

## Surface Properties and Hydrogen Bonds of Mono-functional Polybenzoxazines with Different *N*-substituents\*

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**Abstract** A series of mono-functional benzoxazine monomers with different *N*-substituents were synthesized from phenol, formaldehyde, and various amines (ammonia, methylamine, *n*-butylamine, dodecylamine), named P-am, P-m, P-b, and P-da, respectively. The surface properties of these polybenzoxazine films were proven by contact angle measurements. The hydrogen bond network of the polybenzoxazine systems was studied using the FTIR spectra. And the results showed that the surface free energy increased with increasing the fraction of intermolecular hydrogen bonding when the *N*-substituent was an alkyl chain. However, the rule was not suitable when the *N*-substituent was H. That was because there was one more kind of intramolecular hydrogen bond in the poly(P-am). Based on these findings, we proposed that both the *N*-substituent alkyl group and the fraction of intermolecular hydrogen bonding had effects on the surface free energy.

**Keywords:** Polybenzoxazine; Mono-functional; *N*-substituents; Surface free energy; Hydrogen bonding.

### INTRODUCTION

Polymer materials with low surface free energy played an important role in numerous fields, including aviation, super hydrophobic surfaces, bio-coatings, environmental protection and pollution prevention<sup>[1–7]</sup>. Polybenzoxazines were a fast developing series of low-surface-free-energy materials<sup>[8–10]</sup> possessed many fascinating advantages such as minimal moisture absorption<sup>[11–13]</sup>, good thermal stability<sup>[14–16]</sup>, high char yield<sup>[17–19]</sup>, and molecular design flexibility<sup>[17, 20–27]</sup>. These excellent performances had attracted great attention<sup>[28–35]</sup>.

The polymerization of benzoxazines was performed by thermal open-ring activation, which took place through thermally activated ring opening of the cyclic benzoxazine structure. During the polymerization, intra- and intermolecular hydrogen bonding formed and transformed continuously<sup>[36–38]</sup>, resulting in the changes of the polybenzoxazine films' surface free energy<sup>[39, 40]</sup>. Wang *et al.* reported that strong intramolecular hydrogen bonding between the hydroxyl groups of polybenzoxazines decreased their surface free energies, whereas which could be increased by the intermolecular hydrogen bonding<sup>[39]</sup>. After proposal of this theory, many researchers contributed to the low surface free energy films through reducing proportion of intermolecular hydrogen bonding interactions<sup>[41–44]</sup>. Apart from this, the alkyl group of primary amine also had potential contribution to the surface free energy<sup>[40, 45]</sup>. Ishida *et al.* found that the amine groups could affect the hydrogen-bonding structures of the model benzoxazine dimers<sup>[36, 45]</sup>, while the compactness of a network structure was related to both the basicity and bulkiness of the functional amines<sup>[46]</sup>. Dong *et al.* systematically investigated the effect of *N*-substituents on

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the surface free energy and hydrogen bonding network structure of di-functional polybenzoxazine<sup>[40]</sup>. Their results showed that both the alkyl group and the proportion of intermolecular hydrogen bonding had an effect on the surface energy of the polybenzoxazines, and a transformation mechanism of the intermolecular and intramolecular hydrogen bonding during the progress of cure was proposed simultaneously.

Most studies about the hydrogen bonding network were based on the di-functional benzoxazine. However, the polymerization of mono-functional benzoxazines was different from that of di-functional ones. Therefore, their hydrogen bonding network structure would be different<sup>[47–50]</sup>. Mono-functional benzoxazine had better fluidity property, which was more conducive to the film forming, so the study of monofunctional benzoxazine was important to guide the practical application. In this study, a series of mono-functional benzoxazine monomers with different *N*-substituted groups were synthesized by phenol, formaldehyde, and various amines (ammonia, methylamine, *n*-butylamine, dodecylamine), named 3,4-dihydro-3-*H*-2H-1,3-benzoxazine (P-am), 3,4-dihydro-3-methyl-2H-1,3-benzoxazine (P-m), 3,4-dihydro-3-*n*-butyl-2H-1,3-benzoxazine (P-b), and 3,4-dihydro-3-dodecyl-2H-1,3-benzoxazine (P-da) respectively. The *N*-substituents effects and hydrogen bonding network of these mono-functional polybenzoxazine were studied by contact angle measurement and FTIR curve fitting, and the results demonstrated that both the *N*-substituent alkyl group and the fraction of intermolecular hydrogen bonding had an effect on the surface free energy.

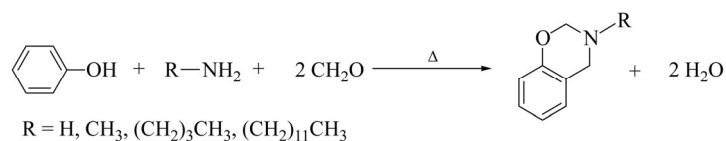
## EXPERIMENTAL

### Materials and Chemical Reagents

Phenol, formaldehyde (37% in water), methylamine, *n*-butylamine, dodecylamine and tetrahydrofuran were purchased from Shanghai Lingfeng Chemical Reagent. Ammonia was purchased from Hubei Debang Chemical Reagent. All chemicals were of analytically pure grade.

### Synthesis of Benzoxazine Monomer

The synthesis method of benzoxazine monomers is shown in Scheme 1<sup>[47]</sup>. 0.4 mol formaldehyde dissolved in 80 mL dioxane, was added in an four-necked flask around ice-water bath. Then 0.2 mol amine (13.62 g 25% ammonia, 24.88 g 25% aqueous solution of methylamine, 14.62 g of *n*-butylamine, and 37.07 g of dodecylamine) dissolved in 20 mL dioxane was slowly dosed, meanwhile the temperature was maintained at 10 °C or less. After stirring 10 min, 0.2 mol phenol (19 g) dissolved in 100 mL dioxane was added, and refluxed for 6 h. After cooling to room temperature, the mixture was dissolved in ether. Then, it was washed with sodium hydroxide solution for three times, followed by wash with water, then dried with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents, the benzoxazine monomers were obtained as transparent, viscous, and yellowish liquids. The yields of benzoxazine monomers P-am, P-m, P-b and P-da were 27.74%, 30.97%, 57.26% and 30.58%, respectively.



Scheme 1 Preparation of benzoxazine monomers

### Preparation of Benzoxazine Monomer Films and Polybenzoxazine Films

The P-am, P-m, P-b and P-da monomers were dissolved into tetrahydrofuran to get the 10 wt% solutions, and then filtered by 0.2 μm microfiltration membranes. Then these solutions were spin-coated onto the treated glass substrates. The treatment method of the glass substrates (1 cm × 1 cm) was as follows: soaked in the cleanser solution overnight, ultrasonic washed by water, ethanol, acetone for 15 min separately, and then dried with the nitrogen gas. Then the filtered solutions were spin-coated onto the treated glass substrates at a speed of 1500 r/m for 45 s, and dried in the vacuum oven at 60 °C for 1 h. Then the monomer films were prepared. After curing for another 1 h at 200 °C, the polybenzoxazine films were obtained. These polymers were named as poly(P-am), poly(P-m), poly(P-b) and poly(P-da).

### **Fourier Transform Infrared Spectroscopy**

The transformation of the chemical interactions during the curing process could be demonstrated by the FTIR of the benzoxazine films cured at different temperatures for different time. The FTIR spectra were recorded by a Nicolet iS10 spectrometer from Thermo Fisher Scientific with 32 scans at  $1\text{ cm}^{-1}$  resolution. The samples of benzoxazine monomers were prepared by dropping P-am, P-m, P-b and P-da onto KBr tablets, and the samples of the polybenzoxazine films were cured at  $200\text{ }^{\circ}\text{C}$  for another 1 h.

### **Nuclear Magnetic Resonance Spectroscopy**

The NMR spectra of all the benzoxazine monomers were recorded on a Varian Mercury Plus 400 MHz NMR spectrometer in deuterated chloroform with tetramethylsilane (TMS) as the external reference.

### **Differential Scanning Calorimetry**

The thermal curing curves of the four benzoxazine monomers were tested by a Pyris Diamond DSC. 3–5 mg benzoxazine monomer samples were heated from  $50\text{ }^{\circ}\text{C}$  to  $250\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ K}\cdot\text{min}^{-1}$  under  $\text{N}_2$  atmosphere. The heat flow curves show the thermal curing process of the benzoxazine monomers.

### **Thermogravimetric Analysis**

The thermal stability was tested by an SDT Q600 V8.3 Build 101 thermogravimetric analyzer. The polybenzoxazine samples were heated from room temperature to  $800\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ K}\cdot\text{min}^{-1}$  under  $\text{N}_2$  atmosphere, and the thermal degradation temperature was obtained when the weight loss reached 5 wt%.

### **Contact Angle Analysis**

The static contact angles of these films were measured by an OCA20 optical goniometer from Dataphysics. The testing liquids were deionized water, ethylene glycol, and diiodomethane (99%), and 2  $\mu\text{L}$  droplet was used with ellipse fitting for CA test. 5 droplets were measured at different regions for each sample, and the static contact angle data were the average values.

Surface free energy was deduced from the contact angle values, and the calculation was based on the OWRK mode in the Owens's three-liquid method<sup>[51]</sup>.

## **RESULTS AND DISCUSSION**

### **Synthesis and Characterization of Benzoxazine Monomers**

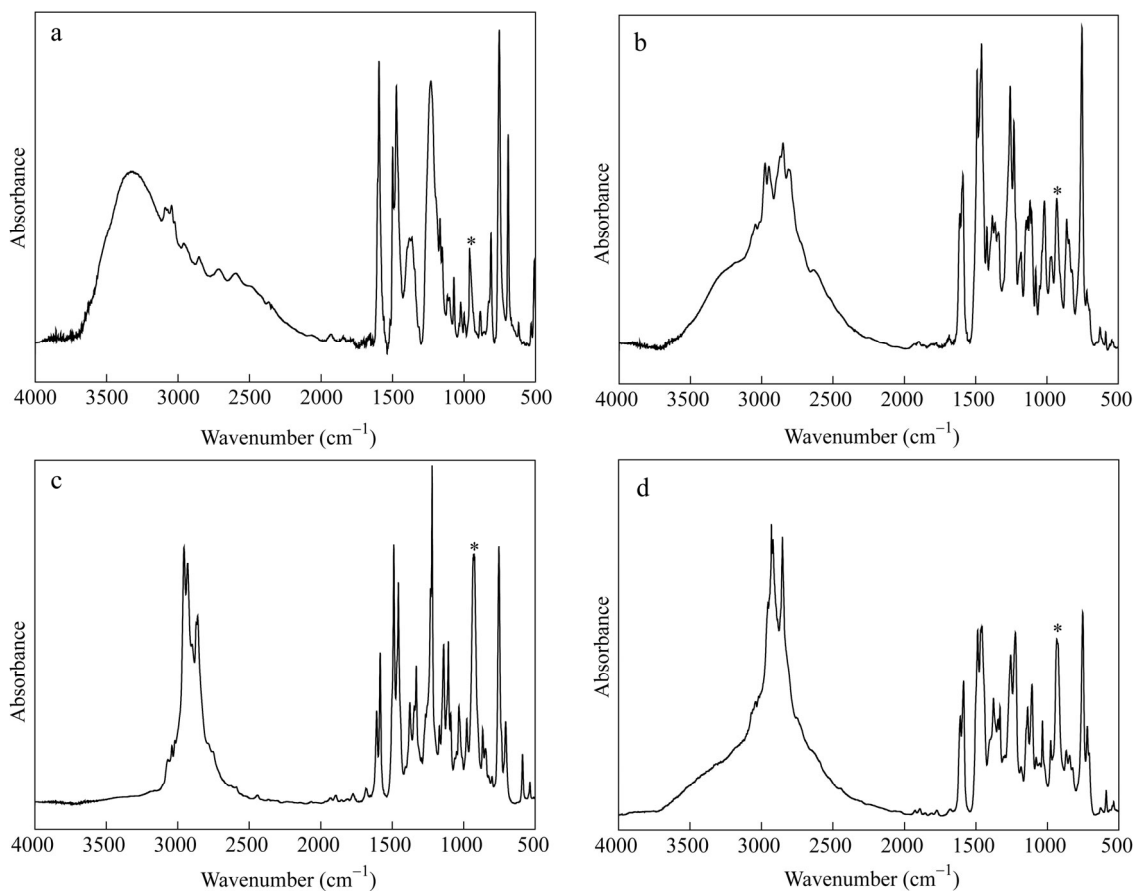
Benzoxazine monomers were prepared from conventional raw materials through Mannich condensation reaction.

The chemical structures of these benzoxazine monomers were confirmed by FTIR and  $^1\text{H-NMR}$ . The FTIR spectra of P-am, P-m, P-b and P-da benzoxazine monomers are shown in Fig. 1 respectively.

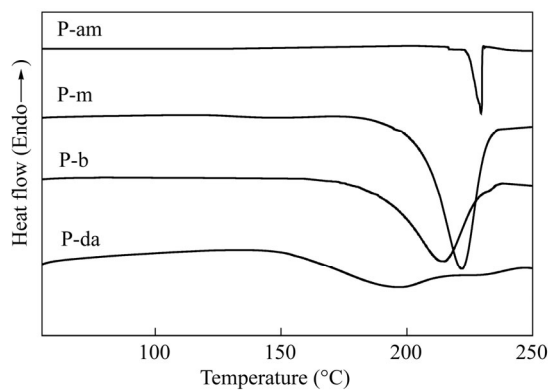
As shown in Fig. 1, the FTIR spectra of these benzoxazine compounds demonstrated that the characteristic absorption bands of P-am, P-m, P-b and P-da appeared at 960, 930, 929, and  $931\text{ cm}^{-1}$ , respectively. The C—O—C asymmetric stretching bands were observed at 1230, 1253, 1219 and  $1255\text{ cm}^{-1}$ , respectively, and the symmetric stretching bands were observed at 1026, 1020, 1033 and  $1034\text{ cm}^{-1}$ , respectively. The  $\text{CH}_2$  wagging bands were observed at 1360, 1330, 1331 and  $1376\text{ cm}^{-1}$ , respectively.

The thermal curing curves of the four benzoxazine monomers are shown in the Fig. 2. The results indicated that the curing temperature decreased with the increase of the *N*-substituent length, and the curing temperatures of P-am, P-m, P-b and P-da were 229.42, 221.76, 213.96 and  $192.62\text{ }^{\circ}\text{C}$ , respectively.

The chemical structures of the benzoxazine monomers were also confirmed by  $^1\text{H-NMR}$ , and the results are summarized in Table 1.



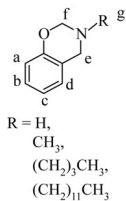
**Fig. 1** FTIR spectra of the four benzoxazine monomers: (a) P-am, (b) P-m, (c) P-b, (d) P-da



**Fig. 2** DSC curves of the four benzoxazine monomers: (a) P-am, (b) P-m, (c) P-b, (d) P-da

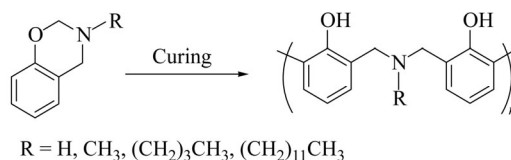
**Table 1.**  $^1\text{H-NMR}$  spectra of P-am, P-m, P-b and P-da

H	P-am	P-m	P-b	P-da
a-d	$\kappa 6.75-7.25_{\text{T}}$	$\kappa 6.70-7.20_{\text{T}}$	$\kappa 6.77-7.11_{\text{T}}$	$\kappa 6.75-7.12_{\text{T}}$
e	4.10	3.96	3.98	3.98
f	4.89	4.87	4.85	4.86
g	1.23	1.21	2.74	2.73
			1.54	1.55
			1.34	1.27
			0.91	0.87



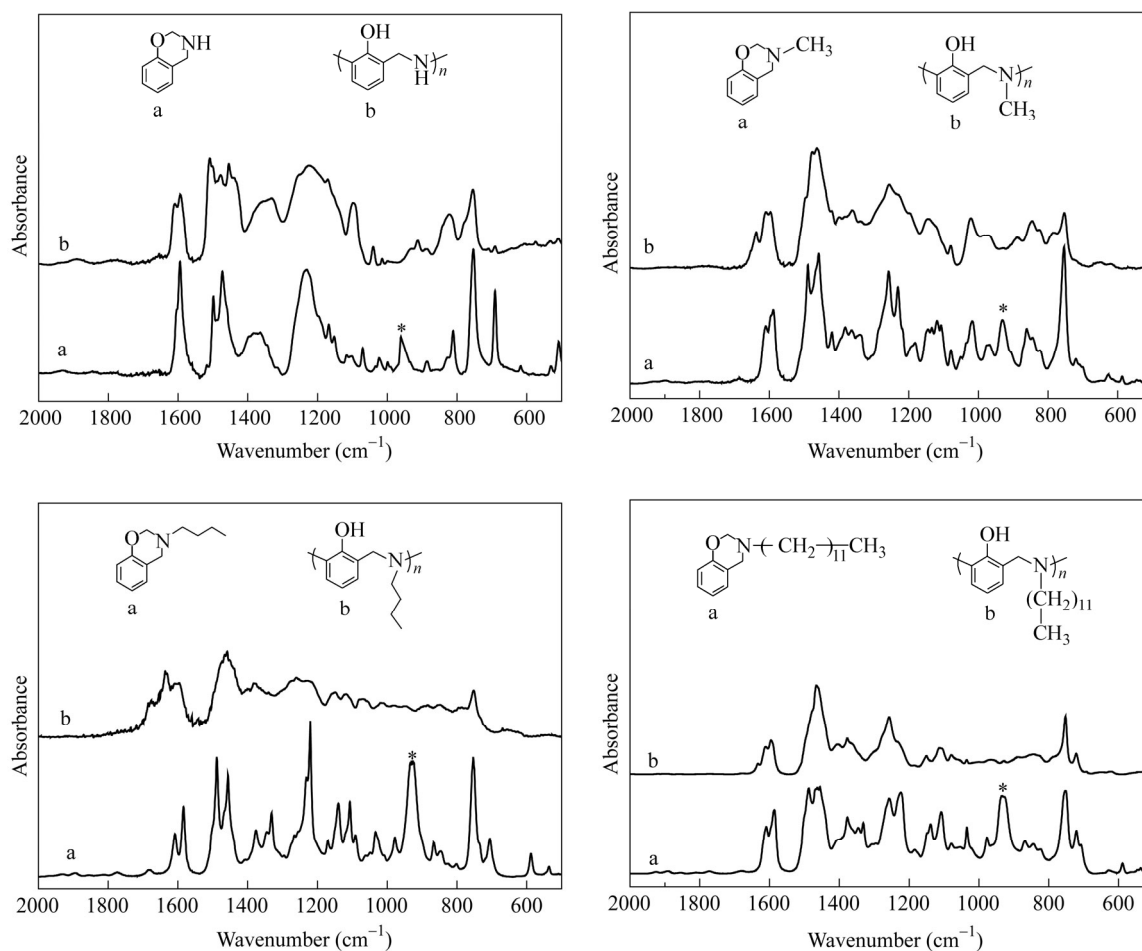
### Preparation of the Polybenzoxazine Films

The polybenzoxazine films were prepared by heat curing (Scheme 2). The benzoxazine monomer films were cured at a certain temperature for a certain time to obtain the polymer films. In this work, the curing temperature was 120–240 °C, and the curing time was 0.5–16 h.



**Scheme 2** Curing progress of the benzoxazines

Figure 3 shows the FTIR spectra of benzoxazine monomers and polymers from 2000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ . As shown in Fig. 3, the absorption peak of benzoxazine ring at 960  $\text{cm}^{-1}$  (930, 929 and 931  $\text{cm}^{-1}$ ) disappeared after curing at 200 °C for 1 h. Meantime, the absorption peak at 1611  $\text{cm}^{-1}$  (1638, 1636 and 1633  $\text{cm}^{-1}$ ) raised on behalf of the characteristic absorption peak of the Schiff base. The results illustrated that the Schiff base had been formed with the ring-open reaction.



**Fig. 3** FTIR spectra of the four benzoxazine monomers (a) and polymers (b)

### Surface Properties of the Polybenzoxazine Films

The surface free energy of polybenzoxazines was studied by the contact angle measurements. These four polybenzoxazine films were prepared by curing at different temperature for 1 h. Then, their surface free energies were evaluated by OWRK mode upon Owens's three-liquid method. The surface free energies of the benzoxazine monomer films were measured firstly (Table 2).

**Table 2.** Contact angles and surface free energies of P-am, P-m, P-b and P-da benzoxazine monomer films

Benzoxazine monomer	Contact angle (°)			Surf. free energy $\kappa(\text{mJ}\cdot\text{m}^{-2})_{\text{T}}$
	Water	Ethylene glycol	Diiodomethane	
P-am	74.1	39.0	13.9	45.93
P-m	75.7	61.9	13.1	36.40
P-b	96.0	74.1	71.8	21.71
P-da	80.2	66.2	17.9	39.83

Subsequently, the surface free energies of the polybenzoxazine films are shown in Table 3.

**Table 3.** Contact angles and surface free energies of poly(P-am), poly(P-m), poly(P-b) and poly(P-da) benzoxazine films cured at different temperatures

Benzoxazine monomer	Curing temp. (°C)	Contact angle (°)			Surf. free energy $\kappa(\text{mJ}\cdot\text{m}^{-2})_{\text{T}}$
		Water	Ethylene glycol	Diiodomethane	
P-am	120	100.3	77.5	66.6	23.11
	150	103.7	80.9	68.5	22.10
	180	107.4	89.5	77.5	16.74
	190	106.7	89.8	78.6	16.13
	200	107.0	89.2	75.1	17.53
	210	106.9	91.0	80.5	15.15
P-m	120	90.2	66.2	17.9	35.83
	150	97.2	72.3	51.6	29.71
	180	103.8	81.5	72.5	20.39
	190	104.3	83.0	65.7	22.48
	200	105.3	85.8	66.7	21.13
	210	105.4	89.2	75.8	16.89
P-b	120	97.5	79.9	72.9	19.80
	150	104.1	86.2	80.5	16.31
	180	101.5	79.4	78.4	18.47
	190	99.1	79.3	78.4	18.42
	200	92.7	73.4	80.8	19.64
	210	94.0	78.4	78.1	19.01
P-da	120	94.2	49.5	36.9	30.63
	150	97.2	72.3	51.6	29.71
	180	103.8	81.5	62.5	24.39
	190	104.3	83.0	65.7	22.48
	200	105.3	85.8	66.7	21.13
	210	105.5	84.7	61.8	23.76

As shown in Table 3, the lowest surface free energies of poly(P-am), poly(P-m), poly(P-b), and poly(P-da) films were 15.15, 16.89, 16.31 and 21.13  $\text{mJ}\cdot\text{m}^{-2}$  respectively, which were cured at 210, 210, 150 and 200 °C for 1 h. In order to compare the surface properties of the four polybenzoxazine films, the surface free energies of these films cured at 200 °C for different time (0.5–16 h) were also measured, and the results are shown in Table 4.

As shown in Table 4, the surface free energies of polybenzoxazine films decreased gradually and then increased upon increasing the curing time from 0.5 to 16 h. The lowest surface free energies of poly(P-am), poly(P-m), poly(P-b), and poly(P-da) films were 17.44, 17.32, 19.65 and 21.47  $\text{mJ}\cdot\text{m}^{-2}$  respectively, which were

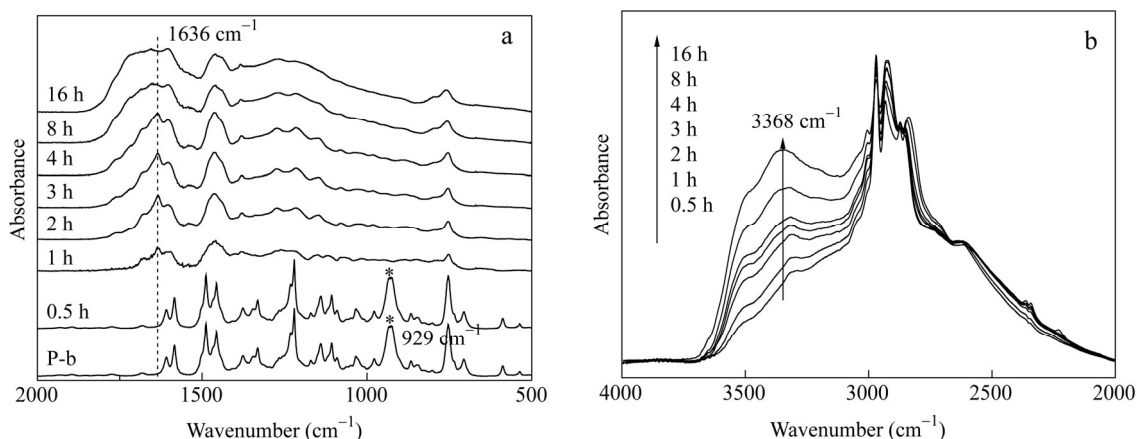
cured for 8, 8, 4 and 1 h. The curing time of poly(P-am), poly(P-m), and poly(P-b) films to get the lowest surface free energies were much longer than that of poly(P-da). Compared to the H, CH<sub>3</sub>, and (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, the long alkyl chain (CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub> had larger steric hindrance, which led to the fast transformation from intra- to intermolecular hydrogen bonds during the curing process. Furthermore, the surface free energies of poly(P-m), poly(P-b), and poly(P-da) films increased with increasing alkyl chain length. As mentioned in the literature<sup>[46]</sup>, the increasing of the alkyl chain length could result in the increasing of intramolecular hydrogen bond length, which was conducive to form the intermolecular hydrogen bond. Thus, the proportion of intermolecular hydrogen bonds increased, and finally the surface free energy increased.

**Table 4.** Contact angles and surface free energies of poly(P-am), poly(P-m), poly(P-b), and poly(P-da) films cured at 200 °C for different time

Benzoxazine monomer	Curing time (h)	Contact angle (°)			Surf. free energy $\gamma_{\text{K}}(\text{mJ}\cdot\text{m}^{-2})_{\text{T}}$
		Water	Ethylene glycol	Diiodomethane	
P-am	$\kappa 1/2_{\text{T}}$	101.5	77.4	51.4	29.20
	1	104.2	82.4	69.4	19.23
	2	104.0	83.8	70.1	19.80
	3	104.9	87.1	70.7	18.99
	4	105.3	89.0	72.1	17.95
	8	104.5	88.2	74.5	17.44
	16	90.6	81.1	67.3	20.89
P-m	$\kappa 1/2_{\text{T}}$	104.9	82.1	63.8	23.87
	1	105.0	83.5	66.9	22.08
	2	102.1	81.4	69.1	21.22
	3	96.5	84.0	70.8	18.94
	4	94.1	85.7	71.4	18.46
	8	105.2	89.7	73.2	17.32
	16	103.0	86.4	68.2	19.51
P-b	$\kappa 1/2_{\text{T}}$	101.9	79.0	48.4	29.27
	1	103.5	80.4	67.6	22.11
	2	103.8	81.6	68.5	21.86
	3	104.0	81.2	70.7	21.22
	4	96.6	80.8	70.8	20.03
	8	92.8	79.9	74.1	19.65
	16	90.8	76.6	75.7	20.40
P-da	$\kappa 1/2_{\text{T}}$	102.6	80.0	68.0	22.29
	1	97.6	78.7	68.6	21.47
	2	86.1	74.7	68.0	23.22
	3	83.0	65.3	71.3	25.40
	4	78.1	71.4	71.3	26.25
	8	67.9	70.9	69.7	33.10
	16	61.7	72.4	62.6	38.80

### Hydrogen Bonding Network Analysis of Polybenzoxazines

The transformation between the intermolecular hydrogen bonds and the intramolecular ones of the polybenzoxazine materials could lead to the low surface free energy<sup>[43, 44]</sup>. Especially for the intramolecular hydrogen bonds<sup>[14, 39, 40, 52]</sup>, it contributes much to the low surface free energy. Normally, there are several kinds of H-bonded species in the polybenzoxazine system<sup>[52–54]</sup>, including —OH...N intramolecular hydrogen bonding (3115 cm<sup>-1</sup>), —OH...O intermolecular hydrogen bonding (3366 cm<sup>-1</sup>), and O<sup>-</sup>...H<sup>+</sup>N intramolecular hydrogen bonding (between 2500 and 3300 cm<sup>-1</sup>). FTIR spectra of poly(P-am), poly(P-m), poly(P-b), and poly(P-da) cured for different time were compared for investigating their hydrogen bonding network. Here we took poly(P-b) cured at 200 °C for example (Fig. 4).

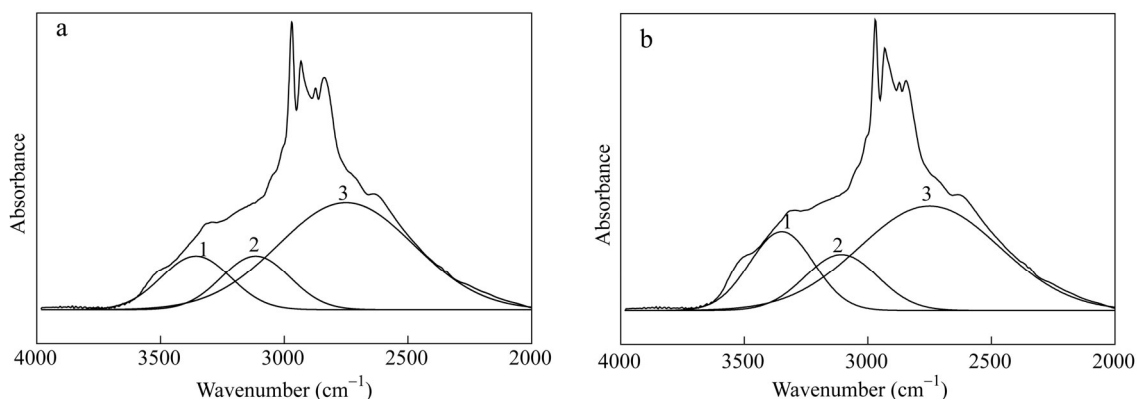


**Fig. 4** FTIR spectra of poly(P-b) cured at 200 °C (0–16 h) in the range of (a) 2000–500  $\text{cm}^{-1}$  and (b) 4000–2000  $\text{cm}^{-1}$

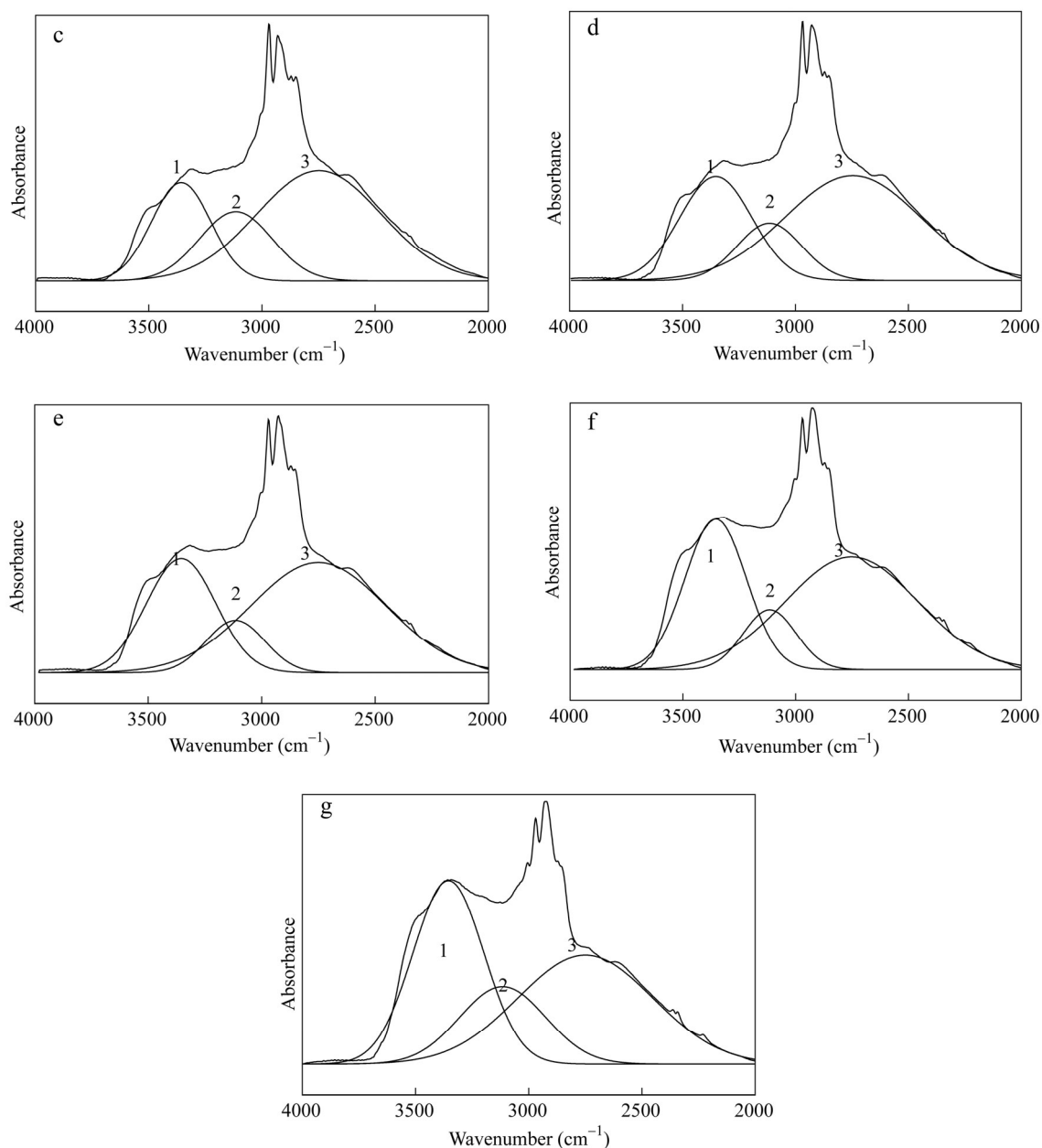
In the range of 500  $\text{cm}^{-1}$  to 900  $\text{cm}^{-1}$  (Fig. 4a), the characteristic absorption of the benzoxazine structure at 929  $\text{cm}^{-1}$  disappeared after curing for 1 h. Meanwhile, the absorbance of the band at 1636  $\text{cm}^{-1}$  increased gradually, which was belonged to free Schiff base ( $\text{C}=\text{N}$ )<sup>[22]</sup>. The polybenzoxazine structure could be thermally degraded at 200 °C, and the generated free Schiff bases and the H-Bonded Schiff bases became the terminated group or the defect structure of the polybenzoxazine.

Figure 4(b) displays the changes of the hydroxyl stretching frequency. The  $\text{O}^{\cdot}\text{H}^{\cdot}\text{N}$  intramolecular hydrogen bonding of the poly(P-b) around 2750  $\text{cm}^{-1}$  appeared during the curing process from 0.5 h to 16 h. And it could be found the proportion of intramolecular H-bond (appeared at 3115  $\text{cm}^{-1}$  and 2750  $\text{cm}^{-1}$ ) was substantially constant after the ring-opening reaction finished (cured about 0.5 h), and the proportion of intermolecular hydrogen bond (appeared at 3368  $\text{cm}^{-1}$ ) changed continuously. To systematically study the changes of intermolecular H-bond with curing time, curve-resolving of FTIR spectra for the corresponding frequencies of each H-bonded species was performed. The results of curve fitting for the FTIR spectra are shown in Fig. 5.

The  $\text{OH}\dots\text{O}$  intermolecular H-bonds of poly(P-b) appeared at 3368  $\text{cm}^{-1}$ . Upon increasing the curing time, the fraction of these intermolecular H-bonds increased continually. Figure 6 shows the fraction of intermolecular hydrogen bonding and surface free energies of poly(P-m), poly(P-b), and poly(P-da). Combining the analyses of the FTIR spectra (Fig. 5a) and the surface free energies (Fig. 6b), it is demonstrated that after the lowest surface free energy, the enhanced intermolecular hydrogen bonding led to the increasing in the surface free energy.



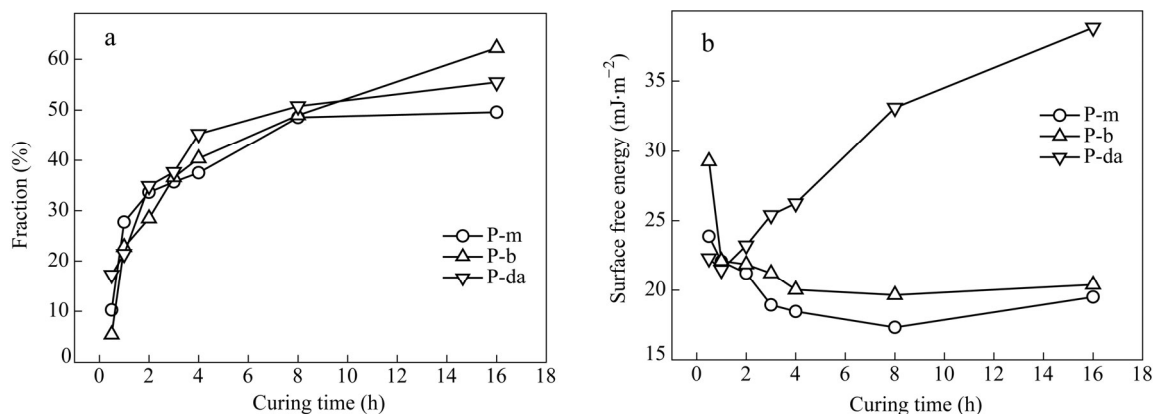




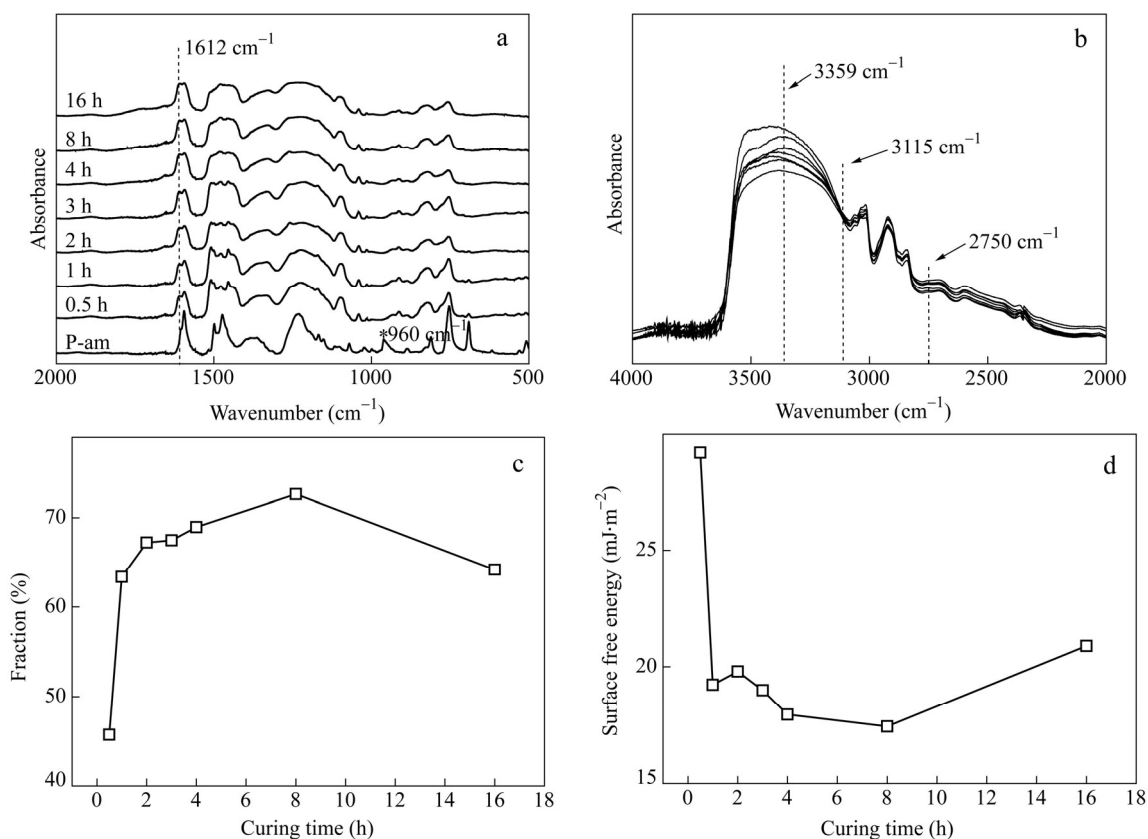
**Fig. 5** Curve fitting for the FTIR spectra of P-b polybenzoxazines cured at 200 °C for (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 8 h and (g) 16 h; (1) OH...O intermolecular hydrogen bonding, (2) OH...N intramolecular hydrogen bonding and (3) O...H<sup>+</sup>N intramolecular hydrogen bonding

The similar research was also done for the poly(P-am), and the results are shown in Fig. 7. The characteristic absorption of the benzoxazine structure at 960  $\text{cm}^{-1}$  disappeared after curing for 0.5 h. Meanwhile, the absorbance of the free Schiff base ( $\text{C}=\text{N}$ ) bond at 1612  $\text{cm}^{-1}$  increased gradually. The proportion of intermolecular hydrogen bond (appeared at 3359  $\text{cm}^{-1}$ ) changed continuously. Similarly, the FTIR spectra curve-resolving of poly(P-am) with respect to the corresponding frequencies of each hydrogen-bonded species was also performed. As shown in Figs. 7(c) and 7(d), upon the increasing of the curing time from 0.5 h to 16 h, the fraction of intermolecular hydrogen bonds increased initially and then decreased, while the surface free energy

was opposite. It may safely draw the following conclusion that strong intermolecular hydrogen bonding decreased the surface free energies of poly(P-am) films, which was inconsistent with the previous studies<sup>[39, 40]</sup>.



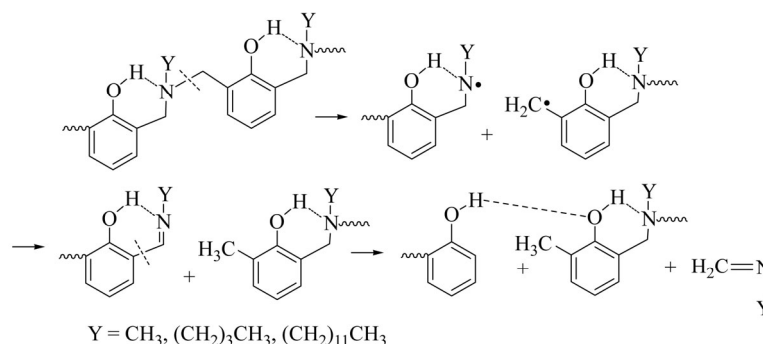
**Fig. 6** Variations of (a) the fraction of intermolecular hydrogen bonding, and (b) the surface free energies of the polybenzoxazines (cured at 200 °C)



**Fig. 7** FTIR spectra of poly(P-am) cured at 200 °C (0–16 h) in the range of (a) 2000–500 cm<sup>-1</sup> and (b) 4000–2000 cm<sup>-1</sup>; Variations of (c) the fraction of intermolecular hydrogen bonding, and (d) the surface free energies of poly(P-am) with curing time (cured at 200 °C)

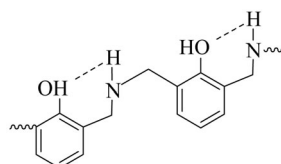
The relationships of the fraction of intermolecular hydrogen bonding and the surface free energies of P-m, P-b and P-da polybenzoxazines were similar but different to that of the P-am polybenzoxazine. This could be

due to their different mechanisms of transformation between intramolecular hydrogen bonding and intermolecular hydrogen bonding. As shown in Scheme 3, when the *N*-substituents were CH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> and (CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, there were strong intramolecular hydrogen bonds between —OH and N—Y. So a stable six-membered ring was formed. Then the C—C bond cleavage formed Mannich base.



**Scheme 3** Transformation mechanism of intramolecular into intermolecular hydrogen bonding in the polybenzoxazine system

But when the *N*-substituent was H, there might be —NH...OH— intramolecular hydrogen bond existed besides the above one in the polymer (Scheme 4). So in the transformation process of intramolecular to intermolecular hydrogen bond, there would appear the —NH...OH— intramolecular hydrogen bond. But the process shown in Scheme 3 was still dominated, that was to say strong intermolecular hydrogen bond would increase the surface free energy. However, the appearance of —NH...OH— intramolecular hydrogen bond made the fraction of intermolecular hydrogen bond decrease, thus led to such a phenomenon that the surface free energy increased with the fraction of intermolecular hydrogen bond decreased (Figs. 7c and 7d) after the lowest surface free energy.



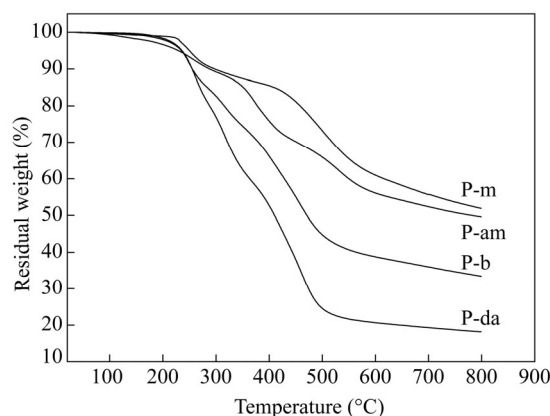
**Scheme 4** The —NH...OH— intramolecular hydrogen bond

As discussed above, the surface free energy was not only affected by the hydrogen bond network but also the *N*-substituted alkyl. After detailed studying for curing conditions of these polybenzoxazine films, it could be concluded that they were all low surface free energy materials. In comparison, the surface free energy of poly(P-da) was higher than that of others, probably because the long alkyl chain was entangled and curled during curing and couldn't stretch on the surface.

#### **Thermal Stability of Poly(P-am), Poly(P-m), Poly(P-b) and Poly(P-da)**

The polybenzoxazines' thermal stabilities were characterized by TGA. Poly(P-am), poly(P-m), poly(P-b), and poly(P-da) were cured at 200 °C for 1 h, then heated under N<sub>2</sub> atmosphere from ambient temperature to 800 °C at the heating rate of 10 K·min<sup>-1</sup>. The results are shown in Fig. 8 and Table 5.

As shown in Fig. 8, a three-stage weight loss process was observed in the TGA result of poly(P-am), while there was a two-stage weight loss process of poly(P-m), poly(P-b), and poly(P-da). The electron donating effect of alkyl chain could strengthen the integration of N atoms and substituents. Meanwhile, the first step of degradation was due to Mannich base cleavage (the cleavage of the C—N bond), resulting in the release of Schiff base (C=N) as reported in the literature<sup>[40]</sup>. The Schiff base in the P-am polybenzoxazine was H<sub>2</sub>C=NH with no alkyl chain linked with N atom, so that it exhibited a TGA curve different from others.



**Fig. 8** TGA thermograms of polybenzoxazines under nitrogen atmosphere

**Table 5.** Thermal resistance of polybenzoxazine measured by TGA

Resin sample	Temperature at 5 wt% loss (°C)	Temperature at 10 wt% loss (°C)	Char yield at 800 °C (%)
P-am	229	288	49.60
P-m	250	298	51.90
P-b	235	255	33.44
P-da	236	256	18.15

As shown in Table 5, the temperature at 5 wt% loss of P-m, P-b and P-da polybenzoxazines decreased with increasing the length of *N*-substituent alkyl chain. That was because the strong electron donating effect of alkyl chain could make Mannich base cleavage more easily. The char yields of these polybenzoxazines are also listed in Table 5, revealing that P-am and P-m polybenzoxazines have good thermal stability.

## CONCLUSIONS

A series of mono-functional benzoxazine monomers with different *N*-substituents were synthesized and characterized. The polybenzoxazine films were prepared by one-step curing method. Their surface free energies were calculated, and the lowest surface free energies of poly(P-am), poly(P-m), poly(P-b), and poly(P-da) films were 15.15, 16.89, 16.31, and 21.13 mJ·m<sup>-2</sup>, respectively.

The hydrogen bonding network of polybenzoxazines curing at 200 °C for different time was investigated by analyzing the curve fitting for FTIR spectra. The results showed that the surface free energies of poly(P-m), poly(P-b), and poly(P-da) would increase continuously with the fraction of intermolecular hydrogen bonds increasing after reaching the lowest surface free energies, but poly(p-am) showed different performance. That was because the *N*-substitute would also affect the surface free energy besides the intermolecular hydrogen bonds. After further study for curing conditions of these polybenzoxazine films, it could be concluded that they were all low surface free energy materials, which indicated their potential applications in the aviation, bio-coatings, and environment protection fields.

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