



Synthesis of high-molecular-weight benzoxazines from various combinations of bisphenols and diamines via Mannich condensation and properties of their thermosets

Yuta Murai¹ · Taichi Uemura² · Yujie Chen² · Takehiro Kawauchi¹ · Tsutomu Takeichi¹

Received: 8 September 2020 / Revised: 5 October 2020 / Accepted: 10 October 2020 / Published online: 29 October 2020
© The Society of Polymer Science, Japan 2020

Abstract

High-molecular-weight (HMW) benzoxazines were synthesized by Mannich condensation with various combinations of bisphenols and diamines, and the mechanical and thermal properties of the polybenzoxazines derived from the HMW benzoxazines were measured by tensile tests and thermogravimetric analysis (TGA) to investigate the structure-property relationship. Free-standing precursor films were easily obtained from the solutions of HMW benzoxazines by a cast method on glass plates, and transparent and very tough polybenzoxazine films were obtained by thermally curing the precursor films at a temperature up to 240 °C. The polybenzoxazine films showed higher tensile strength and larger elongation at break than typical polybenzoxazine, i.e., **PB-a** obtained from low-molecular weight benzoxazine synthesized from bisphenol-A and aniline. In particular, among the HMW polybenzoxazines presented in this work, the **PODP-oda** film derived from 4,4'-oxydiphenol and 4,4'-oxydianiline showed remarkably good mechanical properties ($E = 3.7$ GPa, $s_b = 125$ MPa, and $e_b = 4.5\%$). Moreover, the **PODP-oda** film revealed a higher 5 wt% weight loss temperature ($T_{d5} = 332$ °C) and char yield at 850 °C ($CY_{850} = 58\%$) than **PB-a** ($T_{d5} = 301$ °C and $CY_{850} = 42\%$), as evidenced by TGA, suggesting good thermal stability.

Introduction

Polybenzoxazines are a new type of phenolic resin and are obtained by ring-opening polymerization of benzoxazines synthesized from phenols, amines, and formaldehyde [1, 2]. Polybenzoxazines possess advantageous properties associated with traditional phenolic resins, such as good thermal and flame-retardant properties. In addition, polybenzoxazines

have other properties that are not found in traditional phenolic resins, such as excellent dimensional stability, low water absorption, low dielectric constants, and low surface free energy [3–7]. Due to these properties, polybenzoxazines are expected to be used as the matrix resin for fiber-reinforced plastics, adhesives, rigid printed circuit boards, and other high-tech applications.

However, the major shortcoming of polybenzoxazines is their lack of toughness, which is a common problem for thermosetting resins. To date, various approaches have been proposed to improve the toughness of polybenzoxazines. One approach is alloying with elastomers such as various siloxanes [8–11] and liquid rubber [12, 13]. This approach was successful for the toughening of brittle polybenzoxazines without losing their good thermal properties. A second approach is the molecular design of the benzoxazine monomer by introducing flexible linkages such as aliphatic bridges [14, 15]. This approach was effective for the toughening of cured polybenzoxazines but detrimental to the thermal properties. The third approach is the design of high-molecular-weight (HMW) benzoxazines prepared by the Mannich condensation reaction of bisphenol-A and diamine with paraformaldehyde, affording a polymer containing the benzoxazine moiety in the main chain [16].

Supplementary information The online version of this article (<https://doi.org/10.1038/s41428-020-00438-y>) contains supplementary material, which is available to authorized users.

✉ Takehiro Kawauchi
kawauchi@rins.ryukoku.ac.jp

✉ Tsutomu Takeichi
takeichi@chem.tut.ac.jp

¹ Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

² Department of Materials Chemistry, Faculty of Advanced Science and Technology, Ryukoku University, Oe-cho, Seta, Otsu, Shiga 520-2194, Japan

The polymer containing benzoxazines in the main chain is easily soluble in ordinary solvents and gives flexible and tough uncured films that are easy to handle. Surprisingly, after curing, the films became extremely tough, even though the crosslink density is supposed to be very high [16, 17]. The cured films also showed improved thermal properties. Inspired by the great success of this approach [16–21], various HMW benzoxazines have been developed by utilizing synthetic reactions such as azide-alkyne cycloaddition [22, 23], Diels-Alder reactions [24, 25], and hydrosilylation [26].

HMW benzoxazines are easy to prepare via the Mannich reaction, and many bisphenols and diamines can be used as monomers of HMW benzoxazines. We were interested in examining how much the mechanical properties of HMW benzoxazines obtained from the Mannich reaction can be improved. In this paper, we report the elucidation of the structure-property relationship, focusing mainly on the toughening effect. As a result, we found that the polybenzoxazine obtained from the HMW benzoxazine composed of 4,4'-oxydiphenol and 4,4'-oxydianiline, which incorporated ether linkages in both bisphenol and diamine units, showed remarkably good tensile properties with improved thermal stability.

Experimental section

Measurements

^1H NMR spectra were recorded with a Varian Mercury 300 spectrometer (300 MHz for ^1H) in chloroform-*d* (CDCl_3) at 25 °C using tetramethylsilane as the internal standard. Size exclusion chromatography (SEC) measurements were performed with a Jasco (Hachioji, Japan) PU-1580 liquid chromatograph equipped with a refractive index (Jasco, RI-2031plus) and a UV-visible (254 nm; Jasco UV-1570) detector. Two Shodex (Tokyo, Japan) KF806L SEC columns were connected in series at a flow rate of 1.0 mL/min, and tetrahydrofuran (THF) was used as the eluent. The molecular weight calibration curves were obtained with polystyrene standards (Shodex). Differential scanning calorimetry (DSC) measurements were carried out using a Rigaku (Akishima, Japan) Thermo Plus 2 DSC 8230 instrument, and samples were heated at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Rigaku Thermo Plus 2 TG8120 system, and samples were heated at a heating rate of 5 °C/min under argon. The tensile properties of films with lengths of ~2 cm were determined with an Imada Seisaku-sho (Toyohashi, Japan) Model SV-3 system operated at a crosshead speed of 0.5 mm/min. The tensile properties of each sample were determined from an average of at least ten tests.

Materials

Bisphenol-A (**BPA**), 1,2-ethylenediamine (**eda**), 1,6-hexanediamine (**hda**), 1,4-dioxane, chloroform, and formalin (37%) were purchased from Kishida Chemicals (Japan). Bisphenol-S (**BPS**), 4,4'-oxydiphenol (**ODP**), 4,4'-thiodiphenol (**TDP**), 4,4'-dihydroxybenzophenone (4,4'-carbonyldiphenol, **CDP**), 4,4'-oxydianiline (**oda**), 4,4'-methylenedianiline (**mda**), and paraformaldehyde were obtained from Tokyo Chemical Industry (Japan). 4,4'-Dihydroxybiphenyl (**BP**), 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and THF were purchased from Wako Pure Chemical Industries (Japan). These reagents and solvents were used as received. **B-a**, which is a typical bifunctional benzoxazine, was synthesized from bisphenol-A, aniline and formalin according to the literature [3, 5].

Synthesis of high-molecular-weight benzoxazines

A typical experimental procedure used to obtain **BPA-hda** is described below. Into a 200 mL round-bottom flask equipped with a magnetic stirrer, 50 mL of 1,4-dioxane, 1,6-hexanediamine (1.16 g, 10 mmol), and formalin (37%, 3.24 g, 40 mmol) was added and mixed at room temperature for 20 min. To the suspension, bisphenol-A (2.28 g, 10 mmol) was added at room temperature, and then, the mixture was gradually heated and kept under reflux for 5 h. After the reaction time, the reaction mixture was cooled to room temperature, and the solvent was removed at a reduced pressure by using a rotary evaporator. The residual compound was dissolved in CHCl_3 , and the insoluble part was removed by filtration. The filtrate was washed three times with 1 N NaHCO_3 aq. and several times with pure water until a neutral pH was obtained and then dried with anhydrous sodium sulfate. Chloroform was removed at a reduced pressure by using a rotary evaporator and then by using a vacuum pump at room temperature for 24 h. **BPA-hda** was obtained as a powder (3.34 g, 8.5 mmol) with a 85% yield. The chemical structure of **BPA-hda** was confirmed by ^1H NMR. ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) = 1.36 (- CH_2 -), 1.60 (- CH_3), 2.73 (- N-CH_2 -), 3.96 (Ar- CH_2 -N), 4.83 (O- CH_2 -N), 6.46-7.15 (aromatic).

Other HMW benzoxazines were prepared similarly. The reaction conditions are summarized in Table 1. The ^1H NMR spectra are shown in the Supporting Information.

Preparation and curing of precursor films

A typical procedure used to prepare and cure **BPA-hda** is described below. A DMF solution of **BPA-hda** at a concentration of 15 wt% was cast on a silane-treated glass plate, and the solvent was removed by drying at 50 °C for 10 h under vacuum to afford a free-standing yellowish

Table 1 Synthesis of high-molecular-weight benzoxazines using various combinations of bisphenols and diamines

Code	Solvent	Temp. °C	Time <i>h</i>	Yield ^a %	M_w^b	M_w^b/M_n	Ratio of cyclic structures ^c %
BPA-hda	Dioxane	60	5	85	1700	2.65	80
BPA-eda	Dioxane	Reflux	5	96	1700	4.29	95
BPA-mda	CHCl ₃	Reflux	5	95	2100	4.53	47
BPA-oda	CHCl ₃	Reflux	5	93	1700	2.76	58
BP-hda	Dioxane	90	5	86	1500	3.06	90
BP-eda	Dioxane	70	5	0 ^d	–	–	–
BP-mda	CHCl ₃	Reflux	20	0 ^{d,e}	–	–	–
BP-oda	CHCl ₃	Reflux	20	0 ^{d,e}	–	–	–
ODP-hda	Dioxane	90	5	93	1000	2.70	96
ODP-eda	Dioxane	70	5	96	1500	3.13	89
ODP-mda	CHCl ₃	Reflux	10	93	2200	10.0	59
ODP-oda	CHCl ₃	Reflux	20	90	2000	3.50	70
TDP-hda	Dioxane	Reflux	5	86	1400	2.28	94
TDP-eda	Dioxane	70	5	90	2000	2.68	87
TDP-mda	CHCl ₃	Reflux	5	90	1500	1.96	75
TDP-oda	CHCl ₃	Reflux	10	91	1500	1.52	72
CDP-hda	Dioxane	Reflux	5	93	1200	1.61	83
CDP-eda	Dioxane	60	5	0 ^d	–	–	–
CDP-oda	CHCl ₃	Reflux	20	0 ^d	–	–	–
BPS-hda	Dioxane	Reflux	5	85	1100	1.33	– ^f
BPS-eda	Dioxane	60	5	0 ^{d,e}	–	–	–
BPS-oda	CHCl ₃	Reflux	20	0 ^{d,e}	–	–	–

^aYield of soluble part^bDetermined by SEC using THF as the eluent^cDetermined by ¹H NMR^dInsoluble compound was precipitated^eNo characteristic absorption corresponding to the oxazine ring was observed by IR analysis of the precipitate^fThe signals of the oxazine ring overlapped with signals due to the solvent (Fig. S3 in the Supporting Information)

transparent film. The obtained precursor film was flexible and tough. To control the thickness, the film was pressed between glass plates using a spacer. Gradual thermal curing of the film was performed at 100 and 150 °C for 2 h each under reduced pressure and in a vacuum oven, and then at 200 and 240 °C for 2 h each in an air-circulating oven to give a brown-colored tough **PBPA-hda** film. The other benzoxazines were cured in the same way.

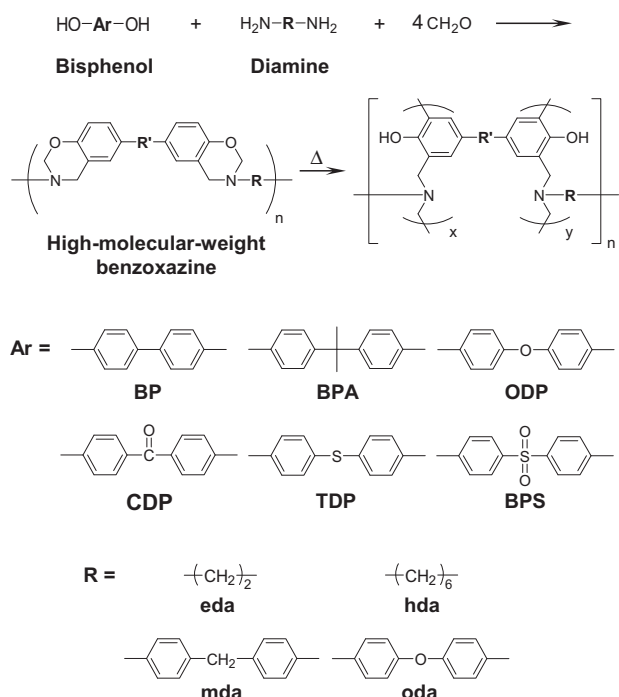
Results and discussion

Synthesis of various high-molecular-weight benzoxazines by combining bisphenol and diamine

The chemical structures of the bisphenols and diamines used in the synthesis of the HMW benzoxazines are shown in Scheme 1. For the bisphenol compounds with different spacers connecting the phenols at the para-position, bisphenol-A (**BPA**), 4,4'-dihydroxybiphenyl (**BP**),

4,4'-oxydiphenol (**ODP**), 4,4'-thiodiphenol (**TDP**), 4,4'-dihydroxybenzophenone (4,4'-carbonyldiphenol, **CDP**), and bisphenol-S (**BPS**) were used. For the diamine compounds, 1,2-ethylenediamine (**eda**) and 1,6-hexanediamine (**hda**) of aliphatic type and 4,4'-methylenedianiline (**mda**) and 4,4'-oxydianiline (**oda**) of aromatic type were used. The Mannich condensation reaction was performed using various combinations of these bisphenols and diamines in organic solvents to synthesize various HMW benzoxazines (Scheme 1). The reaction conditions and yields are summarized in Table 1. The sample code is abbreviated based on the bisphenol and diamine used, such as **BPA-eda**.

When **BPA** was used as the bisphenol compound, the Mannich condensation reaction with the aliphatic diamine proceeded regardless of whether dioxane or chloroform was used as the solvent, and HMW benzoxazines soluble in organic solvents were obtained. On the other hand, when **BPA** was reacted with aromatic diamines, soluble HMW benzoxazines were obtained in chloroform, but an insoluble gel was precipitated as the main product in dioxane.



Scheme 1 Synthesis of polybenzoxazines from high-molecular-weight benzoxazines prepared from various combinations of bisphenols and diamines

Therefore, chloroform was used as the solvent for aromatic diamine.

When bisphenols that have relatively flexible spacers, such as **BPA**, **ODP**, and **TDP**, were used, soluble HMW benzoxazines were obtained in good yields, regardless of which diamine was used. However, when bisphenols that have relatively rigid spacers, such as **BP**, **CDP**, and **BPS**, were used, soluble HMW benzoxazines were obtained only by using **hda** as the diamine compound, and insoluble precipitates were obtained by using **eda** or **oda**. The yield of HMW benzoxazines was higher than 85% except when a rigid bisphenol, such as **BP**, was used. Thus, it was made clear that to obtain soluble HMW benzoxazines, it is necessary to introduce a flexible unit into either the bisphenol or the diamine component, and it is also necessary to appropriately select the solvent for synthesis.

Characterization of high-molecular-weight benzoxazines

The SEC measurement of the HMW benzoxazines using THF as the eluent revealed that the number-average molecular weights (M_n s) were 1000–2000, corresponding to oligomers (Table 1). However, the weight average molecular weights (M_w s) were 5000–20,000 owing to the wide molecular weight distributions. The chemical structure of HMW benzoxazines was confirmed by ^1H

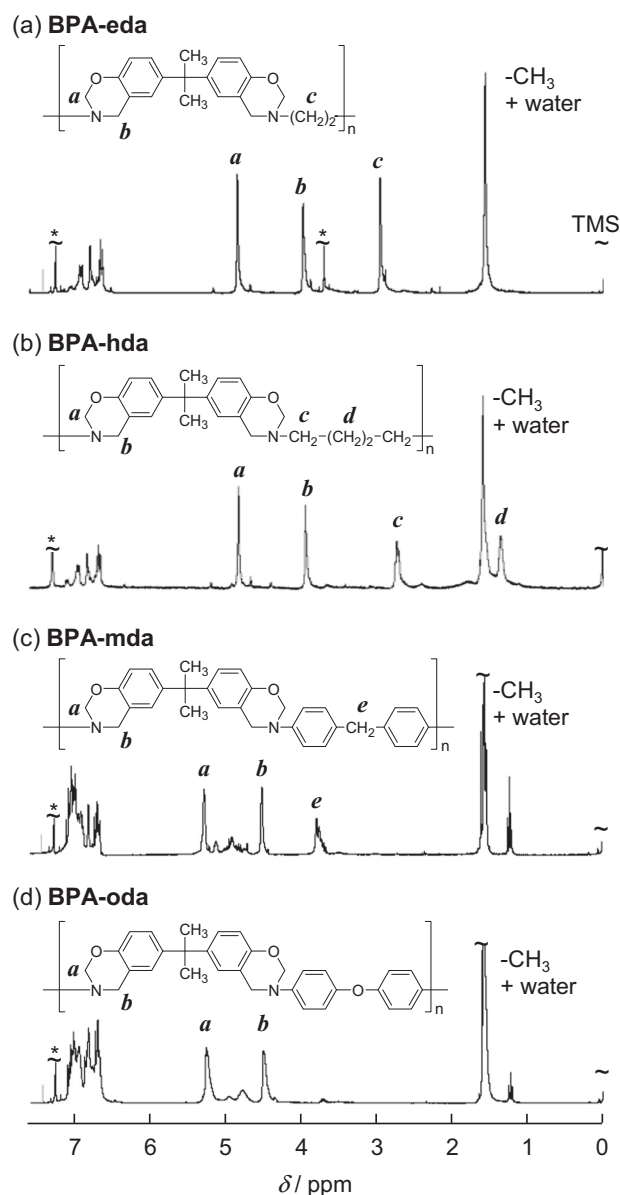


Fig. 1 ^1H NMR spectra of **BPA-eda** (a), **BPA-hda** (b), **BPA-mda** (c), and **BPA-oda** (d) measured in CDCl_3 . The asterisks denote dioxane and chloroform signals

NMR measured in chloroform- d (CDCl_3) or dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$). Fig. 1a shows the ^1H NMR spectrum of **BPA-eda**. The presence of the benzoxazine-ring structure was confirmed by the signals at 4.88 ppm due to O- CH_2 -N (a) and 3.99 ppm due to the Ar- CH_2 -N (b) of the oxazine-ring. The signals due to the methylene protons of the **eda** unit were also observed at 2.98 ppm (c). The integral ratio of the (a) and (c) signals ($A_a/A_c = 380/400$) did not agree with the theoretical value expected from the chemical structure, suggesting that the HMW benzoxazine obtained by Mannich condensation included some defect structures, such as the ring-opened structure

of the benzoxazine unit (Fig. S1 in the Supporting Information), affording phenolic hydroxyl groups [16, 17]. Based on the integration ratio, the ratio of the benzoxazine-ring structure in the chain was estimated to be 95% for **BPA-eda**. The ratios of other HMW benzoxazines are summarized in Table 1. The ratios of HMW benzoxazines obtained from the aliphatic diamines were relatively high (80–95%), while the ratios of HMW benzoxazines obtained from the aromatic diamines tended to be lower (47–75%).

In addition, the chemical shifts of the oxazine-ring signals obtained for **BPA-hda** (4.0 and 4.8 ppm in Fig. 1b) were similar to those of **BPA-eda**. The oxazine-ring signals of **BPA-md** and **BPA-oda** obtained from the aromatic diamines shifted to a lower magnetic field (4.5 and 5.3 ppm, c and d in Fig. 1) than those of **BPA-eda**. This tendency of the oxazine-ring signals to shift was also observed in other HMW benzoxazines (Figs. S2–S4 in the Supporting Information).

The ring-opening polymerization behavior of the HMW benzoxazines was investigated by DSC. Fig. 2 shows some DSC thermograms of the HMW benzoxazines after drying under reduced pressure, together with that of a typical low-molecular-weight benzoxazine, i.e., **B-a** obtained from bisphenol-A and aniline. The DSC curve of **B-a** revealed a sharp exothermic peak corresponding to the ring-opening polymerization of benzoxazine (a in Fig. 2). In contrast, the exothermic peaks of HMW benzoxazines were broadened and shifted toward a lower temperature than that of **B-a** (b–g in Fig. 2). A small amount of the phenolic hydroxyl group of the ring-opened structure might work as an acid catalyst and lower the polymerization temperature.

The solubility of HMW benzoxazines was examined in chloroform, THF, 1,4-dioxane, DMF, and NMP at a concentration of ca. 17 wt%, and the results are summarized in Table 2. The HMW benzoxazines obtained from the relatively flexible bisphenols, **BPA**, **ODP**, and **TDP**, showed high solubilities in the solvents. The solubility tended to decrease when relatively rigid units such as **BP**, **CDP** and **BPS** were introduced. From the result and the boiling point of the solvents, DMF was selected to prepare the precursor film by a cast method.

Preparation and curing of precursor films

DMF solutions of HMW benzoxazines at a concentration of 15 wt% were cast on silane-treated glass plates. The solvent was removed by drying at 50 °C for 10 h under a reduced pressure to give transparent, yellow-colored films. Note that the free-standing tough films were obtained easily, even though the molecular weights were not so high. Such precursor films could not be obtained from typical low-molecular-weight benzoxazine monomers, such as **B-a**.

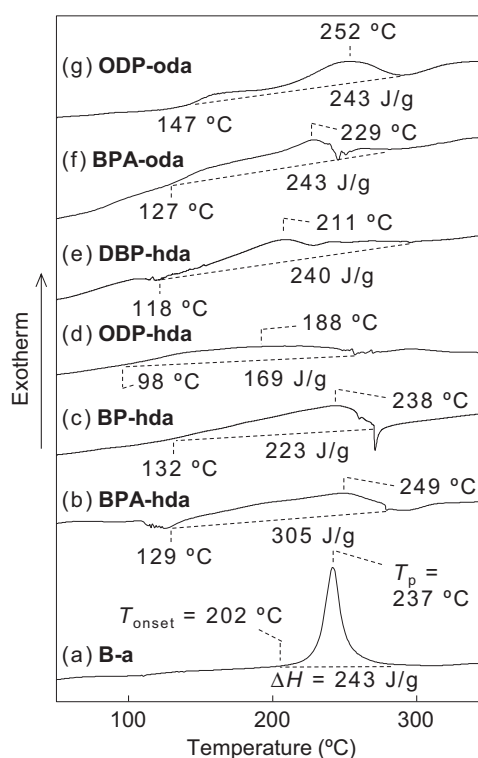


Fig. 2 DSC thermograms of **B-a** (a) and HMW benzoxazines (**b–g**) recorded at a heating rate of 10 °C/min

Table 2 Solubility of HMW benzoxazines in several solvents^a

Code	M_n	CHCl ₃	1,4-dioxane	THF	DMF	NMP
BPA-hda	1700	S	S	S	S	S
BPA-eda	1700	S	S	S	S	S
BPA-md	2100	S	S	S	S	S
BPA-oda	1700	S	S	S	S	S
BP-hda	1500	S ₅₀	S	S	S	S
ODP-hda	1000	S	S	S	S	S
ODP-eda	1500	S	S	S	S	S
ODP-md	2200	S	S	S	S	S
ODP-oda	2000	S	S	S	S	S
TDP-hda	1400	S	S	S	S	S
TDP-eda	2000	S	S	S	S	S
TDP-md	1500	S	S	S	S	S
TDP-oda	1500	S	S	S	S	S
CDP-hda	1200	P	P	P	S ₅₀	S
BPS-hda	1100	P	P	P	P	S

^aThe solubility was examined by adding 2.5 mL of solvent to 0.5 g of the HMW benzoxazines. S: soluble at room temperature, S₅₀: soluble at 50 °C, P: partially soluble at 50 °C

The precursor films were then thermally treated stepwise at 100, 150, 200, and 240 °C for 2 h each. It was confirmed from the DSC measurements of the films that after heat treatment at 240 °C, no exothermic peak was observed,

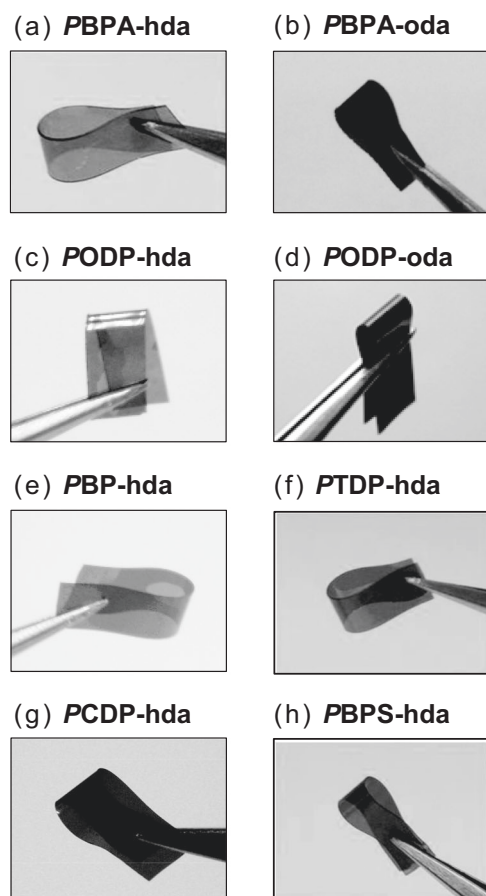


Fig. 3 Appearance of cured HMW benzoxazine films ($3 \times 15 \times 0.07$ mm)

which proves that the temperature was high enough to nearly complete the ring-opening polymerization of benzoxazines (Fig. S5 in the Supporting Information).

After curing at a temperature up to $240\text{ }^{\circ}\text{C}$, the HMW benzoxazine films gave free-standing yellow- to brown-colored transparent polybenzoxazine films (Fig. 3). The polybenzoxazine films were able to bend easily and possessed an extremely improved toughness compared to the typical polybenzoxazine, **PB-a** (Fig. S6 in the Supporting Information). The toughness of the films is described in detail later based on the tensile test results.

The appearance of the cured films is shown in Fig. 3. The **PBPA-hda** film obtained from bisphenol-A and aliphatic diamine was yellow in color (a), while **PBPA-oda** obtained from aromatic diamine was brown (b). Moreover, when **ODP** was used as the bisphenol component, the film obtained from the aromatic diamine, **PODP-oda**, was darker in color (d) than the film obtained using aliphatic diamine (c). The coloring of the film tended to become darker as the aromatic content increased.

Mechanical properties of polybenzoxazines prepared from HMW benzoxazines

The mechanical properties of the polybenzoxazines were investigated by tensile testing of the films. The stress-strain curves are shown in Fig. 4, and the results are summarized in Table 3. The typical polybenzoxazine film, **PB-a**, showed a high tensile modulus ($E = 3.3$ GPa) but low tensile strength ($s_b = 37$ MPa) and elongation at break ($e_b = 1.6\%$), consistent with the brittleness of the film (Fig. 4A). On the other hand, all the polybenzoxazine films obtained from the HMW benzoxazines revealed significantly higher elongation at break than **PB-a** accompanied by an increase in tensile strength, showing that the HMW benzoxazines gave tough and flexible polybenzoxazine films.

To evaluate the effect of the bisphenol structure, the stress-strain curves of polybenzoxazine films obtained by using **hda** with various bisphenols are shown in Fig. 4A. Compared with **PB-a**, the **PBPA-hda** film obtained from bisphenol-A showed a higher tensile strength of 80 MPa and elongation at break of 3.7%. The slight decrease in the tensile modulus of **PBPA-hda** ($E = 2.5$ GPa) compared with that of **PB-a** was attributed to the long aliphatic diamine unit. The other polybenzoxazines shown in Fig. 4A have relatively rigid bisphenol units, and the tensile modulus was improved to 2.8–3.2 GPa without sacrificing the tensile strength and elongation at break.

To evaluate the effect of diamine components, Fig. 4B shows the stress-strain curves of the HMW polybenzoxazines in which bisphenol-A (**BPA**) was fixed as the bisphenol unit and various diamines were used. Among the films, **PBPA-hda** showed the lowest modulus (2.5 GPa) and a high elongation at break (3.7%) because of the long flexible aliphatic **hda** unit. On the other hand, **PBPA-eda** showed the highest tensile modulus (4.0 GPa) and lowest elongation at break (2.1%) because of the short **eda** unit that makes the film relatively rigid. The **PBPA-mda** and **PBPA-oda** films obtained from aromatic diamines showed higher tensile strength and elongation at break than the films obtained from aliphatic diamines. In particular, the use of **ODA** gives the toughest and most flexible films, as evidenced by its having the highest tensile strength (108 MPa) and elongation at break (4.1%). One possible reason for the high toughness of the films composed of aromatic diamines may be the low ratio of ring-closed structures in the HMW benzoxazine chain, as suggested by the ^1H NMR analysis. Another possible reason is that the basicity of the aromatic diamines is weaker than that of the aliphatic diamines, leading to weaker intramolecular hydrogen bonding between the nitrogen of the amine and phenolic hydroxyl group and thus increasing the concentration of the intermolecularly hydrogen bonded species. It is considered that the moderately increased intermolecular

Fig. 4 Stress-strain curves of a **PB-a** film and the polybenzoxazine films obtained from HMW benzoxazines. **a** Influence of the bisphenol unit while fixing the diamine as 1,6-hexanediamine (**hda**). **b** Influence of the diamine unit while fixing the bisphenol as bisphenol-A (**BPA**). **c** Influence of the diamine unit while fixing the bisphenol as 4,4'-oxydiphenol (**ODP**)

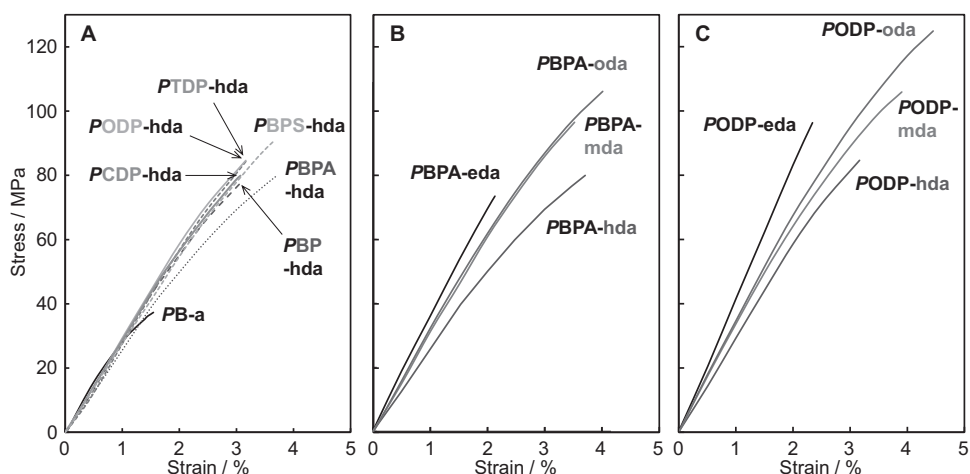


Table 3 Tensile properties of polybenzoxazine films

Code	Modulus GPa	Strength MPa	Elongation at break %
PB-a	3.3	37	1.6
PBPA-hda	2.5	80	3.7
PBPA-eda	4.0	97	2.1
PBPA-mda	3.1	97	3.5
PBPA-oda	3.4	108	4.1
PBP-hda	2.8	77	3.1
PODP-hda	3.0	85	3.2
PODP-eda	4.6	97	2.4
PODP-mda	3.5	106	3.9
PODP-oda	3.7	125	4.5
PTDP-hda	3.1	84	3.1
PCDP-hda	3.2	80	3.1
PBPS-hda	3.0	91	3.7

interaction leads to an increase in the physical crosslinks that make the films tough.

Based on the above results showing that the use of **oda**-containing ether linkage as the diamine unit gave the toughest and most flexible cured films, **ODP**, which also contains an ether linkage, was selected as the bisphenol unit and combined with various diamines. The stress-strain curves are shown in Fig. 4C. The four stress-strain curves in Fig. 4B and 4C look very similar, showing that the tendency of diamines found in the case of **PBPA** is the same as that found in the case of **PODP**. Among the HMW polybenzoxazine films prepared in this study, the **PODP-eda** film showed the highest tensile modulus ($E = 4.6$ GPa), but the tensile strength and elongation at break were not so high. In contrast, the **PODP-oda** film showed the highest tensile strength ($\sigma_b = 125$ MPa) and elongation at break ($\epsilon_b = 4.5\%$) and a high tensile modulus (3.7 GPa), showing that this film was the toughest among

the films examined. Note that both **ODP** and **oda** contain ether linkages.

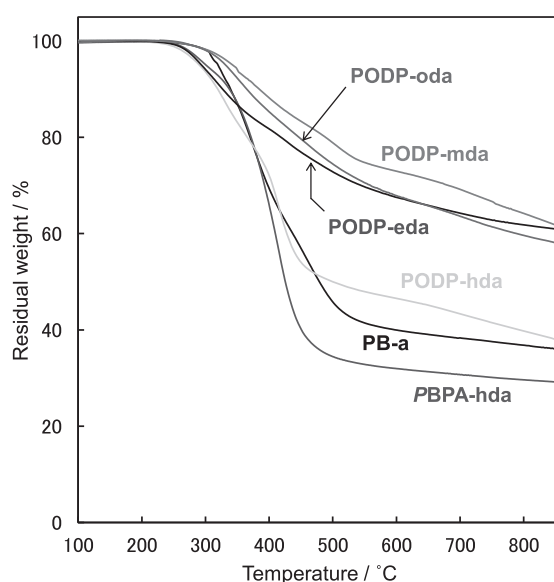
The toughening effect of the ether linkages has been observed in various polymers. In the case of polyimide, the completely rigid-rod polyimide, PI(PMDA/PDA), which can be prepared from pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (PDA), was expected to give films with a very high modulus because of the rigidity of the molecular structure. However, PI(PMDA/PDA) was found to be very brittle and almost impossible to handle as a film [27]. However, by introducing ether linkages, for example, into diamine by using **oda**, the resultant PI(PMDA/ODA) gives surprisingly tough polyimide films with an elongation at break as high as 80–100% [28]. Therefore, PI(PMDA/ODA) films are currently one of the most important commercially available polyimide films.

Thermal stability of polybenzoxazines prepared from HMW benzoxazines

The thermal stability of HMW polybenzoxazine and **PB-a** films was evaluated by TGA under an argon atmosphere, and the 5% weight loss temperature (T_{d5}) and char yield at 850 °C (CY_{850}) are summarized in Table 4. The T_{d5} and CY_{850} of **PB-a** were 301 °C and 42%, respectively. The observed T_{d5} value was consistent with a previous report in which the decomposition and elimination of the amine moiety (aniline unit) occurred at ~300 °C in the initial stage of the thermal decomposition of **PB-a** [29, 30]. In the HMW polybenzoxazines, the diamine moiety is incorporated into the network structure, and a high-temperature shift in the thermal decomposition temperature, such as T_{d5} , is expected. Actually, as shown in the TGA curves (Fig. 5), higher decomposition temperatures were achieved for HMW polybenzoxazines. The exceptions are polybenzoxazines that contain aliphatic diamines (**hda** and **eda**).

Table 4 TGA results of polybenzoxazine films

Code	T_{d5} °C	Char yield at 850 °C %
PB-a	301	42
PBPA-hda	301	29
PBP-hda	306	38
PODP-hda	302	44
PODP-eda	294	61
PODP-mda	342	62
PODP-oda	332	58
PTDP-hda	285	38
PCDP-hda	289	44
PBPS-hda	318	46

**Fig. 5** TGA curves of **PB-a** and polybenzoxazines obtained from HMW benzoxazines measured under an argon atmosphere at a heating rate of 5 °C/min

The effect of the diamine moiety was examined by fixing the bisphenol as **BPA** and using various diamines. It was clearly shown that the use of aliphatic diamines gave lower T_{d5} values, i.e., 301 °C (**hda**) and 285 °C (**eda**), and the use of aromatic diamines gave higher T_{d5} values, i.e., 336 °C (**mda**) and 323 °C (**oda**). The same trend was also observed for CY_{850} ; the use of aliphatic diamines gave lower CY_{850} values, i.e., 29% (**hda**) and 36% (**eda**), and the use of aromatic diamines gave higher CY_{850} values, i.e., 51% (**mda**) and 48% (**oda**). This result indicates that the use of aromatic diamines gives polybenzoxazines with much better thermal stability than those given by the use of aliphatic diamines.

The effect of bisphenols was also examined. Although the effect was not as clear among the bisphenols employed in this study, a difference in CY_{850} was observed. The CY_{850} of polybenzoxazine was the lowest when **BPA**

containing the aliphatic moiety was used as the bisphenol; the CY_{850} of **PBPA-hda** was 29%. However, when bisphenols that do not contain the aliphatic moiety were used, even when using **hda** as the diamine, CY_{850} increased to 38% for **PBP-hda** and **PTDP-hda**, 44% for **PODP-hda** and **PCDP-hda**, and 46% for **PBPS-hda**. The difference also suggests that higher CY_{850} values can be achieved by using bisphenols that do not contain the aliphatic moiety.

It can be concluded that among the HMW polybenzoxazines, **PODP-mda** ($T_{d5} = 342$ °C, $CY_{850} = 61\%$) and **PODP-oda** ($T_{d5} = 332$ °C, $CY_{850} = 62\%$) had excellent thermal stability, giving processable and tough polybenzoxazine films. The reason for this is that the amine and bisphenol moieties were incorporated into the network structure of polybenzoxazine through thermally stable aromatic structures. On the basis of the CY_{850} values, the limiting oxygen index (LOI) of the **PODP-mda** and **PODP-oda** films was estimated to be 42 [31], suggesting that the films had good flame retardancy.

Conclusions

We synthesized various soluble HMW benzoxazines via the Mannich reaction with various combinations of bisphenols and diamines and investigated the structure-property relationship of the polybenzoxazine films derived from the HMW benzoxazines. Free-standing and tough precursor films were easily obtained by casting DMF solutions of HMW benzoxazines on glass plates. By thermally curing the precursor films at temperatures up to 240 °C, transparent and very tough polybenzoxazine films were fabricated. In the tensile test, the polybenzoxazine films showed remarkably higher tensile strength and larger elongation at break than **PB-a**. Comparing the chemical structures shows that the influence of the diamine moiety was greater than that of the bisphenol moiety on the mechanical properties, and the HMW polybenzoxazines composed of aromatic diamines showed higher tensile strength and elongation at break than those composed of aliphatic diamines. In particular, among the HMW polybenzoxazines presented in this study, **PODP-oda** with ether linkages in both bisphenol and diamine units showed remarkably good mechanical properties ($E = 3.7$ GPa, $s_b = 125$ MPa, $e_b = 4.5\%$) as a highly cross-linked thermoset. We would like to emphasize that the introduction of ether linkages in the main chain of HMW benzoxazines is extremely effective for the toughening of polybenzoxazine films. Moreover, the HMW polybenzoxazines composed of aromatic moieties showed good thermal stability: $T_{d5} = 332$ °C and $CY_{850} = 58\%$ for **PODP-oda**. Bisphenol and diamine compounds are raw materials that can be used for various organic compounds, including polymer materials, and are widely used in industry. We reported here that HMW benzoxazines can be tailored

with various combinations of bisphenols and diamines and that the properties of their thermosets can be tuned for different applications. Therefore, the polybenzoxazines derived from HMW benzoxazines can be good candidates for various applications, including for use as matrix resins of advanced composite materials, adhesive films, precision machinery parts, and microelectronics, because of their outstanding mechanical and thermal properties.

Acknowledgements TK acknowledges financial support from the Ryukoku University Science and Technology Fund.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

- Ishida H, Froimowicz P. Advanced and emerging polybenzoxazine science and technology. Amsterdam: Elsevier; 2017.
- Ishida H, Agag T. Handbook of benzoxazine resins. Amsterdam: Elsevier; 2011.
- Ning H, Ishida H. Phenolic materials via ring-opening polymerization: synthesis and characterization of bisphenol-A based benzoxazines and their polymers. *J Polym Sci Part A Polym Chem*. 1994;32:1121–9.
- Ishida H, Allen DJ. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci Part B Polym Phys*. 1996;34:1019–30.
- Shen SB, Ishida H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. *J Appl Polym Sci*. 1996;34:1595–605.
- Takeichi T, Agag T, Yong G. Synthesis and properties of polybenzoxazine based composites. *Recent Res Devel Polym Sci*. 2000;4:85–105.
- Su Y-C, Chang F-C. Synthesis and characterization of fluorinated polybenzoxazine material with low dielectric constant. *Polymer*. 2003;44:7989–96.
- Ardhyananta H, Wahid MH, Sasaki M, Agag T, Kawauchi T, Ismail H, et al. Performance enhancement of polybenzoxazine by hybridization with polysiloxane. *Polymer*. 2008;49:4585–91.
- Ardhyananta H, Kawauchi T, Ismail H, Takeichi T. Effect of pendant group of polysiloxanes on the thermal and mechanical properties of polybenzoxazine hybrids. *Polymer*. 2009;50:5959–69.
- Ardhyananta H, Kawauchi T, Takeichi T, Ismail H. Preparation and properties of polybenzoxazine/poly(dimethylsiloxane-co-diphenylsiloxane) hybrids as high performance polymers. *High Perform Polym*. 2010;22:609.
- Takeichi T, Agag T, Zeidam R. Preparation and properties of polybenzoxazine/poly(imide-siloxane) alloys: In situ ring-opening polymerization of benzoxazine in the presence of soluble poly(imide-siloxane)s. *J Polym Sci Part A Polym Chem*. 2001;39:2633–41.
- Jang J, Seo D. Performance improvement of rubber-modified polybenzoxazine. *J Appl Polym Sci*. 1998;67:1–10.
- Suwitaningsih DN, Katsuta S, Kawauchi T, Furukawa N, Takeichi T. Preparation and characterization of liquid rubber-modified polybenzoxazine. *J Photopolym Sci Technol*. 2015;28:137–43.
- Allen DJ, Ishida H. Physical and mechanical properties of flexible polybenzoxazine resins: effect of aliphatic diamine chain length. *J Appl Polym Sci*. 2006;101:2798–809.
- Baranek AD, Kendrick LL, Narayanan J, Tyson GE, Wand S, Patton DL. Flexible aliphatic-bridged bisphenol-based polybenzoxazines. *Polym Chem*. 2012;3:2892–900.
- Takeichi T, Kano T, Agag T. Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets. *Polymer*. 2005;46:12172–80.
- Takeichi T, Kano T, Agag T, Kawauchi T, Furukawa N. Preparation of high molecular weight polybenzoxazine prepolymers containing siloxane units and properties of their thermosets. *J Polym Sci Part A Polym Chem*. 2010;48:5945–52.
- Chernykh A, Liu J-P, Ishida H. Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain. *Polymer*. 2006;47:7664–9.
- Takeichi T, Uchida S, Inoue Y, Kawauchi T, Furukawa N. Preparation and properties of polymer alloys consisting of high-molecular-weight benzoxazine and bismaleimide. *High Perform Polym*. 2013;26:265–73.
- Uchida S, Kawauchi T, Furukawa N, Takeichi T. Polymer alloys of high-molecular-weight benzoxazine and epoxy resin. *High Perform Polym*. 2014;26:846–55.
- Ohara M, Yoshimoto K, Kawauchi T, Takeichi T. Synthesis of high-molecular-weight benzoxazines having azomethine linkages in the main-chain and the properties of their thermosetting resins. *Polymer*. 2020;202:122668.
- Nagai A, Kamei Y, Wang X-S, Omura M, Sudo A, Nishida H, et al. Synthesis and crosslinking behavior of a novel linear polymer bearing 1,2,3-triazol the main chain by and benzoxazine groups in a step-growth click-coupling reaction. *J Polym Sci Part A Polym Chem*. 2008;46:2316–25.
- Chernykh A, Agag T, Ishida H. Synthesis of linear polymers containing benzoxazine moieties in the main chain with high molecular design versatility via click reaction. *Polymer*. 2009;50:382–90.
- Liu Y-L, Chou C-I. High performance benzoxazine monomers and polymers containing furan groups. *J Polym Sci Part A Polym Chem*. 2005;43:5267–82.
- Chou C-I, Liu Y-L. High performance thermosets from a curable Diels-Alder polymer possessing benzoxazine group in the main chain. *J Polym Sci Part A Polym Chem*. 2008;46:6509–17.
- Kiskan B, Aydogan B, Yagci Y. Synthesis, characterization, and thermally activated curing of oligosiloxanes containing benzoxazine moieties in the main chain. *J Polym Sci Part A Polym Chem*. 2009;47:804–11.
- Takeichi T, Endo Y, Kaburagi Y, Hishiyama Y, Inagaki M. Carbonization and graphitization of polyimide films: effect of size of leaving group at imidization. *J Appl Polym Sci*. 1998;68:1613–20.
- Shirai Y, Takahashi K, Kawauchi T, Takeichi T. Preparation and properties of polyimide-polysiloxane hybrids using sol-gel method. *J Photopolym Sci Technol*. 2013;26:333–40.
- Low H-Y, Ishida H. Mechanistic study on the thermal decomposition of polybenzoxazines: effects of aliphatic amines. *J Polym Sci Part B Polym Phys*. 1998;36:1935–46.
- Low H-Y, Ishida H. Structural effects of phenols on the thermal and thermo-oxidative degradation of polybenzoxazines. *Polymer*. 1999;40:4365–76.
- van Krevelen DW. Some basic aspects of flame resistance of polymeric materials. *Polymer*. 1975;16:615–20.