

## Effect of N-substituents on the surface characteristics and hydrogen bonding network of polybenzoxazines

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### ABSTRACT

In our study, the effect of N-substituents on the surface free energy and hydrogen bonding network structure of polybenzoxazine has been studied systematically. The contact angle measurement results show the surface energies of the polybenzoxazines decrease with the increase of alkyl chain length, and are not affected by the steric factor of the tert-butyl group. However, the FTIR curve fitting results show that both the chain length and bulkiness of alkyl group have an effect on the hydrogen bonding network of the polybenzoxazines, and facilitate the formation of intermolecular hydrogen bonding during the progress of cure. This indicates that both alkyl group and the fraction of intermolecular hydrogen bonding have an effect on the surface energy of the polybenzoxazines. Additionally, the transformation mechanism of the intermolecular and intramolecular hydrogen bonding during the progress of cure is proposed for the first time.

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### 1. Introduction

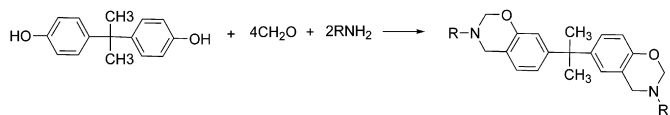
A low surface energy behavior is important for many practical applications in coatings, selfcleaning, and biomaterials [1–6]. Recently, polybenzoxazine has been developed and reported as a novel class of nonfluorine, nonsilicon, low surface energy materials [6,7], having advantages of low cost and easy processability compared with conventional fluoropolymers or silicones [8–11]. It is expected to gain promising future due to their unique advantages, and having a wide range of applications such as super hydrophobic surfaces, in lithographic patterning, and as mold-release materials in nanoimprint technology [8–10].

As mentioned in the literature, polybenzoxazines have been reported to show both inter- and intramolecular hydrogen bonding network structure [12–14]. Wang et al. discovered that the lowest surface free energies of the two polybenzoxazines based on aniline and methylamine were 19.21 and 16.43 mJ/m<sup>2</sup> respectively, which were even lower than that of Teflon (21.0 mJ/m<sup>2</sup>) [7]. They thought that this behavior is due to the presence of strong intramolecular hydrogen bonding matrix in the polybenzoxazines systems, and intramolecular hydrogen bonding leads to a decrease in the surface free energy, whereas increasing the fraction of intermolecular hydrogen bonding leads to opposite effect. Kuo prepared a low-surface-energy polymer material (16.8 mJ/m<sup>2</sup>) by decreasing the

fraction of intermolecular hydrogen bonds between the OH groups in poly(vinyl phenol)/polybenzoxazine blends [15]. Lin et al. discovered that poly(vinyl phenol) (PVPh) also possesses low surface energy (15.7 mJ/m<sup>2</sup>) by decreasing the degree of intermolecular hydrogen bonding between its OH groups after a simple thermal treatment procedure. The manipulation of intermolecular hydrogen bonding interactions had shown a good prospect as a unique and simple approach toward preparing low-surface-energy materials without the need to employ fluoropolymers or silicones.

Although hydrogen bonding is important to control the surface properties in the polybenzoxazine system, the relationship between the surface free energy and the fraction of intermolecular or intramolecular hydrogen bonding remains poorly understood [15]. Up to now, the surface energy of only two polybenzoxazines based on aniline and methylamine were investigated, and a difference in hydrogen bonding network structure and surface energy was observed between methylamine based polybenzoxazines and aniline-based polybenzoxazines. Ishida et al. investigated the correlation between the –OH...N intramolecular hydrogen bonding interaction and amine functional groups in the asymmetric dimers by <sup>1</sup>H NMR spectra, and reported that the differences in the hydrogen-bonded structures of the model benzoxazine dimers is closely related to the amine groups [16]. They also studied that the compactness of a network structure is related to both the basicity and bulkiness of the functional amines [17]. The potential contribution of alkyl group of primary amine to the polymer hydrogen

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**Scheme 1.** Preparation of the benzoxazine monomers (R: methyl; ethyl; butyl; tert-butyl).

bonding network structure and surface free energy were not formally investigated.

In this study, four aliphatic primary amine based benzoxazine monomers were synthesized to explore the effect of N-substituents on the surface energy and hydrogen bonding structure of polybenzoxazine. The effect of aliphatic chain length and steric effect on the polybenzoxazines film-forming property is also probed. Additionally, the thermal stability of the polybenzoxazines was characterized through TGA.

## 2. Experimental

### 2.1. Materials

Bisphenol A and formaldehyde (37% in water), primary amine were supplied by the Sinopharm Chemical Reagent Co of China. All chemicals were used without further purification. In this paper, the benzoxazine monomers were synthesized according to the procedure presented in Scheme 1 [18], R in the structure denotes the substituent of the primary amine. Various primary amines including methylamine, ethylamine, butylamine, and tert-butylamine were used. The monomers will be referred to as B-m, B-e, B-b and B-t, respectively. The crude product was dissolved in ether and washed with aqueous NaOH for three times to remove phenolic oligomers,

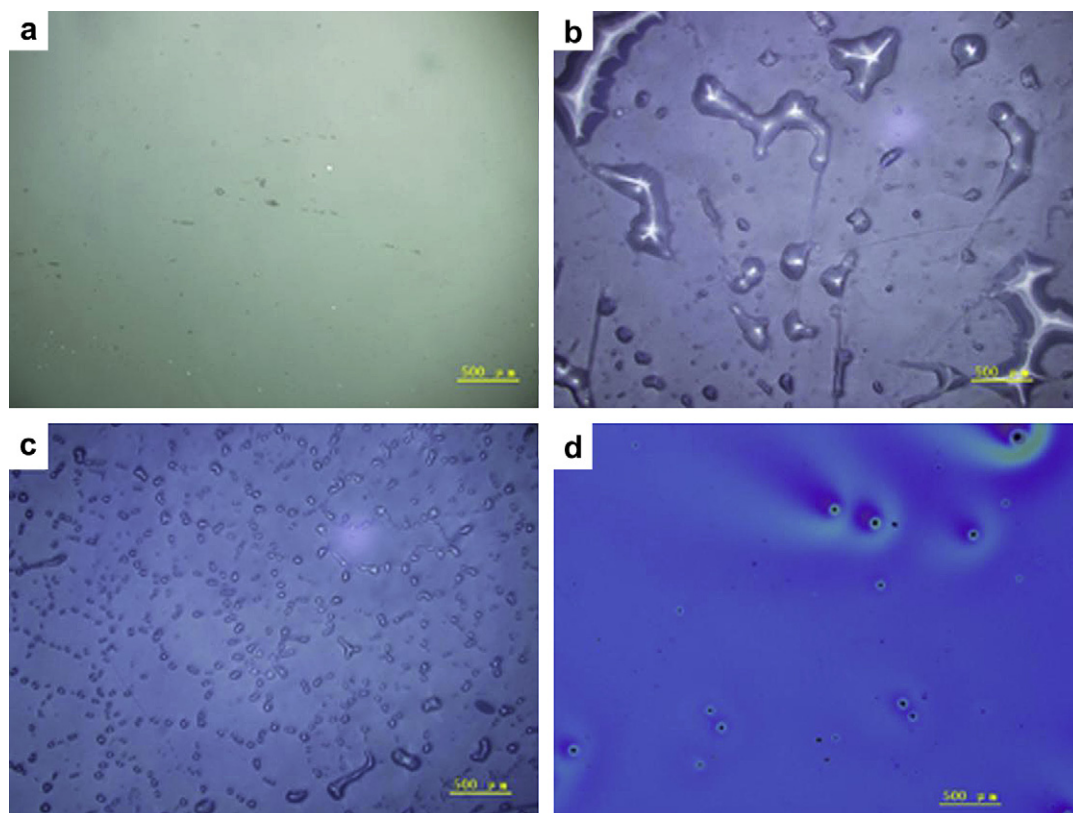
followed by distilled water, and then drying over sodium sulfate. Evaporating the ether resulted in white solid powder for B-m and B-t, and yellow viscous fluids for B-e and B-b respectively. All monomers were refrigerated until the time of use. Successful synthesis and purity were verified by  $^1\text{H}$  NMR and FTIR spectroscopy.

### 2.2. Characterization

The benzoxazine monomer was diluted to 30 mg/ml or 200 mg/ml in THF respectively, and the solution was filtered through a 0.2  $\mu\text{m}$  syringe filter (Celanese, America) before spin coating onto a glass slide ( $100 \times 100 \times 1 \text{ mm}^3$ ). The glass slides were cleaned by Piranha solution (7:3 mixtures (v/v) of 98%  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$ ) at 120  $^\circ\text{C}$  for 30 min before use, and then rinsed by deionized water. The solution was spin-coated at 1500 rpm for 45 s and evaporated in a vacuum oven at 60  $^\circ\text{C}$  for 1 h, then cured in an oven at 180  $^\circ\text{C}$  or 210  $^\circ\text{C}$ . The cured polymers were referred to as B-m, B-e, B-b and B-t polybenzoxazine, respectively. The advancing contact angle measurement of the film was measured using the sessile drop (needle in) technique (OCA20, Data Physics Instruments, Germany) at room temperature. The contact angles of deionized water, ethylene glycol and diiodomethane were further adopted to estimate the surface free energy using van Oss-Good acid/base theory [19,20].

Infrared spectra were acquired with a Nicolet iS10 FTIR spectrophotometer. The sample was prepared by casting the solution directly onto a KBr plate and curing under conditions similar to those used in the film preparation.

Surface profiles of films were acquired with an optical microscope (BX41-P, Olympus). Thermogravimetric analysis (TGA) was conducted with SDT Q600 V5.0 Build 63 under a 40 ml/min flow of nitrogen gas at a scan rate of 10  $^\circ\text{C}/\text{min}$  over the temperature range from 30 to 800  $^\circ\text{C}$ .



**Fig. 1.** Optical microscope of glass slides spin-coated with different benzoxazine monomers after drying at 60  $^\circ\text{C}$  for 1 h a) B-m; b) B-e; c) B-b; d) B-t.

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