Functional 1,3-Benzoxazine Bearing 4-Pyridyl Group: Synthesis and Thermally Induced Polymerization Behavior

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ABSTRACT: 1,3-benzoxazine **1**, bearing 4-pyridyl moiety on the nitrogen atom, was synthesized from *p*-cresol, 4-aminopyridine, and paraformaldehyde. The efficient synthesis was achieved by adding acetic acid to suppress the strong basicity caused by the presence of 4-aminopyridine derivatives. Upon heating **1** at 180 °C, it underwent the thermally induced ring-opening polymerization. The resulting polymer was composed of two types of repeating unit, i.e., (1) Mannich-type one (-phenol-CH_2-NR-CH_2-) that can be expected from the general ring-opening polymerization of conventional benzoxazines and (2) a typical phenolic resin-type one (-phenol-CH_2-phenol-) induced by release of 4-aminopyridine and paraformaldehyde (unit B). Another structural feature of the polymer was that it possessed a benzoxazine moiety at the chain end. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 410–416

KEYWORDS: benzoxazine; heteroatom-containing polymer; metal-polymer complexes; ring-opening polymerization; structure

INTRODUCTION 1,3-benzoxazines have received considerable attention because of their promising practical applications as monomers for high performance materials.[1–3] Their facile and versatile synthesis from relatively abundant materials involving phenols, amines, and formaldehyde is also greatly advantageous from the viewpoint of development of various benzoxazines bearing functional groups.[4–22] Some of these functional groups serve as reactive sites to increase the crosslinking degree so that the thermal and mechanical properties of the obtained poly(benzoxazine)s can fulfill specific requirements.

Another interesting topic in the field of the utilization of functionalized 1,3-benzoxazine monomers is their combination with inorganic materials to fabricate nanocomposites. In these works, the attractive interaction between polar functional groups and inorganic surfaces has been effectively exploited. For example, Yagci et al. have demonstrated the surface functionalization of nanoparticles of magnetite with a benzoxazine bearing carboxyl moiety.[23] Recently, Yagci's group and we collaborated to develop a polybenzoxazine/montmorillonite nanocomposite, where a new benzoxazine bearing 4-pyridyl moiety **1** was used as a key material.[24]

Herein, we report the details of the synthesis of benzoxazine **1**, which possesses 4-pyridyl moiety on the nitrogen atom in the benzoxazine ring, and its thermally induced ring-opening polymerization behavior. Although analogous benzoxazines and naphthoxazines bearing pyridyl moieties have been reported, their polymerization behaviors have been not reported[25–29]. In addition, the ability of the resulting polymer **2** to capture some metal ions such as $Cu^{2+}$and Co^{2+} is also described.

EXPERIMENTAL

Materials

The materials included 4-aminopyridine, purchased from Tokyo Chemical Industry Co. Ltd. Paraformaldehyde and acetic acid were purchased from Kanto Kagaku Co. *p*-Cresol, toluene, cobalt(II) sulfate hepta-hydrate, and copper(II) sulfate penta-hydrate were purchased from Wako Pure Chemical Industries. All materials were used without any further purification. *N*-Phenyl-1,3-benzoxazine **3** was prepared from according to the reported procedure.[30–32]

Measurements

^{1}H NMR spectra were recorded in either chloroform-*d* ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) on a Varian UNITY-INOVA400 (^{1}H, 400 MHz) spectrometer, with tetramethylsilane (TMS) as an internal standard. Melting point was measured by Yanako MP-500D. Number-average molecular

Additional Supporting Information may be found in the online version of this article.

weight (M_n) was estimated by size exclusion column chromatography (SEC) on a Tosoh HLC-8220GPC system, equipped with three consecutive polystyrene gelcolumns (AM4000, AM3000 and AM2500, molecular weight ranges: 1,000,000–500 Da) and refractive index (RI) and ultraviolet (UV, $\lambda = 254$ nm) detectors, using DMF as a eluent and flow rate was 1.0 mL/min. This system was calibrated with polystyrene standards.

Synthesis of 6-methyl-3-(pyridin-4-yl)-3,4-dihydro-2H-1,3-benzoxazine (1)

In a 100-mL round-bottomed flask equipped with a Dean-Stark apparatus, 4-aminopyridine (9.40 g, 100 mmol), *p*-cresol (10.8 g, 100 mmol), acetic acid (6.00 g, 100 mmol), paraformaldehyde (6.00 g, 200 mmol) and 2-methoxyethanol (10 mL) were added in toluene (50 mL) and the mixture was heated under reflux for 14 h with addition of 3.00 g of paraformaldehyde every 2 h. The reaction mixture was cooled to room temperature and washed with 100 mL of 1.5 M NaOH aq. and 100 mL of brine three times each. After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was fractionated by the column chromatography (eluent: acetone) to obtain crude **1**. Crude **1** was further purified by recrystallization from a mixture of acetone and *n*-hexane (volume ratio= 1: 4) to obtain pure **1** (14.7 g, 65 mmol, 65%): mp 136–137 °C.

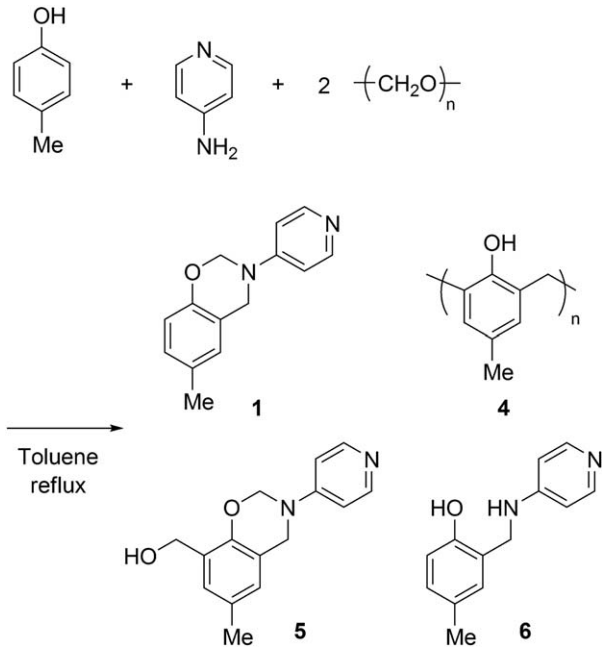
^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ, ppm; 2.26 (s, 3H, CH_3-), 4.60 (s, 2H, Ph-CH_2-N), 5.33(s, N-CH_2-O), 6.73-6.95 (5H, 3,5,6-position H of Ph and 3,5-position H of pyridine), 8.33 (dd, 2H, 2,6-position H of pyridine). ^{13}C NMR (in $CDCl_3$, at 20 °C): 20.8 (*C* H_3-), 48.3 (Ph-*C* H_2-N), 76.3 (N-*C* H_2-O), 110.2, 117.2, 120.0, 127.3, 129.1, 131.0, 150.9, 152.1, and 153.4 (aromatic part). Anal. calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.04; H, 6.12; N, 12.35.

Thermally Induced Ring-Opening Polymerization of 1

Five hundred milligrams each of **1** were taken and each of them was placed in a test tube. Nitrogen inlets were attached to the test tubes and then they were heated in an oil bath at 180 °C. From time to time, these test tubes were taken away from the oil bath one-by-one, and each of the mixture was analyzed by ^{1}H NMR to determine conversions of **1** and the unit ratio. The product obtained by heating the monomer for 14 h was dissolved in DMF, and the solution was poured into ethyl acetate. The resulting precipitate was collected by filtration and was dried *in vacuo* to give corresponding polymer **2a** (180 mg, 36%). In a similar way, the product obtained by heating the monomer for 36 h was treated to obtain polymer **2b** (135 mg, 27%).

Metal ion-Capturing

Two hundred seventy milligrams of **2a** was dissolved in DMF (60 mL) to obtain Solution A. $CuSO_4{\cdot}5H_2O$ (50.0 mg, 0.2 mmol) and $CoSO_4{\cdot}7H_2O$ (56.2 mg, 0.2 mmol) were dissolved into a mixture of deionized water (5 mL) and methanol (15 mL) to obtain Solution B, respectively. Solution A (1 mL) was poured into solution B (1 mL) and stirred for 1 min. The corresponding metal-polymer complexes were precipitated.



SCHEME 1 Synthesis of benzoxazine **1** bearing 4-pyridyl moiety.

RESULT AND DISCUSSION

Synthesis of Benzoxazine Bearing 4-Pyridyl Group

With employing *p*-cresol, 4-aminopyridine, and paraformaldehyde as the starting materials, we surveyed reaction conditions for efficient synthesis of benzoxazine **1** (Scheme 1). Its yields were estimated by ^{1}H-NMR analysis of the reaction mixtures, and the resulting time-yield relationships are shown in Figure 1. The conditions and the corresponding results are summarized in Table 1.

First, we attempted to synthesize **1** by a standard method, i.e., heating a mixture of *p*-cresol, in refluxing toluene (entry 1). The reaction became sluggish, giving a yellow viscous substance insoluble in toluene. Since it was highly polar according to TLC analysis, we speculated that the viscous product was a resol-type condensate **4**, of which formation was promoted by highly basic 4-aminopyridine and its derivatives. As shown in Figure 1, the NMR yield of **1** reached ca. 25% at 27 h. Prolonging the reaction time was not effective to improve the yield. In addition, a benzoxazine bearing hydroxymethyl group **5** was isolated from the reaction mixture in 12% as a byproduct. ^{1}H and ^{13}C NMR of **5** are shown in Figure S1 in Supporting Information. Some plausible mechanisms for the formation of **5** that involve base-catalyzed hydroxymethylation of *p*-cresol and that of the *p*-cresol-derived benzoxazine **1** are shown in Scheme 2.

To suppress these base-catalyzed side reactions, we next attempted addition of acetic acid (entry 2). As shown in Figure 1, the formation of **1** was slightly accelerated. More

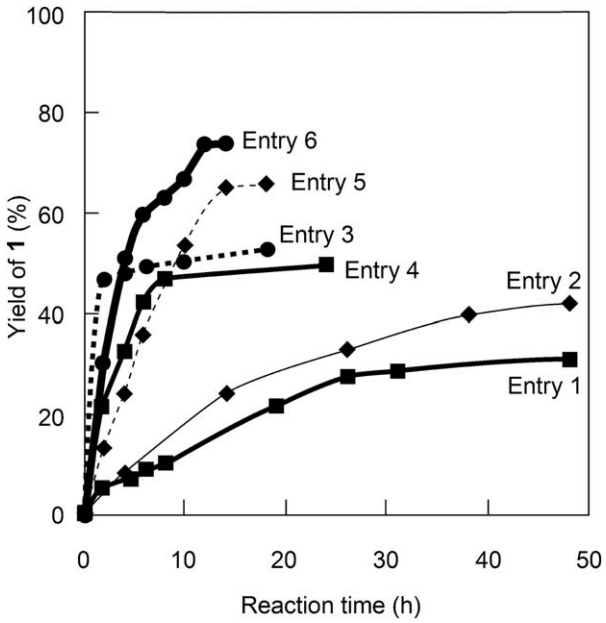
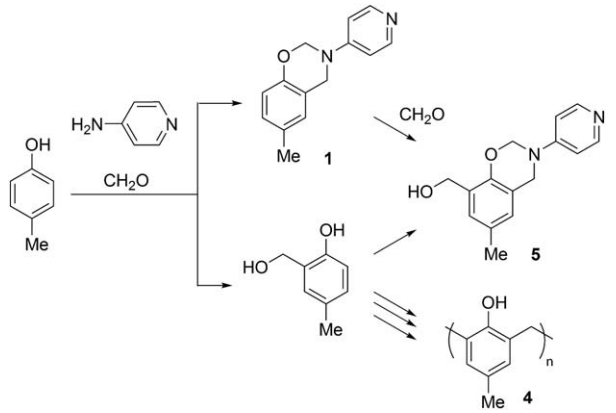


FIGURE 1 Time-dependences of ^{1}H NMR yield of **1**.

remarkably, the formation of the yellow viscous substance was completely suppressed. In addition, the byproduct **5** was not detected in the ^{1}H-NMR analysis of the mixture (Fig. 2).

Upon confirming the remarkable addition effects of acetic acid, we continued further optimization of the conditions. In entry 3, a Dean-Stark apparatus was used for azeotropic removal of water formed during the reaction. As a result, the formation of **1** was significantly accelerated so that its yield reached 50% within 10 h. However, the final yield of **1** after the reaction for 18 h was not satisfactory yet. In this case, a white viscous precipitate formed. TLC analysis of the precipitate revealed that it was a mixture of highly polar compounds. ^{1}H-NMR analysis of the precipitate suggested that the major component of the mixture was an aminomethylated cresol derivative **6** formed by condensation of *p*-cresol, formaldehyde, and 4-aminopyridine, of which further cyclocondensation with formaldehyde gives **1**. Due to the presence of acetic acid, the pyridylamino part would be neutralized and thus converted to a more polar and less soluble salt form, preventing the reaction of **6** with formaldehyde to give **1**.



SCHEME 2 Plausible mechanisms for the formation of byproducts.

For the purpose of preventing the precipitation of the intermediate **6**, 2-methoxyethanol was added as a co-solvent (entry 4). This alcohol was employed because it is enough polar and is less volatile not to be removed from the system during the azeotropic removal of water was added. However, as shown in Figure 1, the rate of formation of **1** was decelerated contrary to our expectation. What we observed in this case was serious sublimation of paraformaldehyde on the condenser. This problem was solved by adding paraformaldehyde in several portions every 2 h (entry 5). Further improvement of the yield of **1** was achieved in entry 6, where the initial concentrations of *p*-cresol and 4-aminopyridine were 10 times larger than those in entry 5. By recrystallization, **1** was isolated as a colorless crystal in 65%.

Besides, we examined another route for the target benzoxazine **1**, which relied on the transformation of 4-aminopyridine into the corresponding triazine derivative and its use. Recently this "triazine-route" has been successfully

TABLE 1 Synthesis of *N*-(4-Pyridyl) 1,3-Benzoxazine[a]

Entry	*p*-Cresol (mmol)	4-Aminopyridine (mmol)	Paraformaldehyde (mmol)	Toluene (mL)	AcOH (mmol)	Dean-Stark apparatus	2-Methoxyethanol (mL)	Reaction time (h)	Yield[b] (%)
1	10	10	20	50	0	Not used	0	48	31 (8[c])
2	10	10	20	50	10	Not used	0	48	42 (30[c])
3	10	10	20	50	10	Used	0	18	53
4	10	10	20	50	10	Used	5	24	50
5	10	10	140	50	10	Used	5	14	66 (52[c])
6	100	100	700	50	100	Used	10	12	73 (65[c])

[a] Temp.: reflux.
[b] Yield estimated by ^{1}H NMR.
[c] Isolated yield.

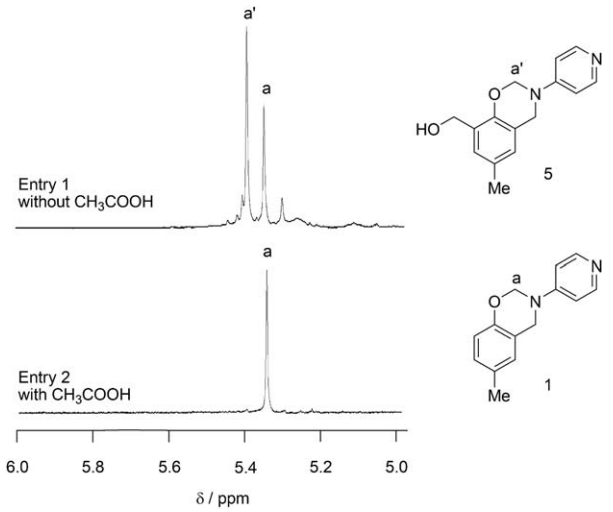


FIGURE 2 ^{1}H NMR spectra of the reaction mixtures (Entries 1 and 2).

applied to the efficient synthesis of benzoxazines.[33] Accordingly, we attempted to synthesize the triazine with varying reaction conditions such as solvent, temperature, and concentration; however, under all the conditions we surveyed, the triazine was not obtained. Instead, the product we got was (4-Py)-NH-CH_2-NH-(4-Py), the 2:1 adduct of 4-aminopyridine and formaldehyde. This adduct was insoluble in all the solvents we examined and this insoluble nature prevented its further reactions.

Benzoxazine **1** was soluble in acetone, ethyl acetate, chloroform, toluene, DMSO and DMF, and was insoluble in *n*-hexane. Figure 3 shows the ^{1}H and ^{13}C NMR spectra of **1**. All the signals, which involve two singlet ones at 4.6 and 5.3 ppm for the two methylene groups in the benzoxazine ring, were successfully assigned. The singlet signal at 8.33 ppm was also assigned for 2,6-position protons of pyridine. The

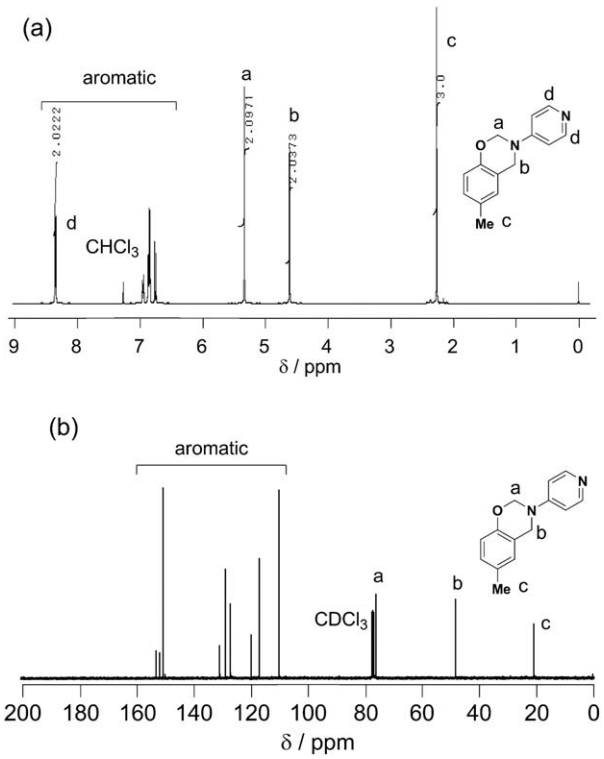
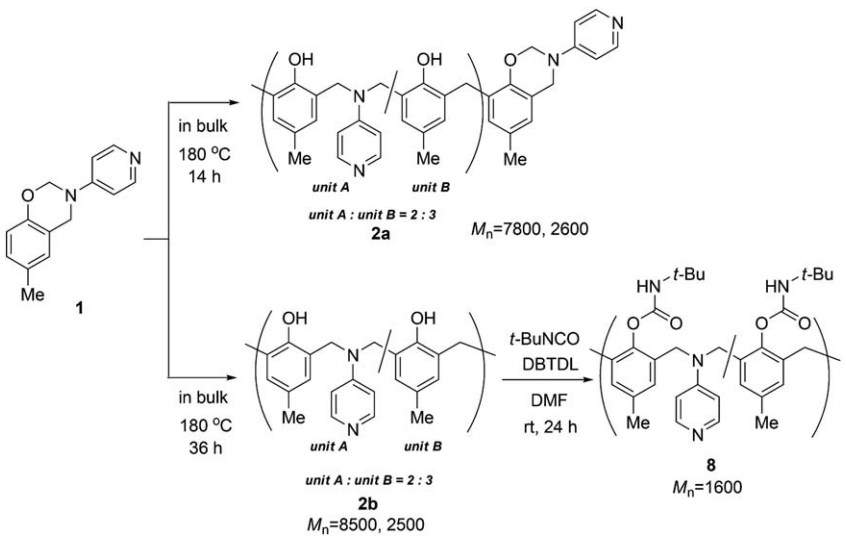


FIGURE 3 ^{1}H and ^{13}C NMR spectra of **1**.

^{13}C NMR spectrum also supported the chemical structure of **1**. The two signals at 76.3 and 48.3 ppm were attributable for the two methylene groups in the benzoxazine ring.

Thermally Induced Polymerization of 1

The thermally induced polymerization of **1** was examined at 180 °C (Scheme 3). As a referential experiment, the thermally induced polymerization of *N*-phenyl-1,3-benzoxazine **3** was also performed under the same conditions. The corresponding time-dependences of monomer conversion are



SCHEME 3 Thermally induced polymerization of **1**.

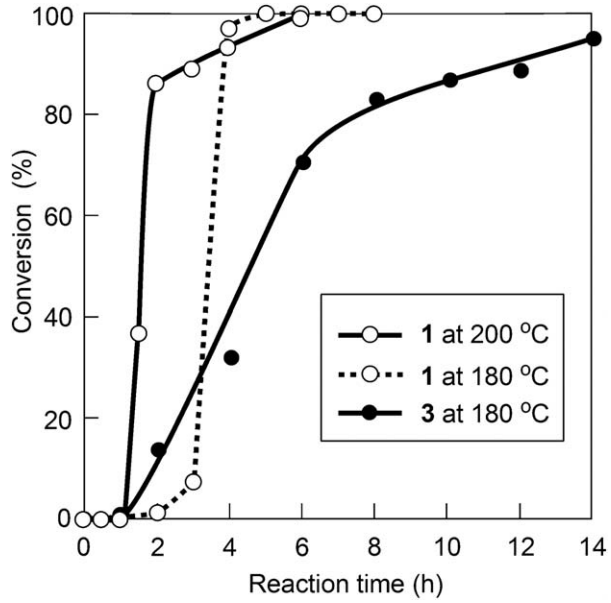


FIGURE 4 Time-dependence of conversion of **1** and that of conversion of **3** in their thermally induced polymerizations at 180 °C.

shown in Figure 4. The consumption rate of **1** was much smaller than that of **3**, suggesting that the electron-withdrawing nature of the 4-pyridyl group affected the polymerization ability of benzoxazine negatively. Such retardation of polymerization by introducing electron-deficient aromatic groups such as 4-chlorophenyl and 4-nitrophenyl groups has been reported.[34]

By heating **1** at 180 °C for 14 h, more than 90% of **1** was consumed. The resulting polymer **2a** was isolated by precipitation from ethyl acetate and then purified by repeating the same precipitation procedure. Figure 5 shows the ^{1}H NMR spectrum of **2a**, which clarified the following structural characteristics of **2a**: (a) The smaller content of pyridyl group than that expected from the standard ring-opening polymerization of benzoxazines without side reactions and (b) the presence of benzoxazine ring at the chain end. The unexpectedly smaller content of pyridyl group was clarified by comparing the integrated intensity of the signals attributable to the pyridyl group at around 8 ppm with that of a broad signal attributable to the methyl group at around 2 ppm. On the other hand, the presence of benzoxazine ring at the chain end was suggested by the presence of two signals at 4.6 and 5.3 ppm, which were attributable to the two methylene groups in the benzoxazine ring. These signals were not observed in the spectrum of polymer **2b**, which was obtained by heating polymer **2a** at 180 °C for 22 h, suggesting that the benzoxazine ring at the terminal of **2a** was consumed by its thermally induced ring-opening reaction. The content of the pyridyl group did not change during this post heating process.

Along with the small content of pyridyl moiety in **2**, a correspondingly small content of the methylene linkages was also suggested by the NMR spectrum. If the polymer **2b** is solely composed of unit A, -cresol-CH_2-N(4-pyridyl)-CH_2-cresol- that can be formed by the standard ring-opening polymerization of benzoxazines, the ratio between the intensity of the signal attributable to the methylene linkages and that of the signal attributable to the methyl groups should be 4:3. However, the ratio estimated by analyzing the spectrum was 1.8:3. From the synchronous lacks of the pyridyl and methylene moieties, we deduced that the polymer contained unit B, a cresol-novolac-type unit.

For more detailed structural analysis of the polymers **2**, their ^{13}C NMR spectra were measured. The resulting spectra are

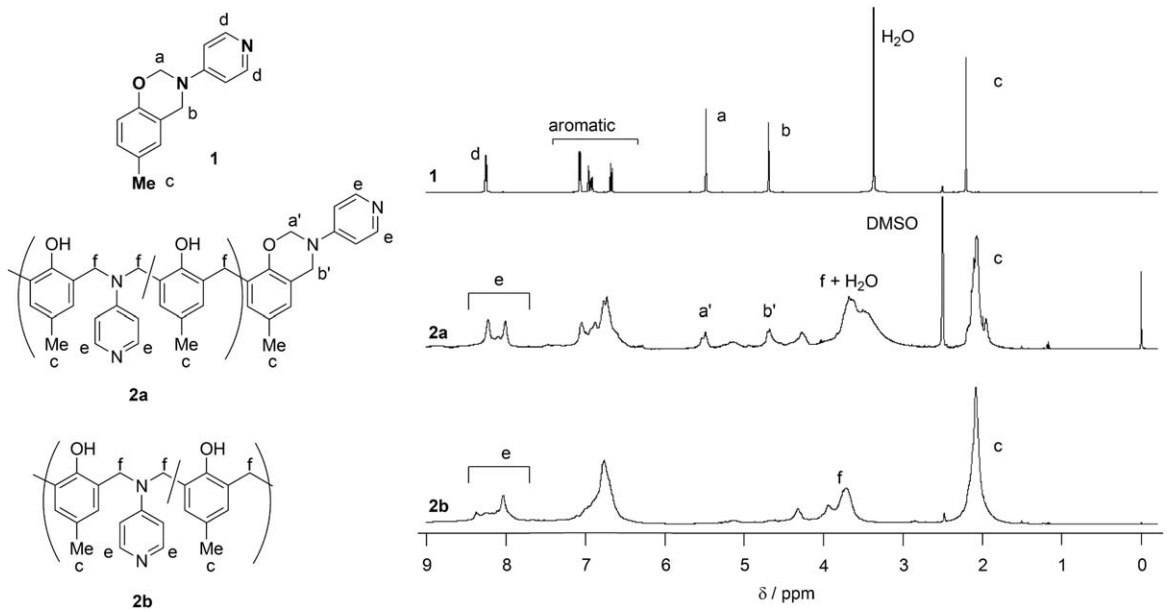


FIGURE 5 ^{1}H NMR spectra of **1**, **2a**, and **2b**.

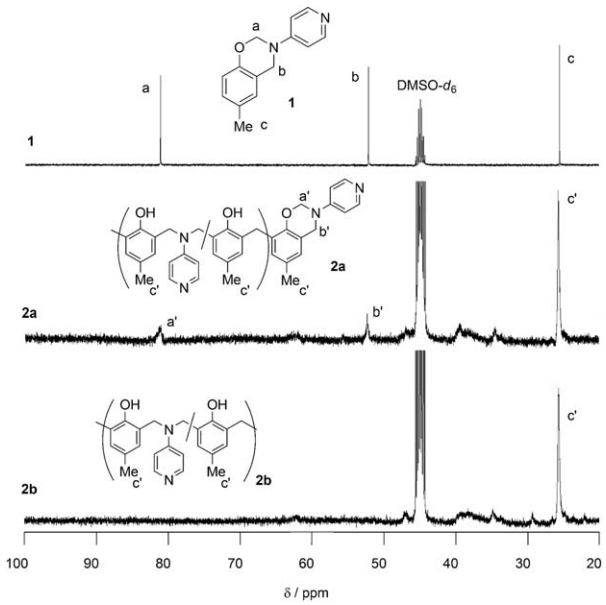


FIGURE 6 ^{13}C NMR Spectra of **1**, **2a**, and **2b**.

shown in Figure 6. The spectrum of **2a** confirmed the presence of benzoxazine moiety at the chain end. On the other hand, the spectrum of **2b** confirmed its disappearance. These results were in good agreement with the information obtained from the ^{1}H NMR analysis.

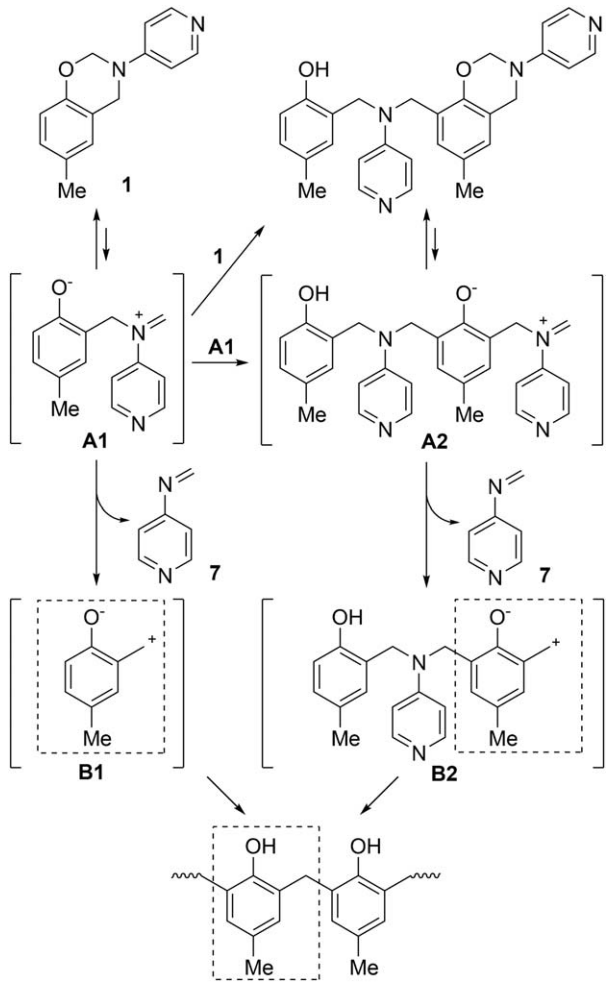
The polymers **2a** and **2b** were isolated as ethyl acetate-insoluble fractions in 36 and 27%, respectively. They were soluble in DMF and DMSO, and insoluble in acetone, ethyl acetate, THF and *n*-hexane.

In addition, the polymerization of **1** was performed at 200 °C. The corresponding time-dependence of the monomer conversion is shown in Figure 4. At this elevated temperature, the consumption rate of **1** was much faster than that observed at 180 °C. Within 4 h, more than 90 % of **1** was consumed. ^{1}H-NMR analysis of the resulting polymer clarified that its structure was quite similar to that of polymer **2b**.

Possible Mechanisms for the Polymerization of 1

Scheme 4 depicts some plausible mechanisms that would be involved in the present polymerization system. Although there should be other pathways, only essential ones that can explain the structural characteristics of the polymer **2** are selected to simplify the discussion. As has been already described, **1** was less reactive than a cresol-derived *N*-phenyl benzoxazine **3**. In the polymerization of benzoxazines, their ring-opening reaction into the corresponding zwitter-ionic intermediates is one of the critical steps. In the case of the polymerization of **1**, this step can be inhibited by introduction of electron-withdrawing 4-pyridyl group on the nitrogen atom, because it destabilizes the iminium cation in the species **A1** that should be formed as a result of the ring-opening reaction.

Once the iminium moiety forms, it can react with the electron-sufficient cresol-derived aromatic ring in the monomer **1**, phenoxide-containing species such as **A1**, and phenolic moieties at the chain ends. The adduct of **A1** and **1** has a benzoxazine moiety, which can remain intact at the chain end or can undergo the ring-opening reaction into a zwitter-ionic species **A2**.



SCHEME 4 Plausible mechanisms for the polymerization of **1**.

Another possible pathway from the zwitter-ionic species such as **A1** and **A2** would be the elimination of imine **7** to give the corresponding methyl cations **B1** and **B2**. Previously we have reported that this elimination process was responsible for the weigh losses during the polymerization of benzoxazines.[35] The resulting methyl cations can react with the electron-sufficient cresol-derived aromatic ring, leading to the incorporation of cresol-novolac-type unit in the resultant polymers.

Estimation of Molecular Weight of Polymer 8

The polymers **2a** and **2b** were analyzed by SEC to estimate their molecular weights. The resulting SEC profiles were bimodal in both the cases. From the two peaks in the profile, M_ns of **2a** were estimated to be 7800 and 2600. In a similar way, M_ns of **2b** were estimated to be 8200 and 2500, which were almost same as those of **2a**.

On the other hand, the SEC profile of polymer **8** obtained by masking the phenolic OH of polymer **2b** by its reaction with *t*-butyl isocyanate was unimodal, and its SEC-estimated M_n was 1600, much smaller than those of **2b**. This significant difference in M_n caused by masking OH implied that (1) the intrinsic molecular weight of **2b** was much smaller than that estimated by SEC and (2) the strong interaction between the phenolic moiety and pyridyl moiety caused aggregation of the polymer chains, leading to the overestimation of molecular weight.

Metal Ion Capturing by Polymer 2

One of the outstanding features of the polymer **2** is the presence of a highly basic 4-aminopyridyl moiety in the side chain. Therefore, we expected that the side chain would have high affinity to metal ions to permit the polymer to capture metal ions efficiently. A DMF solution of **2b** was prepared, and to this solution, a solution of $CuSO_4 \cdot 5H_2O$ in a mixture of water and methanol was added. As a result, a light yellow precipitation appeared in a few minutes (Fig. S2 in Supporting Information), confirming the formation of a complex of polymer **2b** and cupper (II) ion. Similarly, cobalt (II) ion was efficiently captured, leading to the formation of a pink insoluble polymer-metal complex.

CONCLUSIONS

A novel 1,3-benzoxazine, **1**, bearing 4-aminopyridyl moiety was synthesized from 4-aminopyridine, *p*-cresol, and paraformaldehyde, where addition of acetic acid to neutralize the basicity of the system was inevitable. The benzoxazine **1** underwent thermally induced ring-opening polymerization upon heating it at 180 °C. The polymerization was slower than that of an analogous *N*-phenyl benzoxazine derived from *p*-cresol, clarifying the significant deceleration effect by the electron-withdrawing nature of pyridyl moiety. The obtained polymer possessed pyridyl group at the side chain, although its content was lower than that expected from the standard ring-opening polymerization of benzoxazines. The 4-aminopyridyl moiety introduced into the polymer exhibited high affinity to metal ions such as copper (II) and cobalt (II) ions, leading to the formation of the corresponding polymer-metal complexes. Due to this metal-capturing ability, the polymer would be useful as metal scavenging materials and a component for polymer-inorganic hybrid materials.

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