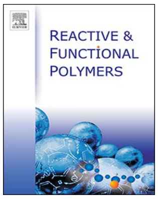
Reactive and Functional Polymers 124 (2018) 139–148

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react



# Structural effects of highly π-conjugated mesogenic Schiff-base moiety on the cationic polymerization of benzoxazine and formation of ordered morphologies

Huan Liu[a,b,*], Qing-Quan Liu[a,b], Li Tian[a,b], Lin-Yan Wang[a,b], Kai Xu[c,**], Qian-Xin Chen[a], Bao-Li Ou[a]

[a] *College of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan 411201, China*
[b] *Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, Hunan University of Science and Technology, Xiangtan 411201, China*
[c] *Key Laboratory of Polymer Material for Electronics, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China*

## ARTICLE INFO

*Keywords:*
Benzoxazines
Schiff-base
Liquid crystal
Ordered porous carbons
Nitrogen-rich

## ABSTRACT

A Schiff-base moiety was introduced into the chemical structure of benzoxazine through the Mannich reaction. With alternative imine groups (C=N) and benzene rings in the chain segment, these highly π-conjugated systems favored the formation of strong intermolecular hydrogen bonds to the hydroxyl groups generated during polymerization, leading to a thermally initiated cationic polymerization mechanism. Compared with the bisphenol-A-based benzoxazine, the benzoxazine with the Schiff-base moiety needs higher energy to facilitate the realization of polymerization and to increase polymerization degree. In addition to the influences on the polymerization, the highly π-conjugated Schiff-base acting as a mesogenic moiety is found to form liquid crystal (LC) phases, like the nematic phase and smectic phase. Interestingly, some LC-rich domains can be stabilized by the polybenzoxazine network, which will contribute to form nitrogen-rich ordered porous carbon at the carbonization stage. For $N_2$ and $CO_2$ adsorption–desorption process, the carbon exhibits an enhanced $CO_2$ adsorption performance, suggesting their capture and separation capacity for $CO_2$.

## 1. Introduction

Polybenzoxazine, as a fast developing class of thermosetting polymer, possesses a number of fascinating advantages such as excellent mechanical and thermal properties [1,2], near-zero volumetric change upon curing [3], low water absorption [4], superior electrical properties [5], low surface free energy [6], and high char yield [7]. These excellent properties make polybenzoxazine a promising candidate as a kind of high-performance polymer. Because the structure of the benzoxazine monomer can be obtained from the Mannich reaction that involves the condensation of phenolic derivative, formaldehyde, and primary amine by the solvent or melt method, some functional structures can be conveniently introduced into polybenzoxazines. On the basis of the chemical structure modification method, advanced functional polybenzoxazines such as self-healing agents [8], shape memory materials [9], hybrid organic inorganic materials [10], photoelectric functional devices [11], and self-cleaning properties [12] have been developed nowadays.

In the case of functional modification of the benzoxazine structure, the study of liquid crystal (LC) benzoxazine is pursued [13–15]. It has been reported that the introduction of mesogenic moieties can produce LC behaviors and some controlled network structures that can facilitate the thermal conductivity of polybenzoxazine [16]. Hence, LC benzoxazines are now expected to be a substitute for LC epoxies in microelectronic devices [17]. Unfortunately, compared with the LC epoxies [18–20], the LC benzoxazines have not yet been considerably developed despite the fact that they have higher thermal properties. In this regard, it is highly desirable to design and tune new benzoxazines with functional transition for designing advanced functional materials and for greatly enhancing performances in terms of LC behavior, catalysis, and gas adsorption and storage.

In our previous study, a Schiff-base moiety having alternate imine groups (C=N) and benzene rings in the main chain was imported into the epoxy backbone through the Mannich reaction [21]. Because the moiety is π-conjugated through rigid molecular scaffolds, it can be involved in the supramolecular structure of stacking interactions.

---

[*] Correspondence to: H. Liu, College of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan 411201, China.
[**] Corresponding author.
*E-mail addresses:* hliu@hnust.edu.cn (H. Liu), xk@gic.ac.cn (K. Xu).

https://doi.org/10.1016/j.reactfunctpolym.2018.01.015
Received 4 December 2017; Received in revised form 16 January 2018; Accepted 17 January 2018
1381-5148/

Depending on the self-assembly ability of the π-conjugated systems, the rigid polymer chains can function as mesogenic moieties with LC properties. Inspired by this work, we intended to introduce the highly π-conjugated Schiff-base moiety into the backbone of benzoxazine for designing a novel benzoxazine monomer, and we expected that the presence of the highly π-conjugated Schiff-base moiety could cause some chemical and physical structural effects in the functional transition of benzoxazine.

First, we consider that the presence of the highly π-conjugated Schiff-base moiety will have effects on the polymerization mechanism of benzoxazine. On one hand, its presence will have an influence on the format of chain initiation, namely, oxazine ring opening. The oxazine ring is opened by the attack of cationic intermediates, resulting in an electrophilic or nucleophilic attack-induced ring-opening polymerization of benzoxazine. When the highly π-conjugated Schiff-base moiety, which exists in two tautomeric forms: enol-imine (E-form) and keto-enamine (K-form) [22,23], is introduced into the benzoxazine backbone, the resulting zwitterion will have an effect on the benzoxazine cationic polymerization. The presence of the zwitterionic structure will create a competition between chain propagation and chain transfer owing to the consequence of proton transfer [24]. Hence, it will be interesting to know how the presence of zwitterion promotes competition and affects the polymerization mechanism of benzoxazine.

On the other hand, the highly π-conjugated Schiff-base moiety will have an influence on the format of the chain propagation. As we know, the polymerization degree of benzoxazine is difficult to be increased [25,26] because when the polymerization degree reaches a vitrified stage, the oxazine ring in contact with each other becomes hard and the polymerization is controlled by diffusion of the benzoxazine molecules. Many oxazine rings, which are not involved into the ring-opening polymerization, will be able to form resonance-stabilized intramolecular hydrogen bonds with the highly π-conjugated Schiff-base moieties [27,28]. It is entirely possible that the highly π-conjugated Schiff-base moiety will induce polymerization to form new active sites or quench the existing active sites through the formation of supramolecular bond [29]. In addition to the hydrogen bond effect, it is more interesting that the Schiff-base moieties can influence rank of the benzoxazine molecular structure. Through the π-π interaction, the benzoxazine molecules will move to get stacked in an order. The formation of an ordered morphology will provide the oxazine rings with a distinctive spatial distribution, which may accelerate or hinder the polymerization. Because of these factors, benzoxazines with various polymerization degrees, such as monomers, oligomers, macromolecules of low cross-linking density, and macromolecules of high cross-linking density, may coexist in polybenzoxazine [30].

Second, in our previous study, LCs phases, like the nematic phase and smectic phase, were found to be formed through the π-π interaction of the highly π-conjugated Schiff-base and could be stabilized by the epoxy polymer network [21]. Combined with the influence of the highly π-conjugated Schiff-base moiety on the benzoxazine polymerization, some short rigid chains such as the monomers, the oligomers, the macromolecules of low cross-linking density still exist in the polybenzoxazine. It is an essential prerequisite for the formation of other ordered morphologies on the basis of the LC template. Hence, we consider that the LC phases may also be found in the benzoxazine and may also be stabilized by the polybenzoxazine network.

For these stabilized LC-rich domains in a polymer matrix, it is relatively unexplored whether they have a structural effect on the formation of special carbon structure or on the formation of ordered morphology. These stabilized LC-rich domains are rich in the highly π-conjugated mesogenic Schiff-base moieties. We found that these moieties in the polymer main chain could be decomposed into the volatile amine and possessed a significant charring tendency for the formation of high residual char during the carbonization stage [31]. Through the volatile amine precursor treatment of an oxidized carbon, nitrogen is incorporated into the carbon through implantation, and this provides a key strategy for the design of the nitrogen-doped carbon [32,33]. Hence, for the formation of the special carbon structure, the Schiff-base moiety is expected to draw the nitrogen into the carbon using implantation during the carbonization stage.

For the formation of ordered morphology, we hope the highly π-conjugated mesogenic Schiff-base moieties can engender supramolecular stacking interactions at high temperatures and form an ordered morphology. With the release of their decomposition volatile products, an ordered hierarchical porous structure may be shaped [34,35]. This is similar to the method of soft-template for the preparation of ordered porous carbons [36,37]. This kind of nitrogen-rich ordered porous carbon prepared by this method will have potential applications in fields of catalysis [38], sensors [39], adsorption [40], and energy generation and storage [41].

## 2. Experimental section

### 2.1. Materials

All reagents and solvents were purchased as reagent grade and were purified or dried by standard methods before use. The preparation and characterization of the SBA was reported in the previous paper [21]. The following reagents were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China): terephthalaldehyde (≥ 98%), *p*-aminophenol (≥ 98%), aniline (≥ 99.5%), and formalin (37%). Analytical grade zinc chloride (≥ 98%) obtained from Aladdin Chemical Reagent Co., Ltd. China was used as catalyst. 4-Dioxane (DOA, ≥ 99.9%) was obtained from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China) and dried with molecular sieves before use. The BA-bz was provided by the Coryes Polymer Science & Technology Co. Ltd. (Chengdu, China) and used without further purification.

### 2.2. Synthesis of the SBA-bz

The synthetic pathway of the SBA-bz is shown in Scheme 1. In a 250-ml flask equipped with a magnetic stirrer and a thermometer, a solution of 40 mmol (3.72 g) of aniline in 20 ml of dioxane was cooled in an ice bath. To this solution, a solution of 80 mmol (6.49 g) of formalin (37%) in 10 ml of dioxane was then added portionwise for 30 min. The solution was kept stirring for 30 min below 5 °C. Thereafter, a solution of SBA (20 mmol, 6.32 g) in 50 ml of dioxane was added. The solution was refluxed at 110 °C for 6 h under a $N_2$ atmosphere. By removal of the solvent using a rotating evaporation instrument at 50 °C, a viscous residue (10.95 g) was obtained, and then, it was dissolved in 100 ml of ether and washed several times with 1 N sodium hydroxide solution and finally with distilled water. A brownish red solid was obtained with 84% yield (9.24 g). SBA-bz: mp, 190–192 °C. $^1$H NMR ($CDCl_3$ with 0.05% v/v TMS, 400 MHz; n′ is the number of symmetrical structures with n): $\delta_H$ 8.50 (2H, s, H1, and H1′), 7.99–7.87 (4H, m, and H10), 7.39 (4H, m, H6, and H6′), 7.23 (2H, s, H9, and H9′), 7.10–6.98 (6H, m, H2, H2′, H3, and H3′), 6.96–6.82 (4H, m, H5, and H5′), 6.77–6.62 (2H, m, H7, and H7′), 5.36 (4H, s, H4, and H4′), and 4.64 (4H, s, H8, and H8′). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta_C$ 159.5 (s, C1, and C1′), 157.3 (s, C5, and C5′), 148.4 (s, C7, and C7′), 144.4 (s, C14, and C14′), 129.2 (s, C9, and C9′), 128.9 (s, C15, and C15′), 126.3 (d, C12, C12′, C13, and C13′), 120.9 (s, C10, and C10′), 118.5 (s, C3, and C3′), 115.1 (s, C8, and C8′), 113.1 (s, C4, and C4′), 79.5 (d, C6, and C6′), and 51.0 (d, C11, and C11′).

### 2.3. Thermally initiated cationic polymerization of the benzoxazine monomers

The benzoxazine monomers (SBA-bz and BA-bz) were poured into a stainless steel mold and then thermally cured in a vacuum oven at 150 °C for 1 h, 190 °C for 2 h, and 230 °C for 3 h. After that, post-curing was carried out for both samples at 260 °C for 1 h. For two of the