Synthesis of Polymers Bearing 1,3-Benzoxazine Moiety in the Side Chains from Poly(allylamine) and Their Crosslinking Behaviors

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ABSTRACT: A polymer bearing 1,3-benzoxazine moiety in the side chain was synthesized successfully from poly(allylamine) based on a stepwise strategy consisted of three steps: (1) treatment of poly(allylamine) with salicylaldehyde to convert the amino group in the side chain into the corresponding *o*-(iminomethyl)phenol moiety, (2) reduction of the *o*-(iminomethyl)phenol to obtain the corresponding *o*-(aminomethyl)phenol moiety, and (3) formation of 1,3-benzoxazine moiety by the reaction of the *o*-(aminomethyl)phenol with formaldehyde. The content ratio of benzoxazine moieties and *o*-(aminomethyl)phenol moieties in the polymer were tunable by varying amount of formaldehyde. The presence of *o*-(aminomethyl)phenol moieties exhibited a significant promoting effect on the crosslinking reaction. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3174–3183, 2011

KEYWORDS: 1,3-benzoxazine; crosslinking; functionalization of polymer; networks; ring-opening polymerization

INTRODUCTION Benzoxazines are a class of heterocyclic compounds capable of undergoing ring-opening polymerization to give the corresponding polymers, which exhibit excellent mechanical strength,[1] thermal stability,[2] and durability under humid environment.[3] Benzoxazines can be easily synthesized by heating a solution of the corresponding phenolic compounds, amines, and formaldehyde.[4] This simple and versatile synthetic method has supported development of a wide range of benzoxazine-type monomers[5–9] involving curable multifunctional ones.[10,11]

Recently, polymers bearing 1,3-benzoxazine moieties have been attracted much attention because of their improved processability and their potential use as prepolymers that undergo crosslinking reactions to afford the corresponding networked polymers with high crosslinking density.[12,13] Several polymers bearing benzoxazine moieties in the main chains have been synthesized by various strategies including polycondensation of bisphenols, diamines and formaldehyde,[14–16] polycondensation of a diol bearing benzoxazine moieties with diacid chlorides,[17,18] and polyaddition of a bisalkyne bearing benzoxazine moieties with bisazide based on the copper (I)-catalyzed alkyne-azide coupling reaction.[19,20] Besides, polymers bearing benzoxazine moieties in the side chains have been developed: For example, benzoxazines bearing polymerizable moieties such as epoxide,[21] maleimide,[22] propargyl,[23] and methacryl groups[24,25] have been synthesized and selectively polymerized into the corresponding benzoxazine-functionalized polymers. Another reliable approach is side chain modification of polymer precursors bearing reactive side chains. For example, poly(4-vinylphenol) was used as a polymeric precursor bearing plural phenol moieties, which were condensed with aniline and formaldehyde to give the corresponding benzoxazine-functionalized polystyrene.[26,27] In another example, the copper-catalyzed azide-alkyne coupling reaction was efficiently used for the attachment of benzoxazine moieties to a polystyrene.[28]

Polymers bearing amino groups in the side chains are attractive precursors for synthesizing polymers bearing benzoxazines in the side chains. Poly(allylamine) is one of such polymeric precursors that can be easily obtained by radical polymerization of allylamine hydrochloric acid.[29] However, there has not been reported the use of poly(allylamine) for benzoxazine synthesis. The current contribution describes our successful use of poly(allylamine) as a precursor for the efficient approach to polymers bearing benzoxazine moieties in the side chains. The present synthetic route that converted the primary amino group into the corresponding benzoxazine moiety consisted of three steps, i.e., 1) condensation of the amino group with salicylaldehyde into the corresponding *o*-(iminomethyl)phenol, 2) its reduction into the corresponding *o*-(aminomethyl)phenol, and 3) its cyclocondensation with formaldehyde to give 1,3-benzoxazine moiety. All the steps proceeded without side reactions to give new linear polymers bearing benzoxazine pendants, and the final step with varying amount of formaldehyde allowed efficient control of content of benzoxazine moieties. Details of the

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synthesis and the crosslinking reactions of the obtained polymers are described herein.

EXPERIMENTAL

Materials

All reagents and solvents were used as received. Allylamine, *n*-propylamine, paraformaldehyde, formaldehyde (37% in water), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50), salicylaldehyde, sodium borohydride, *p*-cresol, hydrochloric acid (35% in water) and sodium hydroxide were purchased from WAKO Pure Chemical Industries.

Measurements

^{1}H NMR spectra were recorded in chloroform-*d* ($CDCl_3$) on a JEOL EX-300 (^{1}H, 300 MHz) spectrometer, with tetramethylsilane (TMS) as an internal standard, acquisition period = 5.45 sec; pulse delay = 1.55 sec; accumulation times = 32. Chemical shifts δ and coupling constants J are given in ppm and Hz, respectively. Thermo-gravimetric analysis (TG) and differential scanning calorimetric analysis (DSC) were performed with a SEIKO EXSTAR6000 (Seiko Instruments). IR spectra were obtained on a JASCO FT/IR-460 plus. Number- and weight- average molecular weight (M_n and M_w) were estimated from size exclusion chromatography (SEC), performed on a Tosoh chromatograph model HLC-8220GPC equipped with consecutive Tosoh TSKgel columns (SuperAW4000, SuperAW3000 and SuperAW2500) using DMF as an eluent at the flow rate of 0.5 mL/min after calibration with polystyrene standards.

Synthesis of Poly(allylamine) (PAA)

PAA was synthesized according to the article.[29] To allylamine (22.8 g, 0.40 mol), prechilled hydrochloric acid (43.8 g, 0.42 mol) was slowly added at 0 °C and the mixture was stirred at 0 °C for 1 h. The resulting solution was concentrated under reduced pressure at room temperature to adjust 70 wt % aqueous solution of allylamine hydrochloride. V-50 (651 mg, 2.40 mmol) was added to the solution, and the mixture was degassed by three freeze-pump-thaw cycles and heated at 50 °C for 50 h under N_2. After cooling to room temperature, the reaction mixture was poured into methanol (800 mL).

The resulting precipitate was collected by filtration with suction, washed with methanol and dried at room temperature under vacuum to yield PAA-HCl **1** (27.5 g, 29.4 mmol, 73%) as a white solid: ^{1}H NMR (in D_2O) δ 3.11 (br, 2H, —C*H*$_2$—NH_3^+), 2.09 (br, 1H, —CH_2—C*H*<), 1.57 (br, 2H, —C*H*$_2$—CH<).

Prechilled 50 wt % aqueous solution of sodium hydroxide (12.3 g, 30.8 mmol) was slowly added to **1** and the mixture was stirred at 0 °C.

After 1 h, the reaction mixture was diluted by adding water to adjust concentration of PAA to 17.5 wt %: ^{1}H NMR (in D_2O) δ 2.64 (br, 2H, —C*H*$_2$—NH_2), 1.56 (br, 1H, —CH_2—C*H*<), 1.27 (br, 2H, —C*H*$_2$—CH<). This aqueous solution of PAA containing about 30 mmol NaCl was stored in refrigerator at 0 °C until use.

Reaction of Poly(allylamine) with Di-*tert*-butyl dicarbonate[30,31]

To the 17.5 wt % aqueous solution of PAA (5.71 g, number of amino groups 17.5 mmol), a solution of di-*tert*-butyl dicarbonate (4.58 g, 21.0 mmol) in dioxane (10 mL) was added and the mixture was stirred at room temperature. After 8 h, 1M aqueous solution of sodium hydroxide (50 mL) was added and the mixture was stirred at room temperature for 12 h. The resulting precipitate was collected by filtration with suction, washed with water, dissolved in THF (15 mL) and poured into hexane (400 mL).

The resulting precipitate was collected by filtration with suction, washed with hexane and dried at room temperature under vacuum to yield **2** (2.21 g, 86%) as a white solid: ^{1}H NMR (in $CDCl_3$) δ 5.60 (br, 1H, —N*H*—), 3.07 (br, 2H, —N—C*H*$_2$—C<), 1.43 (br, 12H, —CH_2—C*H*<, —C*H*$_2$—CH<, —C(CH_3)$_3$); ^{13}C NMR (in $CDCl_3$) δ 157.01 (*C*=O), 78.98 (—*C*(CH_3)$_3$), 44.53 (—N—*C*H_2—C<), 36.09 (—CH_2—*C*H<), 33.48 (—*C*H_2—CH<), 28.79 (—C(*C*H_3)$_3$); IR (KBr) 3365, 2979, 2932, 1699, 1521, 1456, 1392, 1366, 1275, 1251, 1173 cm^{-1}.

Reaction of Poly(allylamine) with *p*-Cresol and Formaldehyde

The 17.5 wt % aqueous solution of PAA (0.65 g, number of amino groups 2.00 mmol) was dried at room temperature under vacuum for 12 h. The residual solid was dispersed in toluene (20 mL), and then *p*-cresol (0.24 mg, 2.2 mmol) and paraformaldehyde (0.34 g, 5.6 mmol) were added. The mixture was refluxed with azeotropic removal of water with using a Dean-Stark apparatus. The resulting precipitate was collected by filtration with suction, washed with toluene and dried to yield **3** (0.30 g) as a white solid: IR (KBr) 2916, 2851, 1670, 1617, 1501, 1457, 1252, 1227, 1118, 936, 814 cm^{-1}.

Synthesis of 2-[(*n*-Propylimino)methyl]phenol (4)

To a solution of *n*-propylamine (3.25 g, 55.0 mmol) in methanol (500 mL), salicylaldehyde (6.10 g, 50.0 mmol) was added and the mixture was stirred at room temperature for 1 h.

The resulting solution was concentrated under reduced pressure and dried at room temperature under vacuum to yield **4** (8.19 g, 99%) as a yellow oil: ^{1}H NMR (in $CDCl_3$) δ 13.69 (s, 1H, —O*H*), 8.34 (s, 1H, —C*H*=N—), 7.32–7.23 (m, 2H, Ar—*H*), 6.95 (d, 1H, J = 8.2 Hz, Ar—*H*), 6.87 (t, 2H, J = 7.4 Hz, Ar—*H*), 3.56 (t, 2H, J = 6.4 Hz, —C*H*$_2$—CH_2—CH_3), 1.73 (m, 2H, —CH_2—C*H*$_2$—CH_3), 0.98 (t, 3H, J = 7.4 Hz, —CH_2—CH_2—C*H*$_3$); ^{13}C NMR (in $CDCl_3$) δ 164.59 (—*C*H=N—), 161.34 (Ar), 131.82 (Ar), 131.12 (Ar), 118.77 (Ar), 118.21 (Ar), 116.78 (Ar), 60.99 (—*C*H_2—CH_2—CH_3), 23.95 (—CH_2—*C*H_2—CH_3), 11.52 (—CH_2—CH_2—*C*H_3); IR (neat) 2963, 2931, 1633, 1583, 1497, 1462, 1417, 1338, 1280, 1210, 1151, 1054, 1032, 1013, 977, 851, 755 cm^{-1}.

Synthesis of *N*-(*n*-Propyl)-1,3-benzoxazine (6)

To a solution of **4** (2.45 g, 15.0 mmol) in THF (150 mL), a suspension of sodium borohydride (1.13 g, 30.0 mmol) in methanol (4.5 mL) was added and the mixture was stirred at room temperature for 0.5 h. Water (15 mL) was added

and the resulting mixture was stirred at room temperature for 12 h. After THF and methanol were removed under reduced pressure, the obtained residue were dissolved in diethylether (20 mL) and washed with water (60 mL) three times.

Diethylether was removed under reduced pressure to yield crude **5** (2.57 g): ^{1}H NMR (in $CDCl_3$) δ 7.16 (t, 1H, J = 5.9 Hz, Ar—*H*), 6.99 (d, 1H, J = 5.5 Hz, Ar—*H*), 6.83 (d, 1H, J = 6.0 Hz, Ar—*H*), 6.77 (t, 1H, J = 5.6 Hz, Ar—*H*), 3.99 (s, 2H, —N—C*H*$_2$—Ar), 2.65 (t, 2H, J = 7.1 Hz, —N—C*H*$_2$—C—), 2.17 (s, 1H, N—*H*), 1.56 (m, 2H, —CH$_2$—C*H*$_2$—CH$_3$), 0.94 (t, 3H, J = 7.4 Hz, —CH$_2$—CH$_2$—C*H*$_3$); ^{13}C NMR (in $CDCl_3$) δ 158.32 (Ar), 128.23 (Ar), 128.09 (Ar), 122.59 (Ar), 118.57 (Ar), 115.95 (Ar), 52.36 (—N—*C*H$_2$—Ar), 50.23 (—*C*H$_2$—CH$_2$—CH$_3$), 22.44 (—CH$_2$—*C*H$_2$—*C*H$_3$), 11.41 (—CH$_2$—CH$_2$—*C*H$_3$); IR (neat) 3320, 3299, 2960, 2933, 1612, 1590, 1492, 1415, 1259, 1186, 1150, 1104, 1034, 754 cm^{-1}.

The crude **5** was dissolved in THF (150 mL), and to this solution, formalin (1.34 g, 16.5 mmol) was added. The mixture was stirred at room temperature for 1 h, and then concentrated under reduced pressure.

The obtained residue was fractionated by column chromatography (hexane/ethyl acetate = 4/1) to yield **6** (1.74 g, 66%) as a colorless oil: ^{1}H NMR (in $CDCl_3$) δ 7.12 (t, 1H, J = 7.4 Hz, Ar—*H*), 6.95 (d, 1H, J = 7.1 Hz, Ar—*H*), 6.86 (t, 1H, J = 7.2 Hz, Ar—*H*), 6.77 (d, 1H, J = 8.2 Hz, Ar—*H*), 4.87 (s, 2H, —N—C*H*$_2$—O—), 3.99 (s, 2H, —N—C*H*$_2$—Ar), 2.71 (t, 2H, J = 7.5 Hz, —C*H*$_2$—CH$_2$—CH$_3$), 1.59 (m, 2H, —CH$_2$—C*H*$_2$—CH$_3$), 0.93 (t, 3H, J = 7.4 Hz, —CH$_2$—CH$_2$—C*H*$_3$); ^{13}C NMR (in $CDCl_3$) δ 154.30 (Ar), 127.23 (Ar), 127.12 (Ar), 120.09 (Ar), 119.95 (Ar), 116.13 (Ar), 82.08 (—N—*C*H$_2$—O—), 52.93 (—N—*C*H$_2$—Ar), 49.87 (—*C*H$_2$—CH$_2$—CH$_3$), 21.04 (—CH$_2$—*C*H$_2$—*C*H$_3$), 11.34 (—CH$_2$—CH$_2$—*C*H$_3$); IR (neat) 2959, 2934, 2873, 1618, 1588, 1502, 1378, 1344, 1321, 1223, 1143, 1120, 939, 909, 814, 745 cm^{-1}.

Synthesis of Polymer Bearing *o*-(Iminomethyl)phenol Moieties (7)

The 17.5 wt % aqueous solution of PAA (9.79 g, number of amino groups 30.0 mmol) containing sodium chloride was dried under vacuum for 12 h. The obtained residue was dissolved in methanol (300 mL). To the solution, salicylaldehyde (4.03 g, 33.0 mmol) was added and the mixture was stirred at room temperature for 3 h. After methanol was removed under reduced pressure, THF (50 mL) was added, and precipitated sodium chloride was removed by filtration with suction. The resulting THF solution of PAA was concentrated under reduced pressure, and the obtained residue was redissolved in THF (30 mL) and poured into methanol (800 mL).

The resulting precipitate was collected by filtration with suction, washed with methanol and dried at room temperature under vacuum to yield **7** (4.14 g, 85%) as a yellow solid: ^{1}H NMR (in $CDCl_3$) δ 13.40 (br, 1H, —O*H*), 8.08 (br, 1H, —C*H*=N—), 7.16–6.70 (br, 4H, Ar—*H*), 3.38 (br, 2H, —N—C*H*$_2$—C<), 1.86–1.30 (br, 3H, —CH$_2$—C*H*<, —C*H*$_2$—CH<); ^{13}C NMR (in $CDCl_3$) δ 166.03 (—*C*H=N—), 161.29 (Ar), 132.24 (Ar), 119.42 (Ar), 118.62 (Ar), 117.92 (Ar), 63.06 (—N—*C*H$_2$—C<), 36.99 (—CH$_2$*C*H<), 33.88 (—*C*H$_2$CH<); IR (KBr): 2915, 1630, 1580, 1497, 1459, 1277, 1210, 1150, 1041, 849, 754 cm^{-1}.

Synthesis of Polymer Bearing *o*-(Aminomethyl)phenol Moieties (8)

To a solution of **7** (3.87 g, number of *o*-(iminomethyl)phenol groups = 24.0 mmol) in THF (240 mL), a suspension of sodium borohydride (1.82 g, 48.0 mmol) in methanol (7 mL) was added and the mixture was stirred at room temperature. After 0.5 h, water (50 mL) was added. The resulting mixture was stirred at room temperature for 12 h. THF and methanol were removed under reduced pressure to obtain a sticky precipitate on the wall of the apparatus. The supernatant aqueous layer was removed by decantation, and the precipitate was dissolved in THF (30 mL) and poured into water (800 mL).

The resulting precipitate was collected by filtration with suction, washed with water and dried at 50 °C under vacuum to yield **8** (3.71 g, 95%) as a white solid: ^{1}H NMR (in $CDCl_3$) δ 7.04–6.68 (br, 4H, Ar—*H*), 5.52 (br, 1H, —OH), 3.79 (br, 2H, —N—C*H*$_2$—Ar), 2.44 (br, 2H, —N—C*H*$_2$—C<), 1.52–1.12 (br, 3H, —CH$_2$—C*H*<, —C*H*$_2$—CH<); ^{13}C NMR (in $CDCl_3$) δ 158.27 (Ar), 128.86 (Ar), 122.84 (Ar), 119.32 (Ar), 116.23 (Ar), 53.24 (—N—*C*H$_2$—Ar, —N—*C*H$_2$—C<), 36.53 (—CH$_2$—*C*H<), 32.88 (—*C*H$_2$—CH<); IR (KBr) 3303, 2846, 2916, 1590, 1489, 1474, 1457, 1411, 1256, 1182, 1102, 1036, 750 cm^{-1}.

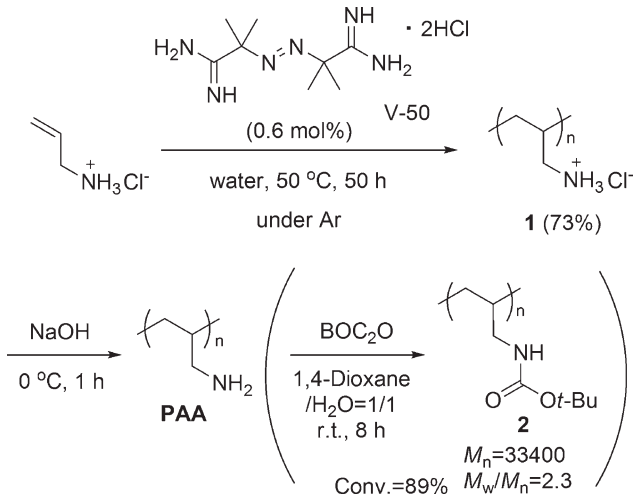
Syntheses of Polymers Bearing 1,3-Benzoxazine Moieties (9)

To a solution of **8** (1.47 g, amount of *o*-(aminomethyl)phenol group = 9.0 mmol) in THF (90 mL), formalin (1.46 g, 18.0 mmol) was added and the mixture was stirred at room temperature. After 2 h, volatiles were removed under reduced pressure. The resulting residue was dissolved in THF (10 mL) and poured into methanol (200 mL).

The resulting precipitate was collected by filtration with suction, washed with methanol and dried at room temperature under vacuum to yield **9a** (1.40 g, 89%) as a white solid: ^{1}H NMR (in $CDCl_3$) δ 7.01–6.71 (br, 4H, Ar—*H*), 4.63 (br, 2H, —N—C*H*$_2$—O—), 3.73 (br, 2H, —N—C*H*$_2$—Ar), 2.45 (br, 2H, —N—C*H*$_2$—C<), 1.61–0.97 (br, 3H, —CH$_2$—C*H*<, —C*H*$_2$—CH<); ^{13}C NMR (in $CDCl_3$) δ 154.52 (Ar), 127.89, (Ar) 120.53 (Ar), 116.58 (Ar), 83.13 (—N—*C*H$_2$—O—), 57.13 (—N—*C*H$_2$—Ar), 50.71 (—N—*C*H$_2$—C<), 39.73 (—CH$_2$—*C*H<), 31.49 (—*C*H$_2$—CH<); IR (KBr) 2905, 2851, 1607, 1583, 1488, 1456, 1333, 1221, 1137, 1106, 1034, 1024, 924, 749 cm^{-1}.

The polymers **9b** and **9c** were prepared similarly from **8** (0.49 g, amount of *o*-(aminomethyl)phenol group = 3.0 mmol). 0.18 g of formalin (2.25 mmol) and 0.12 g of formalin (1.50 mmol) were used for the synthesis of **9b** and **9c**, respectively. **9b** (0.49 g, 95% yield) and **9c** (0.48 g, 94%) were isolated as hexane-insoluble parts.

9b: ^{1}H NMR (in $CDCl_3$) δ 7.00–6.77 (br, 4H, Ar—*H*), 4.65 (br, 1.5H, —N—C*H*$_2$—O—), 3.74 (br, 2H, —N—C*H*$_2$—Ar), 2.42 (br,



SCHEME 1 Synthesis of poly(allylamine).

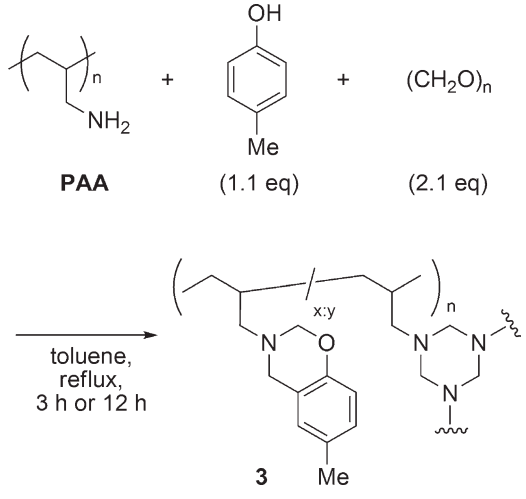
2H, —N—CH_2—C<), 1.53–1.00 (br, 3H, —CH_2—CH<, —CH_2—CH<).

9c: ^{1}H NMR (in $CDCl_3$) δ 7.06–6.71 (br, 4H, Ar—H), 4.64 (br, 1H, —N—CH_2—O—), 3.76 (br, 2H, —N—CH_2—Ar), 2.42 (br, 2H, —N—CH_2—C<), 1.52–1.10 (br, 3H, —CH_2—CH<, —CH_2—CH<).

RESULTS AND DISCUSSION

Synthesis of Poly(allylamine) (PAA)

PAA was synthesized by (1) the radical polymerization of allylamine hydrochloride and (2) treatment of the resulting PAA-HCl salt **1** with an aqueous solution of sodium hydroxide (Scheme 1).[29] To estimate of the molecular weight of PAA by size exclusion chromatography (SEC), PAA was transformed into a less polar derivative **2** by the reaction of the amino side chain with di-*tert*-butyl dicarbonate.[30,31] The estimated number average molecular weight (M_n) of **2** was 33,400, from which M_n of PAA was calculated to be 12,000 based on the equation, (M_n of PAA) = (SEC-estimated M_n of **2**)/(formula weight of the repeating unit of **2**)×(formula weight of the repeating unit of PAA). The ^{1}H- and ^{13}C NMR spectra of the polymers **1**, PAA and **2**, which supported their chemical structures, are shown in Figure S1 (in Supporting Information).



SCHEME 2 1-Step syntheses of polymers bearing benzoxazine moieties from poly(allylamine).

Synthesis of a Polymer Bearing Benzoxazine Moieties 3 by a Conventional Method

Conventionally, various benzoxazines have been synthesized by heating a mixture of the corresponding amines, phenols, and formaldehyde. With expecting that this conventional method would allow us to transform PAA directly into a polymer bearing benzoxazine moieties, a mixture of PAA, *p*-cresol and paraformaldehyde in toluene was heated with azeotropic removal of formed water (Scheme 2). As a result, a solid insoluble in organic solvents such as chloroform, tetrahydrofuran (THF), dimethylsulfoxide, *N*,*N*-dimethylformamide, and methanol was obtained. IR analysis of the solid revealed that it was a networked polymer **3** bearing benzoxazine[32,33] and triazine[34] moieties (Fig. 1), to imply that the amino groups of PAA and formaldehyde underwent condensation, and the cyclotrimerization of the resulting imines afforded the triazine rings as crosslinking points. Generally, triazines undergo thermal dissociation into the corresponding imines, which react with phenols to give the corresponding Mannich-type adducts as precursors of benzoxazines.[35] However, heating the networked polymer **3** in a toluene solution of *p*-cresol for additional 9 h did not induce any consumption of the triazine moieties, suggesting that the insoluble nature of **3** suppressed motion of its triazine moieties to avoid their efficient thermal dissociation. From these results, we concluded that the conventional method for

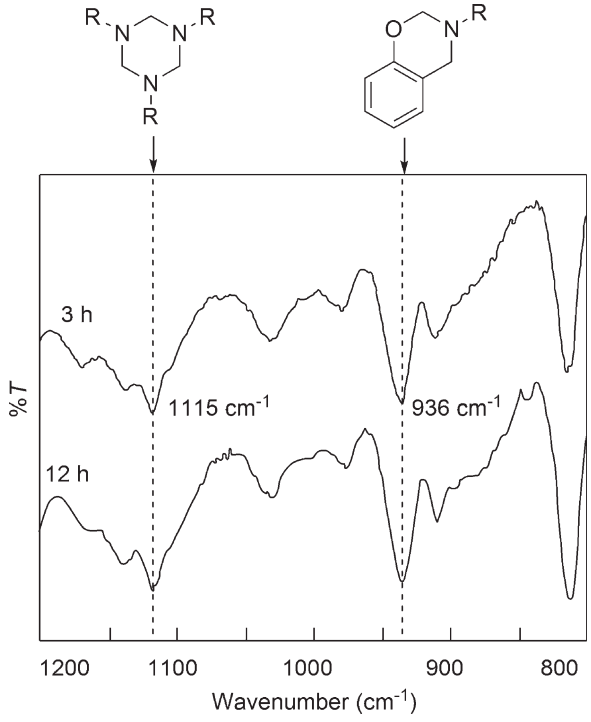
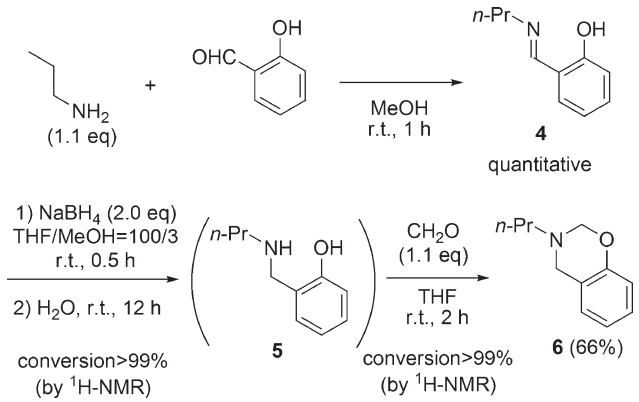


FIGURE 1 IR spectra of the insoluble polymers **3**.



SCHEME 3 A stepwise synthesis of benzoxazine.

benzoxazine synthesis was quite difficult to be applied to selective synthesis of PAA-derived polymers bearing benzoxazine moieties.

Stepwise Approach to Polymers Bearing Benzoxazine Moieties in the Side Chains

The difficulty in synthesizing our target polymer bearing benzoxazine pendants by the conventional method prompted us to investigate a more reliable synthetic approach based on cascading selective chemical transformations starting from PAA: Ronda and coworkers[36,37] have reported a stepwise approach that enabled efficient synthesis of several benzoxazines. The starting materials used therein are amines and *o*-formyl phenols, which underwent condensation to afford the corresponding *o*-(iminomethyl)phenols. The obtained *o*-(iminomethyl)phenols can be readily reduced by sodium borohydride into *o*-(aminomethyl)phenols, and their

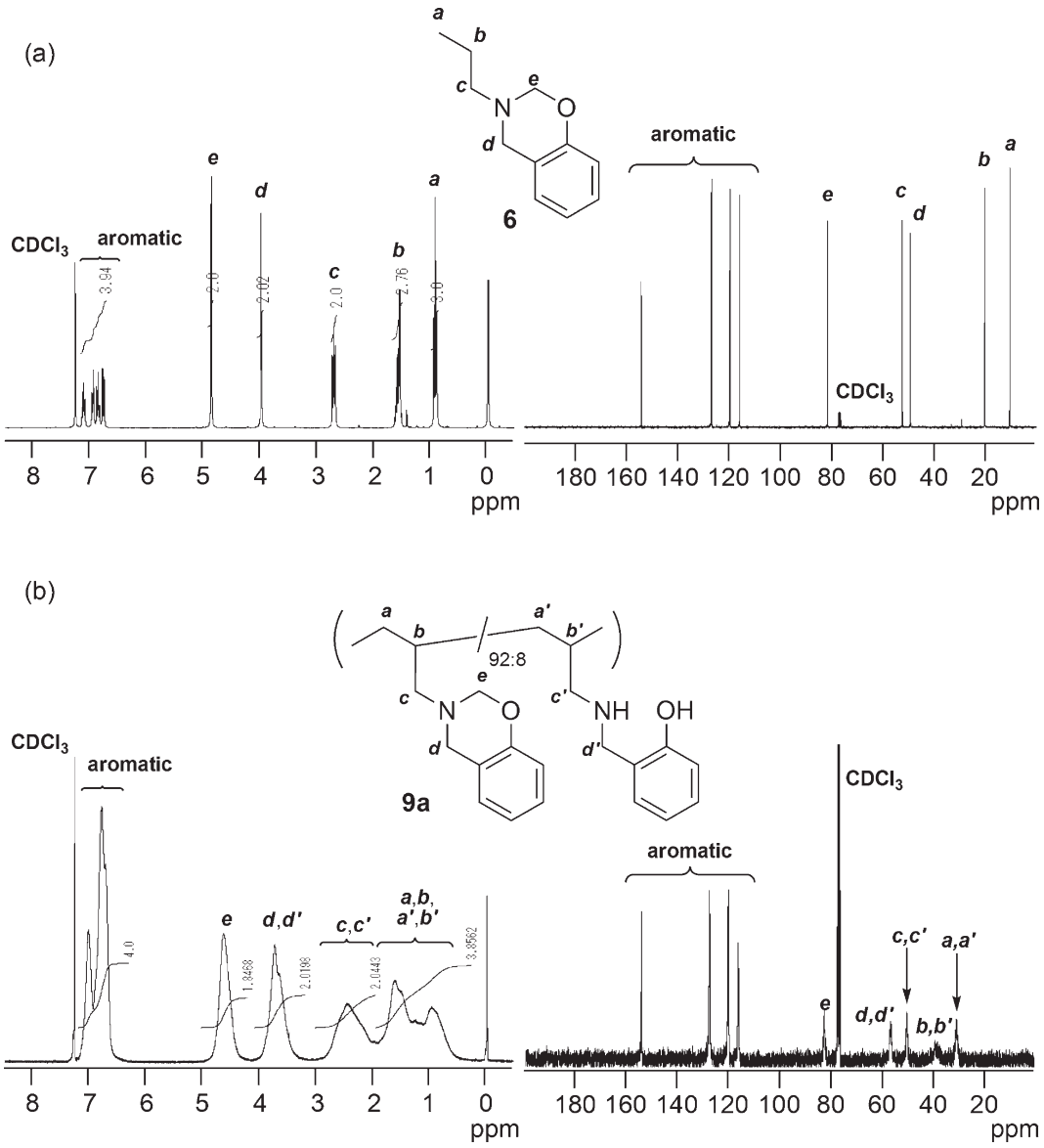
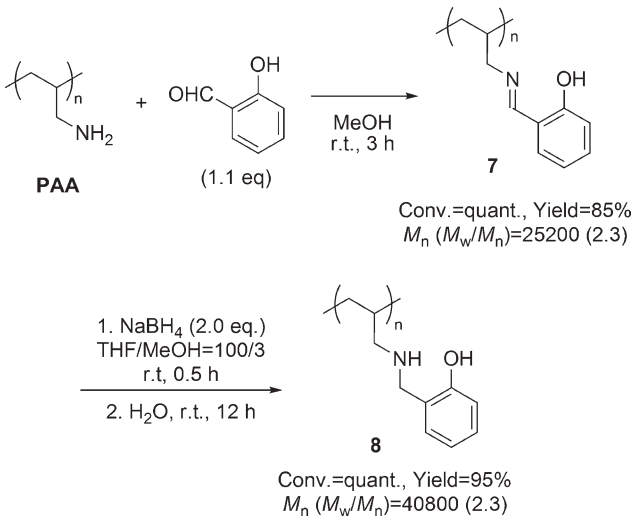


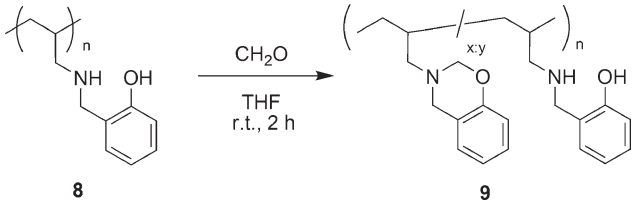
FIGURE 2 ^{1}H and ^{13}C NMR spectra of (a) *N*-(*n*-Pr) benzoxazine **6** and (b) polymer **9a**.



SCHEME 4 Synthesis of polymer **8** bearing *o*-(aminomethyl)-phenol moieties as a precursor for synthesizing polymers bearing benzoxazine moieties.

treatment with formaldehyde gave the corresponding benzoxazines.

Before applying this stepwise approach to the present synthesis of PAA-derived polymers bearing benzoxazine moieties, a series of the relevant reactions starting from *n*-propylamine as a model of PAA were performed to investigate the efficiency in the reaction steps and to clarify the spectroscopic features of the resulting compounds (Scheme 3): In the first step, *n*-propylamine and salicylaldehyde were condensed into *o*-(iminomethyl)phenol **4**. In the second step, the imino group of **4** was successfully reduced by sodium borohydride at room temperature. The reaction mixture was analyzed by ^{1}H NMR to confirm the quantitative conversion of **4** into *o*-(aminomethyl)phenol **5**, which was then used in the final cyclocondensation step without purification. The cyclocondensation of **5** with formaldehyde smoothly proceeded at room temperature to give *N*-propyl benzoxazine **6**. After confirming the quantitative conversion of **5** into **6** by ^{1}H NMR, **6** was isolated by column chromatography. Figure 2(a) shows the ^{1}H NMR spectrum of **6**, which indicated characteristic two singlet signals at 4.87 and 3.99 ppm attributable to the methylene protons of the *N*,*O*-acetal and the benzyl protons, respectively. The ^{13}C NMR also supported the chemical structure of **6** by showing three signals for the propyl group and two signals for the benzoxazine ring at the



SCHEME 5 Syntheses of polymers **9** bearing benzoxazine moieties.

TABLE 1 Syntheses of Polymers **9** Bearing Benzoxazine Moieties in the Side Chain

Entry	Polymer	Amount of CH_2O (eq)	Composition x: y[a]	Yield (%)	M_n[b] (M_w/M_n)[b]
1	**9a**	2.0	92:8	89[c]	27,100 (2.3)
2	**9b**	0.75	72:28	95[d]	30,000 (2.3)
3	**9c**	0.50	50:50	94[d]	32,500 (2.3)

[a] Determined by ^{1}H NMR.
[b] Estimated by SEC (eluent = DMF, polystyrene standards).
[c] Methanol-insoluble parts.
[d] Hexane-insoluble parts.

predicted positions. The ^{1}H and ^{13}C NMR spectra of **4** and **5** are shown in Figures S2 and S3 (in Supporting Information).

The successful model reactions prompted us to apply the same stepwise approach to the synthesis of our target polymers bearing benzoxazine moieties in the side chains. The stepwise chemical transformation of the amino group in the side chain of PAA into *o*-(aminomethyl)phenol moiety is shown in Scheme 4. The first step was the condensation of the amino groups in PAA and salicylaldehyde. The quantitative conversion of PAA into the corresponding polymer **7** bearing *o*-(iminomethyl)phenol moieties was confirmed by ^{1}H NMR. Treatment of **7** with sodium borohydride resulted in the successful reduction of the *o*-(iminomethyl)phenol moieties to afford the corresponding polymer **8** bearing *o*-(aminomethyl)phenol moieties. The polymer **7** and the corresponding model compound **4** shared common spectroscopic features, that is, the ^{1}H NMR signals for the imine proton and the phenol proton were observed at around 8 and 14 ppm, respectively, and the ^{13}C NMR signal for the C=N group was observed at around 166 ppm (Fig. S2 in Supporting Information). Similarly, the comparison of the spectra of the polymer **8** with those of the model compound **5** confirmed its chemical structure (Fig. S3 in Supporting Information). M_n and M_w/M_n of the polymers shown in Scheme 4 were estimated by SEC.

With using the polymer **8** as a precursor, the target polymers **9** bearing benzoxazine moieties were synthesized based on the cyclocondensation reaction of *o*-(aminomethyl)phenol moieties with formaldehyde (Scheme 5). In this reaction step, content of the benzoxazine moieties in the formed polymer **9** was successfully controlled by varying amount of formaldehyde used for the reaction (Table 1). In entry 1, an

TABLE 2 DSC Profiles of the Crosslinking Reactions of Polymers **9**

Entry	Polymer (Composition x: y)[a]	T_{onset} (°C)[b]	$T_{peak\ top}$ (°C)[b]	Heat Evolution (J/g)[b]
1	**9a** (92:8)	181	251	480
2	**9b** (72:28)	162	242	310
3	**9c** (50:50)	150	227	270

[a] Determined by ^{1}H NMR.
[b] Obtained by DSC in a dynamic mode (heating rate = 10 °C/min).

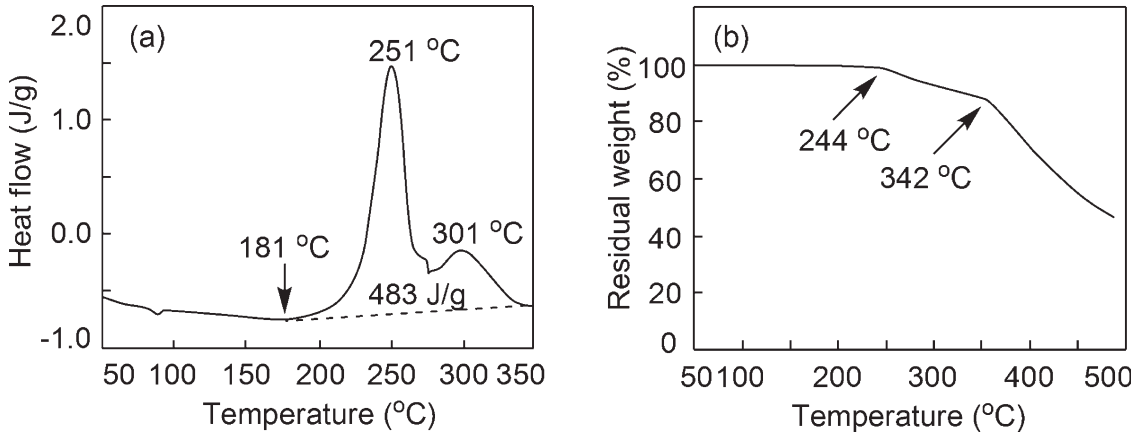


FIGURE 3 (a) DSC and (b) TG thermograms of the polymer **9a**.

excess amount of formaldehyde (2.0 equivalent to the amount of *o*-(aminomethyl)phenol moieties) was used. The cyclocondensation reaction proceeded smoothly at room temperature to afford the polymer **9a** bearing benzoxazine moieties. The ^{1}H NMR of **9a** indicated a broad signal at around 4.6 ppm attributable to the methylene protons of the *N*,*O*-acetal moiety [Fig. 2(b)]. By comparison of the intensity of this signal with the integrated signal intensity for the aromatic protons, the composition ratio x:y of **9a** was calculated to be 92:8. The presence of the methylene group between the nitrogen and oxygen atoms was also confirmed by the ^{13}C NMR spectrum [Fig. 2(b)]. In entries 2 and 3, reduced amounts of formaldehyde (0.75 and 0.5 equivalents to the number of the *o*-(aminomethyl)phenol moieties, respectively) were used. As a result, the corresponding polymers **9b** and **9c**, of which content ratios x:y were 72:28 and 50:50, respectively, were obtained. These content ratios were determined by ^{1}H NMR similarly to the case of **9a**. The corresponding spectra are shown in Figure S4 (in Supporting Information).

Thermally Induced Crosslinking Reaction of Polymers 9 Bearing Benzoxazine Moieties

With using polymer **9a**, thermally induced ring-opening reaction behavior of benzoxazine moieties was investigated by DSC measurement [Table 2 and Fig. 3(a)]. In parallel, weight loss behavior was also investigated by TG measurement [Fig. 3(b)]. In the DSC thermogram, two exothermic peaks were observed, and their peak top temperatures were 251 °C and 301 °C, respectively. The former one was attributable to ring-opening reaction of benzoxazine moieties to crosslink the polymer **9a** into the corresponding networked polymer, while the latter one was attributable to degradation of the unconsumed benzoxazine moieties (Scheme S1 in Supporting information).[38] In fact, the TG thermogram clarified that the weight loss gradually occurred from 244 °C until 342 °C, and this temperature range was in good accordance with the temperature range of the second exothermic peak observed in the DSC chart.

Next, rate of the consumption of the benzoxazine moieties was evaluated. Polymer **9a** was heated at 180 °C or 200 °C for *t* (hours), and the resulting sample was analyzed by DSC to detect heat evolution $\Delta H_{(t)}$ due to reactions of the residual benzoxazine moieties. By varying *t*, a series of the corresponding DSC profiles were collected, from which $\Delta H_{(t)}$ values were obtained (Fig. 4). As increasing the heating time, the exothermic peak in a range from 210 to 270 °C diminished to imply the consumption of the benzoxazine moieties. Conversions were calculated according to the following

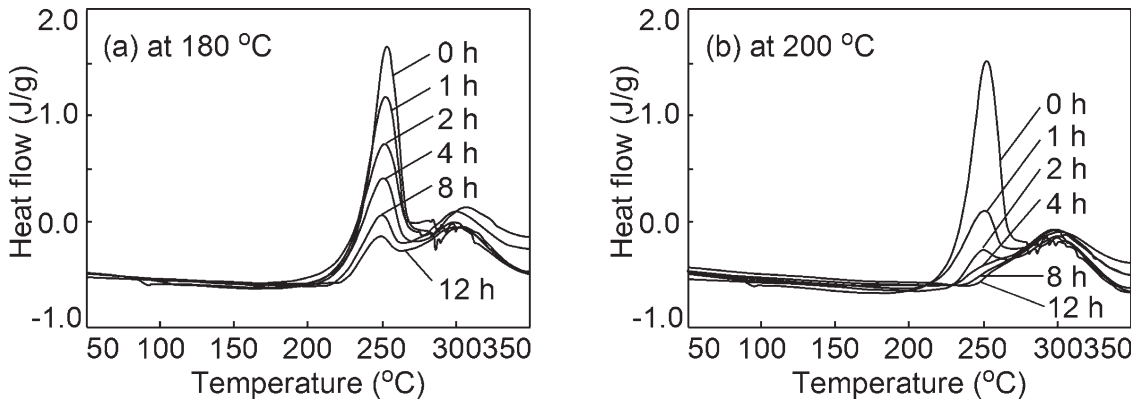


FIGURE 4 Heat evolution profiles of the polymer **9a** after heat treatment (a) at 180 °C and (b) at 200 °C.

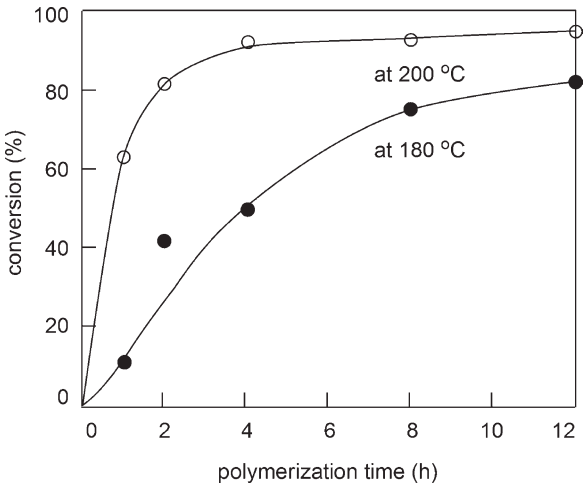


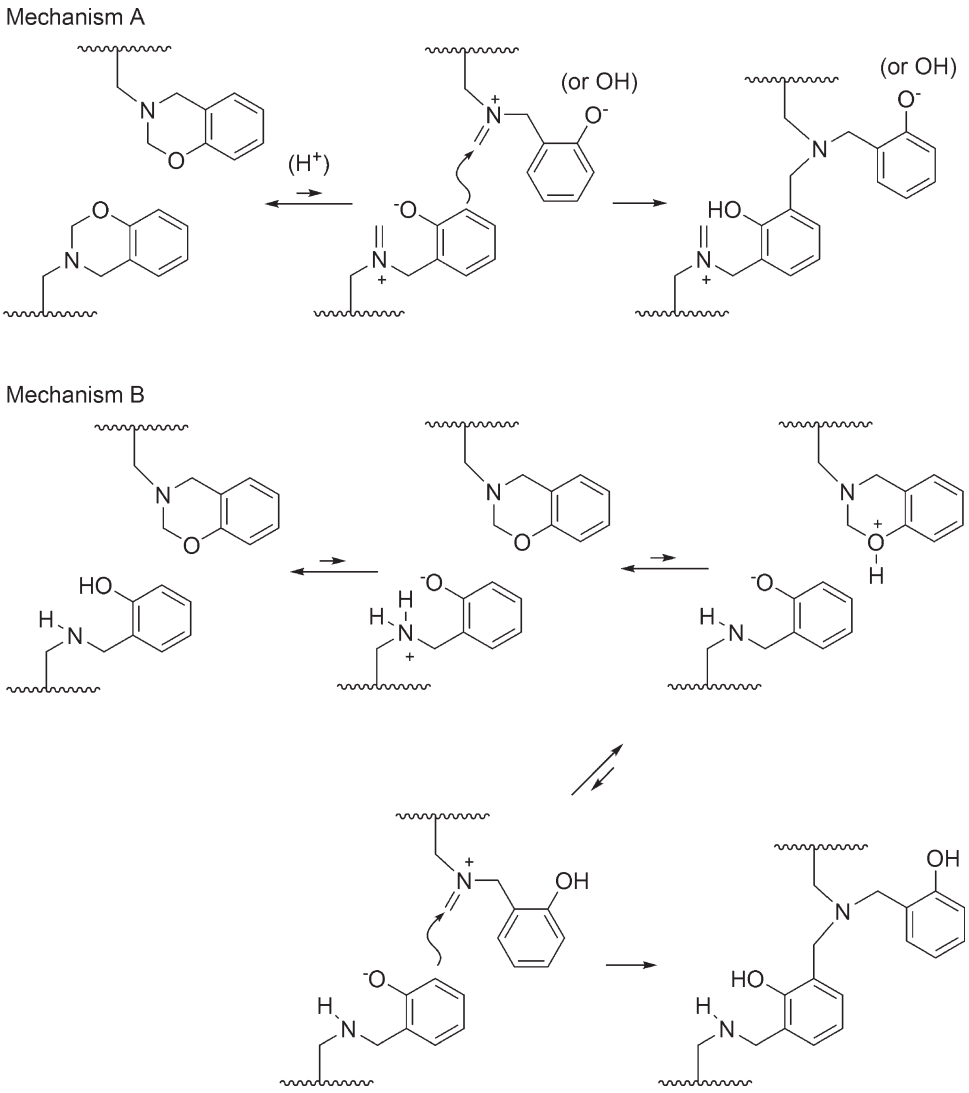
FIGURE 5 Time-conversion relationships for ring-opening reactions of the polymer **9a**. The conversions of benzoxazine moieties were calculated according to the following equation, conversion = $100(1 - \Delta H_{(t)}/\Delta H_{(0)})$.

TABLE 3 Thermal Properties of the Crosslinked Polymers Obtained by Heating Polymer **9a** (x: y = 92:8) at 180 or 200 °C

Entry	Temp. (°C)	Time (h)	T_{d5} (°C)[a]	T_{d10} (°C)[a]	Residual Weight Ratio at 450 °C (%)[a,b]
1[c]	–	–	275	309	45
2	180	12	290	335	41
3	200	4	295	341	43

[a] Measured by TG/DTA.
[b] [Weight after heating up to 450 °C]/[initial weight].
[c] Data for the pristine **9a**.

equation, conversion of benzoxazine moieties = $100(1 - \Delta H_{(t)}/\Delta H_{(0)})$, and were plotted against t (Fig. 5). Upon heating **9a** at 180 °C, the benzoxazine moieties were gradually consumed and the conversion reached 80% at 12 h. Much faster consumption of the benzoxazine moieties was achieved by heating **9a** at 200 °C.



SCHEME 6 Plausible reaction pathways involved in the crosslinking reaction of polymer **9**.

The thermal stabilities of the samples obtained by heating **9a** were investigated (Table 3). In the TG/DTA analysis of **9a**, temperature for 5% weight loss (T_{d5}) and that for 10% weight loss (T_{d10}) were observed at 275 °C and 309 °C, respectively (entry 1). By heating **9a** at 180 °C for 12 h, T_{d5} and T_{d10} increased to 290 °C and 335 °C, respectively (entry 2). Furthermore, higher T_{d5} and T_{d10} values were achieved by heating **9a** at 200 °C for 4 h (entry 3). These results clarified that the crosslinking reaction of **9a** based on the ring-opening reactions of the benzoxazine moieties contributed to the improvement of the thermal stability.

Based on these results, a cast film of polymer **9a** was prepared from its THF solution on a glass plate and heated at 200 °C for 4 h under air. The resulting polymer film became insoluble in organic solvents such as DMF, THF, and chloroform, to imply **9a** was crosslinked successfully.

Next, DSC analyses of the polymers **9b** and **9c** in a dynamic scan mode (heating rate = 10 °C /min) were performed. These polymers had higher contents of *o*-(aminomethyl)phenol moiety than **9a**, and its effects on the crosslinking behaviors were of our interest. Supporting Information Figure S5 shows the resulting DSC profiles, and some essential data extracted from them are listed in Table 2. As increasing the content of *o*-(aminomethyl)phenol moiety in the order of **9a** (8%) < **9b** (28%) < **9c** (50%), the peak top temperatures were lowered in the order of **9a** (251 °C) > **9b** (242 °C) > **9c** (224 °C). The onset temperatures and the heat evolutions were also lowered in the same order. These results suggested that the *o*-(aminomethyl)phenol moiety served as a promoter for the crosslinking reaction. Possible mechanisms for this promoting effect are discussed in the next section.

Crosslinking Reaction Mechanism

In Scheme 6, only a few selected mechanisms for the crosslinking reaction of polymer **9** bearing benzoxazine pendants are shown, because space is lacking for a full depiction of all the possible mechanisms. Mechanism A involves a reversible heterolytic scission of cyclic *N*,*O*-acetal moiety to form the corresponding zwitterionic intermediate (ZI).[39–43] This ring-opening reaction can be promoted by protonation of the oxygen atom.[44] In the case of polymers **9b** and **9c**, their *o*-(aminomethyl)phenol would be the source of proton and thus their crosslinking reactions would have been promoted. The phenoxide moiety would readily undergo intermolecular Mannich reaction with an iminium moiety of another ZI to crosslink the polymers. In addition, the resulting structure has an iminium and phenoxide moieties, of which reactions can contribute to increase number of crosslinking points.

Mechanism B involves a reaction of *o*-(aminomethyl)phenol with benzoxazine. *o*-(Aminomethyl)phenol would be in an equilibrium with a zwitterionic form bearing a phenoxide and ammonium moieties. The former is a nucleophile that can readily react with imminium moiety, while the latter can act as a proton source. In the presence of such a proton source, the ring-opening reaction of benzoxazine can be promoted through protonation of its oxygen atom. This dual role of *o*-(aminomethyl)phenol as a reactant and a proton source would be the reason for the promoted crosslinking reactions of **9b** and **9c**.

SUMMARY

From poly(allylamine) as a starting material, a sequence of modifications of the amino pendants allowed development of a series of new crosslinkable polymers bearing benzoxazine moieties in the side chains. In the final step of the synthetic route, the benzoxazine moieties were prepared from the corresponding *o*-(aminomethyl)phenol moieties by their reactions with formaldehyde, and thus the content ratio between benzoxazine and *o*-(aminomethyl)phenol moieties were controllable by varying amount of formaldehyde. The polymer with 8% *o*-(aminomethyl)phenol content readily underwent the crosslinking reaction by heating it at 200 °C. On the other hand, the polymers with higher o-(aminomethyl)phenol contents were crosslinkable at lower temperatures due to the dual role of o-(aminomethyl)phenol as a reactant and a proton source that promoted the ring-opening reaction of the benzoxazine moieties.

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