz)	
AH	bisphenol A+1,6-diaminohexane	2.61±0.01 (10 GHz)	0.0053±0.0001 (10 GHz)	
TAM	bisphenol A+ p-tert-butylphenol +4,4′-diaminodiphenylmethane	2.66±0.01 (10 GHz)	0.0091±0.0001 (10 GHz)	
TM	bisphenol A+ p-tert-butylphenol	2.82±0.01 (10 GHz)	0.0113±0.0001 (10 GHz)	
AM	bisphenol A + 4,4′-diaminodiphenylmethane	3.53±0.01 (10 GHz)	0.0243±0.0001 (10 GHz)	

A rough comparison between our prepared benzoxazine resins and various other types of benzoxazine resins based on the dielectric properties is shown in Table S1. Generally, for dielectric performance enhancement of benzoxazine resins, the preparation of less polar monomers, binary, ternary and tetra-copolymer systems, and inorganic-organic composites have become increasingly attractive.[1-21] It is noted that the low-k ($k < 3.0$) fluorine-free benzoxazine resins under high-frequency (> 300 MHz) have been rarely reported. In particular, scarce research has focused on the reduction of *f* for low dielectric thermosetting resins. In our laboratory, the aromatic and aliphatic main-chain benzoxazine copolymers with high-frequency low-*k* values have been reported.[19-21] However, the *f* values of designed and prepared benzoxazine resins are still not satisfactory. Very recently, Lin reported that poly(2,6-dimethyl phenyl oxide) (PPO) containing benzoxazine resin can reach the high-frequency requirement of *f* value below 0.005 (1GHz), due to the main component of thermoplastic PPO.[18] In this paper, we first report, to the best our knowledge, the pure thermosetting benzoxazine resins owning low *k* (< 3) and ultra-low *f* (< 0.005) values under high frequencies (5 & 10 GHz).

Table S2 The breakdown strength and T_g* data of cured benzoxazine polymers.

Samples	AH	TH	TAH	AM	TM	TAM
Breakdown Strength (MV m^{-1})	-	-	57.89	-	-	111.3
T_g / ^oC (DSC)	206	127	172	227	132	174

*: T_g values were measured from the midpoint of the heat capacity change of DSC curves based on Figures S9 and S10.

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