

# Synthesis of liquid–crystalline benzoxazines containing a biphenyl group in the mesogenic moiety



Masayoshi Ito<sup>a</sup>, Takehiro Kawauchi<sup>a,1</sup>, Koichi Sakajiri<sup>b</sup>, Tsutomu Takeichi<sup>a,\*</sup>

<sup>a</sup> Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan

<sup>b</sup> Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 2-12-1, Japan

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## ABSTRACT

In this work, we describe a process to synthesize novel liquid–crystalline (LC) benzoxazines from a LC phenol that contains biphenyl, ester and azomethine groups in the mesogenic moiety, various alkyl amines and formaldehyde. The LC behavior of the biphenyl-containing benzoxazines was investigated by differential scanning calorimetry and polarized optical microscopy and compared with analogous phenyl-containing LC benzoxazines containing phenyl, ester and azomethine groups in the mesogenic moiety. While the LC benzoxazines containing the phenyl groups only exhibited a nematic phase upon heating, the LC benzoxazines containing biphenyl groups exhibited a smectic phase as well as a nematic phase. Additionally, the LC-isotropic transition temperatures were over 100 °C higher than that for the phenyl-containing LC benzoxazines. A film obtained by curing the biphenyl-containing LC benzoxazine at 180 °C for 1 h exhibited birefringence. Finally, the thermal diffusivity of the cured LC benzoxazines was also investigated.

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## 1. Introduction

Polybenzoxazines are a new type of phenolic resin and are obtained by the ring-opening polymerization of cyclic benzoxazine monomers synthesized from phenols, amines and formaldehyde [1–7]. The structures of B-a, which is a typical benzoxazine monomer, and its polymer (PB-a) are shown in Scheme 1. Polybenzoxazines possess advantageous properties associated with traditional phenolic resins, such as high thermal and flame retardant properties. Additionally, polybenzoxazines have other properties that are not found in traditional phenolic resins, such as excellent dimensional stability, low water absorption, low dielectric properties and low surface free energy. The polymerization of benzoxazine proceeds by thermal curing without a catalyst and without generating any volatiles. The wide variation in raw materials, phenols and amines allows tremendous flexibility in the molecular design of the cyclic monomers [8–20]. Due to these properties, polybenzoxazines are expected to be used as the matrix resin for carbon fiber reinforced plastics, adhesives, rigid printed circuit boards and other high-tech applications in the future.

Recently, thermal conductivity enhancement of materials has become a requirement in the micro-electronics field as a result of

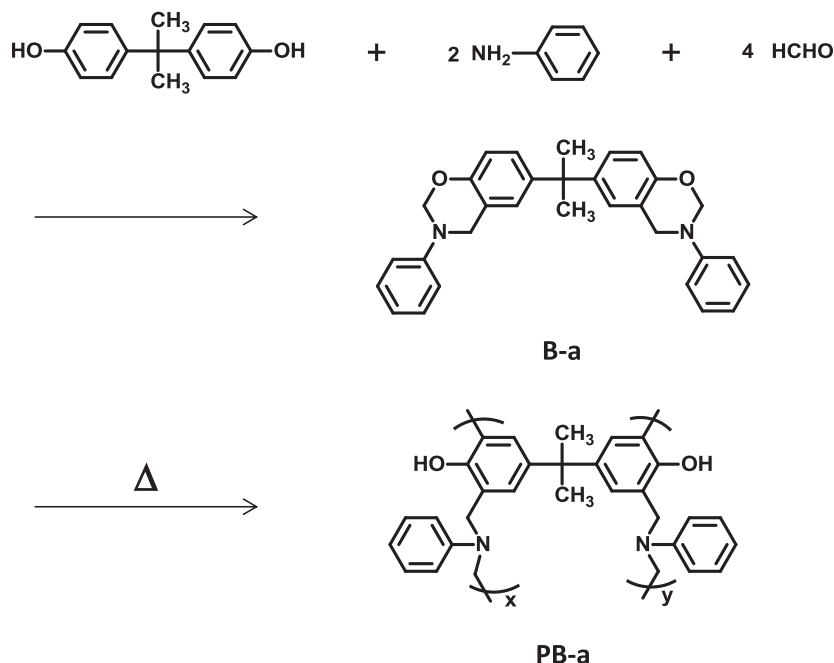
the demand for miniaturizing electronic devices [21]. Generally, resins are typically used for insulating materials. However, resins have low thermal conductivities, usually one to three orders lower than ceramics and metals, and can prevent heat transfer [22,23]. To improve the thermal conductivity of resins, one approach is to place high thermal conductivity fillers into resins [24–32]. However, the amount of filler that can be placed into the resins is limited because the resin viscosity increases with the amount of the filler that is used [33]. Additionally, the enhancement of the thermal conductivity of the resin itself effectively enhances the thermal conductivity of the composite that the resin is used in [33]. It has been reported that liquid–crystalline (LC) epoxy resins exhibit high thermal conductivities because of the rigid mesogen and the network structures that are controlled by the LC behavior [34,35]. However, there has been no examination of the enhancement of the thermal conductivity of polybenzoxazines using LC benzoxazines.

Ishida et al. reported on LC benzoxazines containing a cyanobiphenyl group in the mesogen. The benzoxazines exhibited an LC phase only during the cooling cycle and did not show any LC phase during the heating cycle [36]. Recently, we synthesized LC benzoxazines that exhibited an LC phase not only during the cooling cycle but also during the heating cycle, indicating the presence of enantiotropic LC benzoxazines [37]. The fact that the benzoxazines exhibit an LC phase during the heating cycle is advantageous for controlling the polybenzoxazine network structure via thermal curing. The LC temperature ranges of the LC benzoxazines increase as the length of alkyl

\* Corresponding author. Tel.: +81 532 44 6815; fax: +81 532 48 5833.

E-mail address: [takeichi@ens.tut.ac.jp](mailto:takeichi@ens.tut.ac.jp) (T. Takeichi).

<sup>1</sup> Present address: Frontier Research Center, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan.



**Scheme 1.** Preparation of B-a and PB-a.

chains connected to the mesogenic moiety decreases. The highest LC-isotropic transition temperature in the previous study was 126 °C, and the benzoxazine transformed into its isotropic phase at this temperature during the heating cycle. Because the onset of polymerization of the LC benzoxazine was found to take place at 195 °C, the polymerization proceeded in the isotropic state.

To polymerize benzoxazines in the LC state, decreasing the polymerization temperature by adding a catalyst and increasing the LC temperature range are considered. In this study, we attempted to increase the LC temperature range by introducing more of the rigid biphenyl group instead of the phenyl group into the mesogenic moiety. We investigated the liquid crystallinity of the obtained LC benzoxazines by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The polymerization behavior of the LC benzoxazines was also investigated. Furthermore, the thermal diffusivity of the polybenzoxazines obtained from the LC benzoxazines was also examined.

## 2. Experimental section

### 2.1. Materials

Raw materials, such as 4-(heptyloxy)-4'-biphenylcarboxylic acid, thionyl chloride, *p*-hydroxybenzaldehyde, pyridine (dehydrated), methylamine (40% in methanol), butylamine, octylamine, tetrahydrofuran (THF, super dehydrated and stabilizer free), *N,N*-dimethylformamide (DMF, dehydrated), methanol, ethanol, and chloroform, were purchased from Wako Pure Chemicals (Osaka, Japan) and were used in the as-received state. Additionally, *p*-aminophenol was obtained from Wako Pure Chemicals and was purified by sublimation. Sodium sulfate (anhydrous) and formalin (37%) were purchased from Kishida Chemicals (Osaka, Japan) and were used without any further purification.

### 2.2. Synthesis of 7BEA

Thionyl chloride (17.8 g, 0.150 mol) was added to a solution of 4-(heptyloxy)-4'-biphenylcarboxylic acid (4.69 g, 0.0150 mol) in

THF (40.0 mL) at room temperature in a nitrogen atmosphere and heated to reflux to yield a black solution. A catalytic amount of DMF was added to the black solution, and the mixture was refluxed for 12 h. Excess thionyl chloride, THF and other volatiles were evaporated using a diaphragm pump for 2 h and a vacuum pump (15 Pa) for 3 h at 45 °C to give black solid. To this solid, *p*-hydroxybenzaldehyde (1.83 g, 15 mmol) and THF (15 mL) were added and stirred at room temperature. Pyridine (1.19 g, 15 mmol) was then added to the mixture and stirred at 50 °C for 24 h in a nitrogen atmosphere. A brown solid precipitated as the mixture was stirred. The brown solid was collected by filtration and washed with methanol. The solid was dissolved into chloroform (500 mL) and washed three times with water using a separating funnel. Then, the chloroform solution was dried overnight with sodium sulfate (anhydrous). After removing the sodium sulfate by filtration, the chloroform solution was concentrated using a rotary evaporator. The solution was evaporated with a vacuum pump to yield a dry brown solid of 67% 7BEA (4.18 g, 10 mmol).

The spectroscopic data for 7BEA using IR ( $\text{cm}^{-1}$ ) are as follows: 1728 ( $\nu_{\text{C=O}}$ ) and 1707 ( $\nu_{\text{CH=O}}$ ). The  $^1\text{H}$  NMR spectra for 7BEA are as follows ( $\text{CDCl}_3$ , rt, 400 MHz,  $\delta$ ): 0.91 (t,  $\text{CH}_3$ , 3H), 1.22–1.64 (m,  $\text{CH}_2$ , 8H), 1.75–1.89 (m,  $\text{CH}_2$ , 2H), 4.02 (t,  $\text{CH}_2$ , 2H), 7.01 (d, CH, 2H), 7.44 (d, CH, 2H), 7.61 (d, CH, 2H), 7.72 (d, CH, 2H), 7.99 (d, CH, 2H), 8.24 (d, CH, 2H) and 10.0 (s, CH, 1H).

### 2.3. Synthesis of 7BEAP

To synthesize 7BEAP, ethanol (240 mL) and 7BEA (1.50 g, 3.60 mmol) were added to a flask and stirred at the reflux temperature. *p*-Aminophenol was added to the resulting yellow solution (0.472 g, 4.32 mmol) and refluxed for 12 h. A brown solid, precipitated during refluxing, was collected by filtration, washed with ethanol (300 mL), and dried with a vacuum pump to yield 64% 7BEAP (1.17 g, 2.3 mmol).

The spectroscopic data for 7BEAP using IR ( $\text{cm}^{-1}$ ) are as follows: 3447 ( $\nu_{\text{O-H}}$ ), 1734 ( $\nu_{\text{C=O}}$ ) and 1602 ( $\nu_{\text{C=N}}$ ). The  $^1\text{H}$  NMR spectra for 7BEA are as follows ( $\text{CDCl}_3$ , rt, 400 MHz,  $\delta$ ): 0.91 (t,  $\text{CH}_3$ , 3H), 1.16–1.61 (m,  $\text{CH}_2$ , 8H), 1.72–1.91 (m,  $\text{CH}_2$ , 2H), 4.02 (t,  $\text{CH}_2$ , 2H),

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