Low melting point, high thermal stable branched benzoxazines resin derived from mixed-substituted phosphazene core

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Abstract. Six fluorine-containing, mix-substituted phosphazene-based branched benzoxazine monomers with a low melting point were successfully prepared and their chemical structures were verified by ¹H, ¹³C, ³¹P and ¹⁹F nuclear magnetic resonance (NMR). These branched benzoxazine resins underwent thermal ring-opening polymerization to form cured polymers with high thermal stability both in N₂ atmosphere and in air. The co-substituents, both *m*-CF₃PhOH and *p*-CF₃PhOH, imposed significant effects on processing, thermal, and surface properties of corresponding polybenzoxazines. Non-isothermal differential scanning calorimetry (DSC) under diverse heating rates was adopted to investigate the curing kinetics and determine the activation energy of polymerization. DSC results indicate that the *m*-CF₃PhO–/*p*-CF₃PhO– groups have the potential to lower ring-opening polymerization temperature. Glass transition temperatures (*T*_gs) of polybenzoxazines derived from *p*-CF₃PhOH are higher than that of polymers derived from *m*-CF₃PhOH due to different steric hindrance and crosslinking density. More interesting, all polybenzoxazines show relatively high dielectric constant but exhibit low dielectric loss at ambient temperature.

Keywords: thermosetting resins, branched benzoxazine monomer, phosphazene-core, low melting point, high thermal stability

1. Introduction

1,3-Benzoxazine, a monomer of newly developed thermosetting resins called polybenzoxazines (PBZ), can be synthesized conveniently from primary amine, formaldehyde, and phenol by one-pot Mannich condensation [1, 2]. Due to the wide range of selectivity of raw materials, it provides benzoxazines with molecular design flexibility and can meet the practical requirement by designing different monomer structures [3–20]. For example, the tetra-functional fluorene-based benzoxazine resin (t-BF-a-c) was synthesized, which exhibits an exothermal peak at 276 °C, and displays good processability and wide process window (60 °C) due to the incorporation of cardanol

[21]. The main merits of PBZs include excellent mechanical and thermal properties, high char-formation ability [2, 22], low dielectric loss [23], low water absorption [24–28]. The furan-containing tetrafunctional fluorene-based benzoxazine monomer (t-BF-f) was prepared, which exhibits extremely higher glass transition temperature (440 °C) and better thermal stability than difunctional furan-containing fluorene-based polybenzoxazine, ascribed to its higher crosslinking density of poly(t-BF-f) [29]. Besides, most PBZs possess excellent dimensional stability due to their high crosslinking density, and this character makes it a suitable polymer matrix resin for polymer composites. Many benzoxazine-based composites

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have been studied [30–34]. However, most benzoxazine resins appear as high melting point powders, and organic solvents [35] are always needed when preparing benzoxazine composites. Obviously, organic solvent will bring about environmental issues and make the process complicated. Water was also used as a processing aid for benzoxazine composite preparation, but before curing, water still need to be removed from the system [33]. Another approach to lower the melting point of benzoxazine resin is introducing flexible chain [36–38] or functional group [39] into benzoxazine structure, but the improvement of processability is obtained at the sacrifice of the mechanical and thermal properties to some extent. Hence design and preparation of benzoxazine monomer with a low melting point but without decreasing its properties is a current challenge.

It has been proved that the incorporation of fluorinated substituents into polybenzoxazines [40, 41] can improve the thermal stability [42] and lower its dielectric constant [43, 44] due to the small dipole moment and low polarizability of the C–F bond [45]. Thus the fluorine content in main-chain polybenzoxazines leads to better hydrophobic property [46, 47], which seemed very suitable for oil–water separation driven by gravity [48–50]. Undoubtedly, fluorinated benzoxazines have attracted many attentions and gradually become a research focus [51–53].

Recently, our group focused on preparing organic–inorganic hybrid polybenzoxazines based on cyclotriphosphazene core, and this kind of resins exhibited excellent thermal stability and easy preparation [54–57]. Though these monomers have higher molecular weights (>1490 g/mol) compared that with traditional bisphenol-A based benzoxazine monomer, but some of them showed relatively low melting point (32–84 °C) [57] and have the potential to be used as a matrix resin for composite preparation. With the aid of high molecular design flexibility of phosphazene-based benzoxazine, we try to introduce fluorine-containing high polar group, such as *m*-CF₃PhOH/*p*-CF₃PhOH, into cyclotriphosphazene core to prepare mixed-substituted phosphazene-based benzoxazine derivatives to obtain benzoxazine monomers with a low melting point or even liquid-like monomers. In this research, six benzoxazine monomers with branched structure (Figure 1) and different functionality were obtained by a nucleophilic reaction. These benzoxazine monomers appear as liquid or low melting point solid suitable for

composites preparation. More attractively, after polymerization, all fluorine-containing polybenzoxazines show high heat resistance both in N₂ and in air atmosphere, and the highest glass transition temperature is as high as 218 °C.

2. Experimental

2.1. Materials

Salicylaldehyde (≥98%), sodium borohydride (96%≥), 4-aminophenol (≥98%), paraformaldehyde (≥95%), potassium carbonate and sodium hydroxide were all gained from Guoyao Chemical Reagent Co., Ltd., Shanghai, China. *m*-CF₃PhOH[3-(Trifluoromethyl)phenol](≥98%), *p*-CF₃PhOH[4-(Trifluoromethyl)phenol](≥98%), were supplied by Alfa Aesar Reagent Co, Ltd., Missouri, USA. Hexachlorocyclotriphosphazene [N₃P₃Cl₆, *trimer*] was recrystallized before utilization. All other reagents were used directly after received.

2.2. Measurements

Chemical structure of all compounds was identified by Proton (¹H), Carbon (¹³C), Phosphorus (³¹P) and Fluorine (¹⁹F) NMR spectroscopy which recorded on Bruker AV400 NMR spectrometer (Bruker, Co., Ltd., Switzerland) and taking deuterated solvent DMSO-*d*₆ as the solvent. FTIR (Fourier transform infrared) spectra were taken on Bruker Vertex 70 FTIR spectrometer (BrukerDaltonics, Inc., USA) with a resolution of 4 cm⁻¹ between 4000–400 cm⁻¹. The rheological behavior was studied with a rotational rheometer (MCR302 SN81054732, Beijing Hongchangxin Technology co., LTD, Beijing, China) at 100 °C. Thermal transitions were monitored with DSC instrument NETZSCH Model 404F3 from NETZSCH, Inc. (Bavaria, Germany) within the temperature range of 30–300 °C at a scanning rate of 10 °C/min, nitrogen flow rate of 50 ml/min. Thermal stability of polybenzoxazines was investigated through thermogravimetric analysis on NETZSCH High-Resolution STA 409PC thermogravimetric analyzer (TGA) (NETZSCH instrument manufacturing co., Ltd., Selb, Germany) under nitrogen purging rate of 60 ml/min, at a heating rate of 10 °C/min and scanning temperature range between 30 to 900 °C. The bulk properties of polybenzoxazines were measured on a dynamic mechanical thermal analysis apparatus (Diamond DMA, PerkinElmer Inc., Waltham, USA) in 3-point bending mode with specimens dimension of 50×10×1.0 mm. The thermal transition

of samples was investigated in the temperature scope of 30–300 °C, with a frequency of 1 Hz and heating rate of 4 °C/min. A contact angle goniometer, POW-EREACH JC2000C1 (Shanghai Zhongchen digital technology equipment co., Ltd., Shanghai, China), was employed to measure the advancing contact angle (θ_a) and the receding contact angle (θ_r) of film samples at 25 °C. During θ_a measurement, drop volume increased from 3 to 7 μ l, when measuring θ_r , drop volume decreased to 3 μ l. In the course of measuring both θ_a and θ_r , the needle always maintained within the droplet. For each sample, a minimum of three different readings was recorded. *n*-Hexadecane and deionized water were used as a standard. Dielectric properties of film samples were recorded on Agilent 4294A Precision Impedance Analyzer (Agilent Technologies, Inc., Palo Alto, USA) at ambient temperature in the frequency range of 100 Hz–1 MHz. Before each measurement, the samples were coated with InGa electrodes. The size of the samples was about 20×10×2 mm. Monomers were compressed into tablets, 12 mm in diameter, the thickness of 2 mm.

2.3. Curing kinetic analysis

Non-isothermal DSC (differential scanning calorimetry) method was used to study the curing behavior. The activation energy of polymerization was calculated separately by Kissinger, Ozawa and Flynn–Wall–Ozawa's method [58] based on the DSC data taking at a heating rate of 2, 5, 10, 15, and 20 °C·min⁻¹.

2.4. Monomer synthesis: Preparation of monomer 4m, 3m, 2m, 4p, 3p and 2p

Six monomers were prepared according to the reported procedure [57]. The reaction details and chemical structure of six branched monomers with phosphazene core were presented in Figure 1. The monomers were named as *Nm* and *Np*. (*N* = 4, 3, 2, which express the number of co-substituent, *m/p* represents *m/p*-CF₃PhOH).

General procedures for preparing the monomers:

Preparation of 4m [N₃P₃(O-BOZ)₂(OC₆H₅-*m*-CF₃)₄]: [N₃P₃Cl₆] (4.00 g, 11.5 mmol, 1 eq), activated K₂CO₃ (12.72 g, 92 mmol, 8 eq) and acetonitrile (150 ml) were charged into a three-necked 500 ml round-bottom flask with vigorous agitation under ice-water bath at 0 °C, then a calculated amount of

HO-BOZ (5.26 g, 23 mmol, 2 eq) dissolved in 100 ml acetonitrile was added dropwise into the suspension. Then, the mixture was agitated under an ambient condition in an argon atmosphere for nearly 5 h, and the process was monitored by TLC (thin-layer chromatography). After the HO-BOZ was consumed completely, the excess amount of *m*-CF₃PhOH (or *p*-CF₃PhOH) (5.67 g, 60 mmol, 4 eq) in 100 ml CH₃CN was dropped slowly into the reaction mixture under vigorous agitation, then let the temperature rose to 85 °C and kept at this temperature for 10 hours. Then cooled the reaction mixture to ambient temperature, solid salts (remaining K₂CO₃ and produced KCl) were filtered out and the filtrate was condensed under vacuum at 40 °C by rotary evaporation. The residue was dissolved in CH₂Cl₂ (120 ml), extracted three times with 5% sodium hydroxide and finally washed with pure water until the water phase was neutral. The CH₂Cl₂ solution was dried by anhydrous MgSO₄ overnight. Then the solvent was removed by rotary evaporation at under vacuum to give pale yellow viscous liquid (target product N₃P₃(O-BOZ)₂(OC₆H₅-*m*-CF₃)₄ 13.03 g, yield 92.0%). The other monomers were prepared with similar procedure. The chemical structures of six benzoxazines are shown in Figure 1.

4m: pale yellow viscous liquid, yield 92%, ¹H NMR (ppm, DMSO-*d*₆, TMS): 4.64(s, 4H, CH₂N), 5.43 (s, 4H, OCH₂N), 6.75–7.53(m, 32H, CH). ³¹P NMR (δ, DMSO-*d*₆): 8.77–9.03. ¹⁹F NMR (δ, DMSO-*d*₆): -61.64–61.38(CF₃).

3m: pale yellow viscous liquid, 91% yield, ¹H NMR (ppm, DMSO-*d*₆, TMS): 4.62 (s, 6H, CH₂N), 5.41 (s, 6H, OCH₂N), 6.63–7.54 (m, 36H, CH). ³¹P NMR (δ, DMSO-*d*₆): 8.97–9.13, ¹⁹F NMR (δ, DMSO-*d*₆): -61.59–61.29(CF₃).

2m: light yellow powder, 87% yield, mp. 35.7 °C. ¹H NMR (D ppm, MSO*d*₆, TMS): 4.60 (s, 8H, CH₂N), 5.39 (s, 8H, OCH₂N), 6.70–7.45 (m, 40H, CH). ³¹P NMR (δ, DMSO*d*₆): 9.45–9.70. ¹⁹F NMR (δ, DMSO-*d*₆): -61.39–61.24(CF₃).

4p: light yellow powder, 91.0% yield, mp. 40.2 °C. ¹H NMR (D ppm, MSO-*d*₆, TMS): 4.61 (s, 4H, CH₂N), 5.40 (s, 4H, OCH₂N), 6.71–7.51 (m, 32H, CH). ³¹P NMR (δ, DMSO-*d*₆): 8.99–9.22. ¹⁹F NMR (δ, DMSO-*d*₆): -60.71–60.43(CF₃).

3p: light yellow powder, 89.0% yield, mp. 46.3 °C. ¹H NMR (ppm, DMSO-*d*₆, TMS): 4.62 (s, 6H, CH₂N), 5.41 (s, 6H, OCH₂N), 6.72–7.51 (m, 36H,

Figure 1. Synthesis of cyclotriphosphazene-based mixed substituted benzoxazines.

CH). ^{31}P NMR (δ , $\text{DMSO-}d_6$): 9.22–9.31, ^{19}F NMR (δ , $\text{DMSO-}d_6$): -60.96–60.46(CF_3).

2p: light yellow powder, 87% yield, mp. 56.2 °C. ^1H NMR (ppm, $\text{DMSO-}d_6$, TMS): 4.60 (s, 8H, CH_2N), 5.40 (s, 8H, OCH_2N), 6.95–7.65 (m, 40H, CH). ^{31}P NMR (δ , $\text{DMSO-}d_6$): 9.22–9.59. ^{19}F NMR (δ , $\text{DMSO-}d_6$): -60.71–60.43(CF_3).

2.5. Curing reaction of benzoxazine monomers

The six monomers were added to six aluminum foil molds and heated up to 120 °C under vacuum for 1 h. Later, the samples were cured in an air-circulating temperature-controlled oven as following: 200 °C/2 h, 220 °C/2 h, 230 °C/2 h, 240 °C/2 h then post-cured at

250°C for 1 h. When finishing curing, the temperature was allowed to bring back gradually to room temperature to prevent samples cracking. Then six polymers (P4*m*, P3*m*, P2*m*, P4*p*, P3*p* and P2*p*) were obtained.

3. Results and discussion

3.1. Chemical structure characterization of the six benzoxazines

The proposed chemical structures of six monomers were collected in Figure 1 and were thoroughly analyzed by NMR technology. The ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra (DMSO as solvent) of monomer 4*m* are shown in Figure 2 and the corresponding data of all six monomers are collected in Table 1. Signals (Figure 2a) at 4.60–4.64 ppm ($\text{Ar}-\text{CH}_2-\text{N}$) and 5.39–5.43 ppm ($\text{O}-\text{CH}_2-\text{N}$) for benzoxazine structure [59] are observed in all monomers. The multiple peaks at 6.63–7.67 ppm are ascribed to the aromatic protons. The theoretical ratio of the hydrogen atom of $\text{Ar}-\text{CH}_2-\text{N}$, $\text{O}-\text{CH}_2-\text{N}$ and all aromatic hydrogen in monomer 4*m* is 4:4:32 based on its chemical structure, and the experimental ratio according to the integrated peak area of ^1H NMR signals is 4.00:3.99:32.81, which proves that there are two benzoxazine units and four *m*- CF_3PhO - on cyclotriphosphazene ring in 4*m*. In ^{13}C NMR spectrum of 4*m* (Figure 2b), the characteristic carbon

resonances of the oxazine ring appear at 49.48 ($\text{Ar}-\text{CH}_2-\text{N}$) and 79.16 ppm ($\text{O}-\text{CH}_2-\text{N}$), respectively.

Because the six monomers were mix-substituted by HO-BOZ and *m*- CF_3PhOH /*p*- CF_3PhOH , the chemical environment of phosphorus atoms in the same monomer is different for its asymmetric nature, so the ^{31}P NMR signals of 4*m* appeared as multiple peaks around 9.0 ppm (Figure 2c). For there are no other peaks were found, we can conclude that the substitution reaction of cyclotriphosphazene was complete. Besides, the ^{19}F NMR spectrum of 4*m* (Figure 2d) shows the characteristic resonance of fluorine atoms of $-\text{CF}_3$ at –60 to –62 ppm, which indicates that the *m*- CF_3PhOH (or *p*- CF_3PhOH) has been successfully introduced into phosphazene ring. The NMR data of the other five monomers were collected in Table 1.

3.2. Curing reaction of six monomers scanned by DSC

From Table 2, we can find out that all six mixed-substituted monomers show low melting point (<60 °C), and more surprisingly, the monomer 4*m* and 3*m* are pale yellow viscous liquids at room temperature, even if the theoretical molecular weight of six monomers are as high as 1231.8 g/mol (4*m*), 1297.0 g/mol

Figure 2. ^1H NMR (a), ^{13}C NMR (b), ^{31}P NMR (c) and ^{19}F NMR (d) spectra of monomer 4*m*.

Table 1. The data of nuclear magnetic resonance (NMR).

	Monomer					NMR [ppm]		
	Ar-CH ₂ -N		O-CH ₂ -N		Aromatic	Founded ratio of H atom (a:b:Aromatic)	³¹ P	¹⁹ F
	¹ H	¹³ C	¹ H	¹³ C				
4 <i>m</i>	4.64	49.48	5.43	79.16	6.75–7.53	4.00:3.99:32.81	8.77–9.03	-61.64–61.38
3 <i>m</i>	4.62	49.48	5.41	79.19	6.63–7.54	6.00:6.10:36.84	8.97–9.13	-61.59–61.29
2 <i>m</i>	4.60	49.50	5.39	79.29	6.70–7.45	8.00:7.92:40.75	9.45–9.70	-61.39–61.24
4 <i>p</i>	4.61	49.45	5.40	79.28	6.71–7.67	4.00:3.99:31.90	8.99–9.22	-60.71–60.45
3 <i>p</i>	4.62	49.44	5.41	79.21	6.72–7.62	6.00:6.01:36.71	9.22–9.31	-60.96–60.46
2 <i>p</i>	4.61	49.46	5.40	79.30	6.95–7.60	8.00:8.08:40.31	9.22–9.59	-60.71–60.43

(3*m*), 1362.1 g/mol (2*m*), 1231.8 g/mol (4*p*), 1297.0 g/mol (3*p*), 1362.1 g/mol (2*p*), respectively. *m*-CF₃PhOH owns the melting point more effectively than *p*-CF₃PhOH because of its asymmetric structure. Furtherly, we measured their viscosity at a shear rate of 60 s⁻¹ at 100 °C (this temperature is far below the onset polymerization temperature of all monomers), the corresponding viscosities are 0.31 (4*m*), 1.41 (3*m*), 11.30 (2*m*), 16.40 (4*p*), 70.10 (3*p*), 133.80 Pa·s (2*p*), respectively. Hence, the low melting point and low viscosity provided them with good processing performance and made them suitable for composite preparation.

The polymerization behaviors of six monomers were probed by DSC as depicted in Figure 3, and the corresponding data were collected in Table 2. Their onset polymerization temperatures *T*₀ are as high as 225 °C (4*m*), 229 °C (3*m*), 240 °C (2*m*), 235 °C (4*p*), 235 °C (3*p*) and 248 °C (2*p*), we can figure out that all monomers possess wide processing window ($\Delta T > 189$ °C, please see Table 2 for details) and this character will benefit composites preparation. From the DSC curves of six monomers (Figure 3), the peak temperature (*T*_{max}) of heat release due to

ring-opening polymerization of monomer 4*m* to 2*p* centered at 246, 248, 259, 253, 252 and 265 °C, respectively. The monomer 4*m* (or 4*p*) which contains four *m*-CF₃PhO- (or *p*-CF₃PhO-) groups shows lower *T*_{max} compared with 2*m* (or 2*p*) which only contains two *m*-CF₃PhO- (or *p*-CF₃PhO-) groups, and the trend is consistent with the onset polymerization temperature. It means that the *m*-CF₃PhO-/ *p*-CF₃PhO-groups possess the ability to lower the ring-opening polymerization temperature, and the more the co-substituted groups, the lower the onset polymerization temperature of the corresponding monomer.

For the sake of understanding the details of ring-opening polymerization, non-isothermal DSC methodology was adopted to study the curing behavior of six monomers by different mathematic model. The non-isothermal DSC curves of monomer 3*m* were presented in Figure 4a. It can be observed that monomer 3*m* shows only one exothermic peak under different heating rates and the exothermic peak moves to a higher temperature with increasing heating rate. For example, the exothermic peak locates at 218 °C at a heating rate of 2 °C/min, it reaches 265 °C when heating rate increases to 20 °C/min. From these curves, some curing parameters concerning the nature of the ring-opening polymerization of monomer 3*m* such as onset polymerization temperature (*T*₀), maximum polymerization temperature (*T*_p), and the end-up polymerization temperature (*T*_m) at different heating rates could be figured out. The relationship between curing parameters (and heating rate (ϕ)) is shown in Figure 4b. By extrapolating the heating rate to zero, the corresponding values of *T*₀, *T*_p and *T*_m for monomer 3*m* are 185, 219 and 237 °C, respectively. In the same way, curing parameters of other five monomers at zero heating rate are obtained and listed in Table 2 (marked in green color).

The activation energy (*E*_a) of monomer 3*m* was computed according to Kissinger (*E*_K), Ozawa (*E*_O) and

Figure 3. DSC plots of the six benzoxazine monomers under scanning rate of 10 °C/min.

Table 2. The properties of monomers and their corresponding polymerization activation energies.

Monomer						^f Curing parameters			E_a [kJ/mol]			
	^a T_m [°C]	^b Viscosity [Pa·s]	^c T_o [°C]	^d ΔT [°C]	^e T_{max} [°C]	T_o [°C]	T_p [°C]	T_m [°C]	E_K	E_O	E_{F-W-O}	Average
4 <i>m</i>	liquid	0.31	225	>225	246	197	217	236	87.5	90.3	90.8	89.5
3 <i>m</i>	liquid	1.41	229	>229	248	185	219	237	97.7	100.9	102.2	100.3
2 <i>m</i>	35	11.30	240	204	259	216	231	249	98.8	102.2	100.1	100.4
4 <i>p</i>	40	16.40	235	195	253	206	223	241	101.7	104.0	98.8	101.8
3 <i>p</i>	46	70.10	235	189	252	195	222	241	113.7	115.0	114.6	114.7
2 <i>p</i>	56	133.80	248	192	265	228	242	256	120.5	122.0	119.7	120.5

^a T_m : Melting point of benzoxazines;

^bThe viscosity at the shear rate of 60 s⁻¹ at 100 °C;

^cOnset temperature of the exothermic peak by DSC;

^d $\Delta T = T_o - T_m$;

^eMaximum of the polymerization exotherm by DSC;

^fCuring temperatures obtained by using $T - \phi$ extrapolation method.

Flynn–Wall–Ozawa method (E_{F-W-O}), respectively. The corresponding data are presented in Figure 4c–4f. The E_a value of monomer 3*m* is 97.7 kJ/mol by Kissinger equation, 100.9 kJ/mol by Ozawa method, and 102.2 kJ/mol by Flynn–Wall–Ozawa method. Three methods give similar results, and the average value of E_a is 100.3 kJ/mol. The E_a values of the remaining five monomers are obtained by the same procedure, and the results are collected in Table 2. Based on these data, we can deduce that co-substituent, both *m*-CF₃PhOH and *p*-CF₃PhOH groups, can lower down the activation energy of polymerization to some extent.

3.3. Thermal properties of the six polybenzoxazines

Thermal property of thermosetting resins is one of the key factors for their practical applications. The six fluorine-containing polybenzoxazine samples were prepared according to the described conditions in the experimental section. All the cured polybenzoxazines are transparent with a deep-red appearance. The gel fractions (or percentage of cured polymer that is insoluble in chloroform) of the six samples were measured by the standard solvent-extraction method. These values were used to evaluate the conversion rate of monomers. All cured polymers possessed high gel fraction (over 99%), and these results indicated that nearly all monomers joined together to form crosslinked network due to their high molecular weight nature.

Heat resistance of six cured benzoxazine resins was inquired by TGA (Figure 5). The carbon residue (or char yield) was defined as a solid residue remained

at 850 °C which was estimated using TGA curves in nitrogen (N₂) atmosphere (Figure 5a) and in an air atmosphere (Figure 5b). The corresponding data for all polybenzoxazines are summarized in Table 3. It was found that 5 and 10% weight-loss temperatures of all polybenzoxazines were above 350, 365 °C, respectively, not only in N₂, but also in air atmosphere. And char yield of all polymers is more than 45% in N₂, and more than 10% in air. Such results are really inspiring because it means that all six polymers show outstanding thermal stability both in nitrogen and in air atmosphere compared with that of previous reports [60, 61]. It is thought that the stable inorganic phosphazene core benefits the thermal stability of the polymers. Moreover, the number of benzoxazine moiety on phosphazene, which provide crosslinking sites also affected the thermal stability of polymers. Hence, the higher the benzoxazine ring contents, the better the thermal stability of the corresponding polybenzoxazines. After curing at the same condition, the gel fraction of six polymers is greater than 99%, and it meant that a highly crosslinked polymer was obtained after the curing reaction.

It is also found that the char yields of cured benzoxazines deriving from *p*-CF₃PhOH are a little higher than those of polybenzoxazines from *m*-CF₃PhOH. For example, the char yields of P2*p* are about 61.1% (in N₂) and 51.0% (in air), respectively. Meanwhile, the char yields of P2*m* which has a similar structure to P2*p* are 48.9% (in N₂) and 22.4% (in air), respectively. The difference was also found in other polybenzoxazines couples, such as among P4*m* and P4*p*, P3*m* and P3*p*. The possible explanation is that the steric hindrance of the *m*-CF₃PhOH is higher than that

Figure 4. (a) The DSC curves of Monomer 3m at different curing rates. (b) Relationship curves of curing parameters and heating rates. (c) Representation of Ozawa's and Kissinger's methods to calculate activation energy. (d) Conversion as a function of curing temperature. (e) $\ln \phi \sim 1000/T$ curves (α = Degree of curing). (f) Representation Flynn–Wall–Ozawa's methods to calculate activation energy.

of the *p*-CF₃PhOH, consequently leads to lower crosslinking density (Table 3). As known, increasing the crosslinking density of thermosets is one of the most popular methods to improve the thermal stability of traditional polymers, such as in rubber curing.

3.4. Dynamic mechanical analysis of the polybenzoxazines

DMA is widely used to analyze the dynamic mechanical properties of polymers. Based on DMA results

(Figure 6), we can figure out T_g , storage modulus, and crosslink density of the six polymers. The corresponding data were displayed in Table 3.

The co-substituent groups show notable effects on the properties of cured polymers according to data listed in Table 3. Though all polybenzoxazines possess relatively high T_g (over 128 °C), the T_g values of polybenzoxazines deriving from *p*-CF₃PhOH are little higher than that of polybenzoxazines from *m*-CF₃PhOH. The storage moduli and cross-linking

Figure 5. TGA curves of six polybenzoxazines. a) In N_2 , b) in air.

Table 3. Thermal and Mechanical properties of six polybenzoxazines.

Samples	^a $T_{5\%}$ [°C]		^b $T_{10\%}$ [°C]		^c Y_c [%]		^d T_g [°C]	^e E' [GPa]	^f $(T_g + 40)$ [K]	^g E'_1 [MPa]	^h v_e [mol·m ⁻³]
	N_2	air	N_2	air	N_2	air					
P4m	352	351	372	420	45.8	20.3	128	1.3	441	8.9	809
P3m	373	403	411	418	46.2	10.9	147	0.7	460	9.4	818
P2m	373	369	421	413	48.9	22.4	175	1.1	488	12.9	1058
P4p	358	352	365	368	47.5	26.6	221	2.6	534	31.2	2342
P3p	357	362	368	397	58.0	30.2	210	1.8	513	29.0	2265
P2p	358	350	370	369	61.1	51.0	228	1.6	541	37.2	2757

^a5% weight loss temperature;

^b10% weight loss temperature;

^cthe Char yields at 850 °C;

^dthe glass transition temperature by DMA;

^ethe storage modulus at 50 °C;

^fKelvin temperature of $(T_g + 40)$ K;

^gstorage modulus at $(T_g + 40)$ K;

^hthe crosslinking density at $(T_g + 40)$ K respectively from DMA values.

density show a similar trend as T_g . Such result is attributed to the reason that *m*-CF₃PhOH possesses greater steric hindrance than *p*-CF₃PhOH, hence the polybenzoxazines deriving from *m*-CF₃PhOH have higher free volume at low temperature compared with the polymers deriving from *p*-CF₃PhOH. It means

that segment movement of polymers deriving from *m*-CF₃PhOH is easier than that of polymers from *p*-CF₃PhOH, so *m*-CF₃PhOH-containing polybenzoxazines show relatively lower T_g . The storage moduli of the polymer depend on chemical structure and cross-linking density. These six polymers show

Figure 6. Storage moduli (a) and $\tan \delta$ (b) of the polybenzoxazines.

similar chemical structure, and their storage modulus mainly depends on the crosslink density. As mentioned above, the larger steric hindrance of *m*-CF₃PhOH prohibits the network formation during ring-opening polymerization and leads to a thermosetting resin with low crosslink density. The theoretic calculation of crosslinking density also gives solid support for this explanation. According to well-established rubber elasticity theory [62, 63], the crosslinking density (ν_e) of a crosslinked network can be estimated using Equation (1):

$$\nu_e = \frac{E_1'}{3RT} \quad (1)$$

where, E_1' is the storage modulus at a temperature of ($T_g + 40$) degree in the form of absolute temperature [K], so the ν_e is less influenced by the hydrogen bonding. R is the gas constant.

Although the equation was first put forward for lightly crosslinked materials, such as cured rubber, now it has been adopted widely to estimate the crosslink density of different polybenzoxazines. The crosslink densities of the six polybenzoxazines are shown in Table 3, it's very clear that crosslink density of *p*-CF₃PhOH series polybenzoxazines (2342, 2265, 2757 mol·m⁻³ for P4*p*, P3*p*, P2*p*, respectively) are much higher than that of the *m*-CF₃PhOH series (809, 818, 1058 mol·m⁻³ for P4*m*, P3*m*, P2*m*, respectively), which supports the speculation that *m*-CF₃PhOH series polymers have lower T_g compared with *p*-CF₃PhOH series polybenzoxazines.

Here, we can conclude that carefully select the co-substituent, we can obtain high-performance polybenzoxazines with different properties. For example, *m*-CF₃PhOH-derived polybenzoxazines show low T_g , but we can imagine that this group of polymers will show high impact strength for its low crosslinking density; meanwhile, *p*-CF₃PhOH-derived polybenzoxazine showed excellent thermal properties for its high crosslinking density.

3.5. Dielectric properties of monomers and cured polymers

One of the potential application fields of polybenzoxazines is electronics packaging materials, hence evaluate the dielectric property of polybenzoxazines is necessary. The tests of dielectric properties of all six polybenzoxazines (Table 4) were carried out at room temperature in the frequency range of 100 Hz ~ 1 MHz. Monomer 4*m* and 3*m* are viscous liquid

therefore are not suitable for testing. All other monomers can be compressed into a tablet for the measurement. The dielectric constant of 2*m* (having two *m*-CF₃PhO- groups) is 7.5, 4*p*, 3*p* and 2*p* which has four, three and two *p*-CF₃PhO-groups, their dielectric constants are 7.1, 7.3, 7.4, respectively. Interestingly, all six samples show relatively high dielectric constant compared with that of previous reported fluorinated polybenzoxazines (2.42–2.19 [64], 2.3 [65]). From P4*m* to P2*p*, the dielectric constants at 1 MHz are 5.0, 5.6, 5.7, 5.3, 5.8 and 5.9, respectively. The dielectric constant of materials depends directly on its polarizability, increasing the polarizability benefits to improve dielectric constants. Obviously, polymer's dielectric properties rely strongly on its chemical structure. Therefore, the high dielectric constant of six polymers is possibly due to orientational polarization of two kinds of polar groups present in cured polymers: polar co-substituents (*m/p*-CF₃PhOH) and the end-capped phenol groups resulting from ring-opening of benzoxazines. CF₃– is a strong electron-withdrawing group, both *m*-CF₃PhOH and *p*-CF₃PhOH possess high polarity whether the CF₃-group locates on meta- or para-position. For monomer 4*m* and 4*p*, which have higher *m*-CF₃PhOH/*p*-CF₃PhOH content, they play dominated role in corresponding high dielectric constant polybenzoxazines. For monomer 2*m* and 2*p*, which possess higher BOZ content, the high dielectric constant of corresponding polymers depends mainly on polar phenol group attached to the network (Figure 7). These two benzoxazine monomers possess molecular weight as high as 1362.1 g/mol, which will lead to high viscosity mixtures at the initial stage of polymerization and then hinder the formation of uniform cross-linking network. Some polar phenol groups appear at the chain end and take place orientational polarization under an applied voltage. Certainly, the co-substituent also contributed to the dielectric constant of P2*m* and P2*p*.

In addition to the dielectric constant, dielectric loss is another key factor for dielectric materials, and low dielectric loss is beneficial for electronic applications. From Table 4 we can find out that all six polybenzoxazines show a low dielectric loss at 1 MHz (0.016, 0.0089, 0.0084, 0.014, 0.0097, and 0.0067, respectively). Among them, the dielectric loss of P4*m* and P4*p* are a little higher than that of the other four polymers, which is attributed to lower crosslinking density of P4*m* and P4*p*. The dielectric loss of

Figure 7. The polar end-phenol group formation during thermal polymerization.

Table 4. Dielectric property of monomers and polymers.

Samples	4 <i>m</i>	3 <i>m</i>	2 <i>m</i>	4 <i>p</i>	3 <i>p</i>	2 <i>p</i>	P4 <i>m</i>	P3 <i>m</i>	P2 <i>m</i>	P4 <i>p</i>	P3 <i>p</i>	P2 <i>p</i>
ϵ (1 MHz)	–	–	7.5	7.1	7.3	7.4	5.0	5.6	5.7	5.3	5.8	5.9
$\tan \delta$ (1 MHz)	–	–	0.020	0.028	0.024	0.023	0.016	0.0089	0.0084	0.014	0.0097	0.0067

–: undetectable

monomers is higher than their corresponding polymers.

3.6. The surface properties and water absorption of polybenzoxazines

The properties of thermosets are affected by moisture in the air during storage and in service, such as electric properties. So, the water absorption/penetration ability of the polymer is very crucial to its practical utilization as electric materials. In recent years, the polybenzoxazines have been regarded as a new kind of low surface energy materials for its high hydrophobic nature and low water absorption character. The surface wettability characteristics of the six samples were investigated by water contact angle (WCA) measurement [66]. The advancing contact

angle (θ_a), receding contact angle (θ_r) and surface free energy of six novel polybenzoxazines were displayed in Table 5. θ_r is more sensitive to the surface condition than θ_a , therefore the θ_a -related data are suitable for calculating the surface free energy. Compared with reported results [67, 68], the six new polymers don't show high hydrophobic properties, and all θ_a values of six polymers are not more than 90° . Wang *et al.* [67] attributed these results to the perfect hydrogen-binding network which resulting in high hydrophobicity in polybenzoxazines was disrupted by higher curing temperatures, and concluded that the ratio of intra- and intermolecular hydrogen bonds affected the surface property seriously. From the FTIR spectra of six polybenzoxazines (Figure 8), we can find out three different kinds of hydrogen bonds:

Table 5. The surface properties of six polybenzoxazines.

Sample	θ_a [°]		γ [mJ/m ²]	Water		Water absorption (13 d) [%]	
	Water	Hexadecane		θ_r [°]	CAH [°]	RH = 33%	RH = 75%
P4 <i>m</i>	85±0.5	25±1.0	30.2	65±2.0	20	0.65	0.67
P3 <i>m</i>	78±1.0	23±1.5	32.3	56±3.0	22	0.82	0.79
P2 <i>m</i>	76±1.5	24±1.5	34.5	52±2.5	20	0.85	0.86
P4 <i>p</i>	90±0.5	28±2.0	27.9	68±2.0	22	0.19	0.21
P3 <i>p</i>	88±1.0	31±1.5	28.2	60±1.5	28	0.23	0.29
P2 <i>p</i>	81±1.5	27±2.5	31.7	57±2.5	24	0.38	0.41

Figure 8. FTIR spectra of six polybenzoxazines.

3550 cm^{-1} indicating $\text{—OH}\dots\pi$ intramolecular hydrogen bonds, 3400–3370 cm^{-1} indicating $\text{—OH}\dots\text{O}$ intermolecular hydrogen bonds, 3180 cm^{-1} indicating $\text{—OH}\dots\text{N}$ intramolecular hydrogen bonds. These results are consistent very well with reported data; the surface free energies of the six polymers are higher than 27 mJ/m^2 .

Before water absorption test, all samples were dried under vacuum at 90 °C for 24 h to constant weight and placed in a testing box (33% and 75% RH, at room temperature) for different times. The water absorption content of the samples was listed in Table 5. Though the six polybenzoxazines are somewhat hydrophilic, all samples show relatively low humidity absorption ability whether the relative humidity is low (33%) or high (75%), which makes the branched polybenzoxazines suitable for some special applications, such as underfilling in the electronic packaging encapsulation. Analyzing these results, we can find out that the water absorption ability of *m*- CF_3PhOH -derived polybenzoxazines is bigger than that of *p*- CF_3PhOH -derived polybenzoxazines. The result is consistent very with above-mentioned facts, that is, *m*- CF_3PhOH -containing polybenzoxazines has lower crosslinking density compared with *p*- CF_3PhOH -containing ones.

4. Conclusions

In this paper, we provide a novel route to prepare branched benzoxazine resins with low melting point and still hold excellent thermal and mechanic properties. Though the molecular weight of six benzoxazine monomers is larger than 1230 g/mol, two of them appear as a liquid at 25 °C and the melting point of the other four monomers is below 60 °C. All six monomers also possess high solubility in common

organic solvent; these merits make them easily processable both in melt and in solution. Polybenzoxazines derived from *p*- CF_3PhOH exhibit higher T_g and thermal stability than *m*- CF_3PhOH -derived polybenzoxazines. Unlike the traditional bisphenol-A derived polybenzoxazines which normally shows a low dielectric constant and low dielectric loss, the newly developed cyclotriphosphazene-based polymers show relatively high dielectric constant but still remain low dielectric loss. Though all polybenzoxazines contain CF_3 group, they don't show high hydrophobic properties.

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