Self Termination of Ring Opening Reaction of *p*-Substituted Phenol-Based Benzoxazines: An Obstructive Effect *via* Intramolecular Hydrogen Bond

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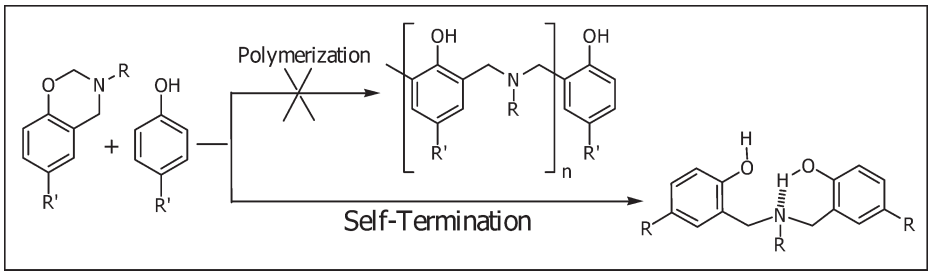

The ring opening polymerizations of *p*-substituted phenol-based benzoxazines are self-terminated as soon as dimers form. The polymerization of benzoxazine monomers does not proceed according to the theoretical mechanism even though the conditions, temperature, molar ratio, solvent polarity, and reactant ratio are varied. The speculated mechanism, involving the unique structure of a dimer with inter- and intramolecular hydrogen bonds, is applied to explain an obstructive effect on ring opening polymerization. In this article, we clarify an important case which the stereo structure of the compound controls the reaction and prevents the polymerization expected from the theoretical mechanism.

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INTRODUCTION

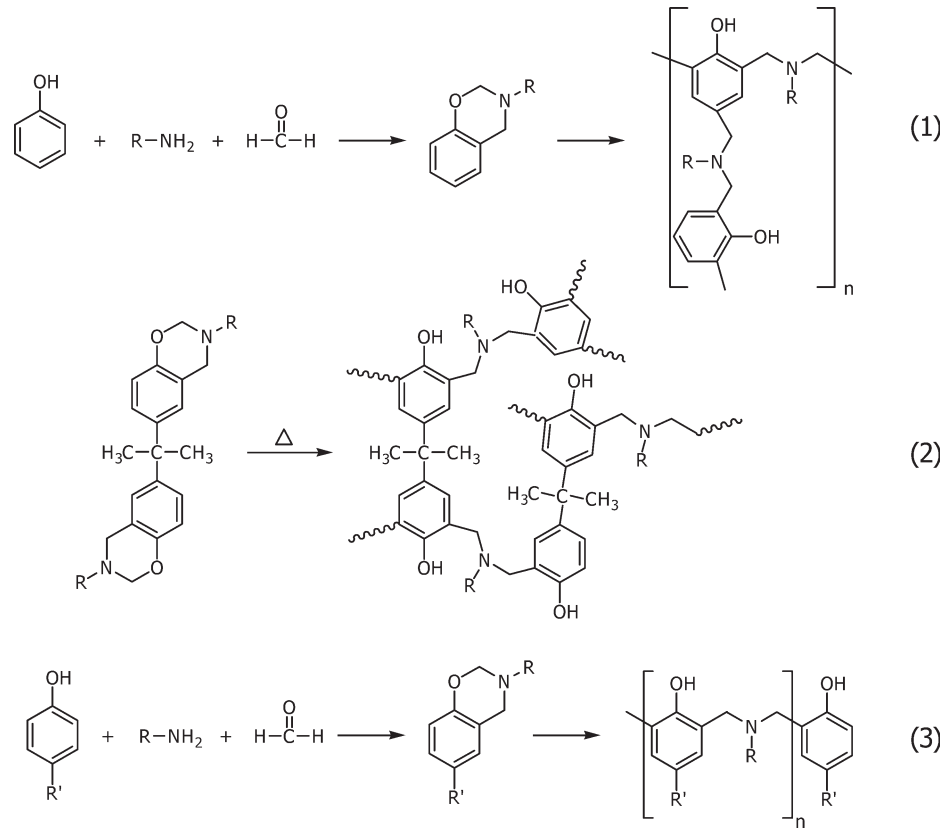
3,4-Dihydro-1,3-2*H*-benzoxazines are known as heterocyclic compounds obtained from *p*-substituted phenols, formaldehyde, and primary amines in a molar ratio of 1:2:1 *via* the Mannich reaction [1]. Theoretically, benzoxazines act as a monomer that undergoes the ring opening reaction to obtain a polymer chain with methylene-amine-Mannich bridges at both the ortho and para positions [2–6] [eq. (1), Scheme 1]. Kopf and Wagner [7] proposed the oxazine-derived phenolics as a potential precursor in synthesis of novolacs. Benzoxazines are reported as polybenzoxazines for the first time when Ning and Ishida [6] demonstrated novel phenolic resins obtained from a series of bisphenol A-based benzoxazine monomers. The success in polymeric material of bisphenol A-based polybenzoxazines might be related to the crosslink structure generated from the two hydroxyl groups belonging to a single bisphenol ring [eq. (2), Scheme 1] [6].

It is important to note that, although the reaction and mechanism of ring-opening benzoxazines [2] have been studied since 1952, *p*-substituted phenol-based benzoxazines and azamethylene phenols have rarely been reported. Based on the reverse Mannich reaction [8], *p*-substituted phenol should produce a high-molecular-weight linear polymer, since the aza-methylene linkage is occurred at only the ortho positions in the structure [eq. (3), Scheme 1].

Riess *et al.* [5] attempted the polymerization of phenol by using various conditions, which are the type of phenols, reaction temperatures, molar ratios, and phenol initiator concentrations. The reactions were done in bulk using NMR and vapor pressure methods to find that the degree of polymerization of the main products were about at the level of tetramer to hexamer. Although the reason why polymerization terminated was not clarified, the reaction was explained in terms of the kinetics and mechanisms [5].

Until now, there is no report about the linear polybenzoxazines even the mechanism insists the stepwise reaction to produce a chain of aza-methylene-phenol polymer. For the past few years, our group has paid attention onto the linear chain of polybenzoxazines, however, to our surprise the polymerization of *p*-substituted phenol-based benzoxazines does not proceed as expected. As will be describe here, the many reactions we have carried out allows us to conclude that the ring opening of *p*-substituted phenols provide neither linear oligomer nor polymer (Scheme 2), but only dimers.

Scheme 1



This article, thus, are to clarify (i) if indeed we never get the linear or cyclic compounds from the *p*-substituted based benzoxazine monomers as written in the formula, (ii) why the *p*-substituted based benzoxazine monomers give only dimer, and (iii) what obstructs the polymerization. By solving these questions, we are able not only to point out a rare example of a polymerization that could not proceed according to theory but also to design a synthesis pathway considering the factors involved at the monomer level.

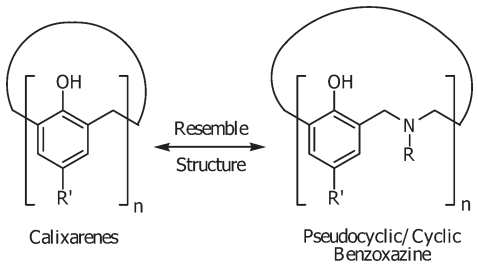
RESULTS AND DISCUSSION

Ring opening polymerization. Carboxylic acids and phenol derivatives are known as acid catalysts for the ring opening reaction of benzoxazines [5,9]. Ning and Ishida [6] reported that the ring opening is preferable in high-dielectric constant solvents such as methanol.

After the mixture of **1a** and *p*-cresol (molar ratio of 20:1) was refluxed in MeOH for 8 h, a white precipitate appeared. The TLC of the MeOH solution shows two spots at R_f for 0.48 and 0.56, referring to *p*-cresol and **1a**, respectively. This confirmed that only starting materials were present. However, the white precipitate gives an R_f for 0.30, implying a new product. The HPLC chromatograms exhibit the results corresponding to TLC. As shown in Figure 1, a new single sharp peak at (t_R) 3.430 min is observed for the white product, whereas those for **1a** and *p*-cresol are found at t_R 3.344 and 3.418 min, respectively.

From FTIR spectra (Fig. 2), the white product gives rise not only to the band at 3226 cm^{-1} but also to a broad band at 3100–2600 cm^{-1}. Lin-Vien *et al.* [10] reported a broad band at 3200–2600 cm^{-1} corresponding to the strong OH···N bond. Thus, we speculate that the white product with a free hydroxyl group in an open ring benzoxazine forms an intermolecular hydrogen bond with another free hydroxyl group and an intramolecular hydrogen bond with an aza group. The band at

Scheme 2



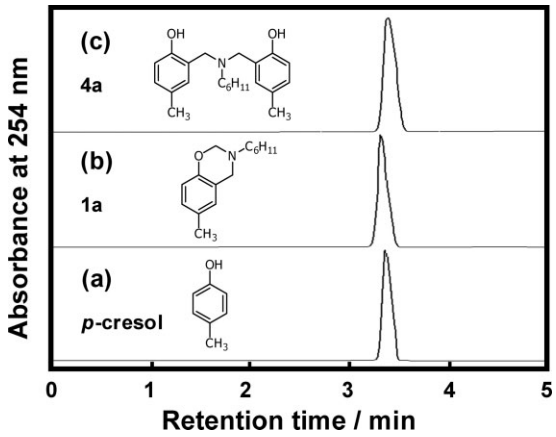


Figure 1. HPLC chromatograms of (a) *p*-cresol, (b) **1a**, and (c) **4a**.

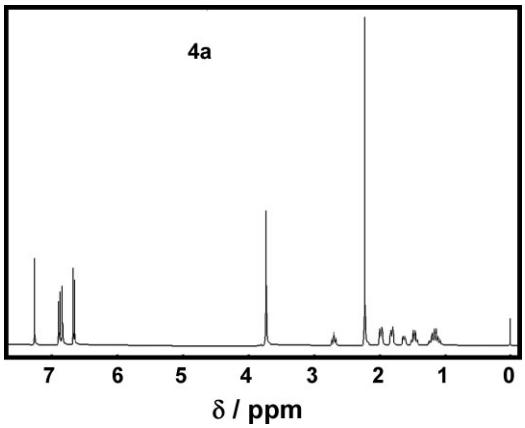


Figure 3. ^{1}H NMR spectrum of **4a**.

1502 cm^{-1} in both **1a** and the product corresponds to a vibrational mode of a trisubstituted benzene. It is important that no tetrasubstituted benzene band at 1485 cm^{-1} was observed. The ^{1}H NMR spectrum of **1a** shows two singlet peaks at $\delta_H = 4.07$ and 4.95 ppm, whereas that of the white precipitate (Fig. 3) shows a singlet resonance at $\delta_H = 3.75$ ppm belonging to methylene groups. This suggests the existence of the aza-methylene linkage in the product as a result of a ring opening reaction. If the product is a polymer, four species of aromatic protons could be observed; however, only three protons at δ_H 6.65 (d), 6.8 (s), and 6.90 (d) ppm resulted. Thus, we speculated that the product was not a polymer but rather a dimer as shown in **4a**.

Elemental analysis (EA) supports our conclusion. Elemental analysis is C 77.90, H 8.56, and N 4.16, which reflects exactly the dimer unit of **4a**.

Effect of solvent and temperature. Bruke *et al*. [4] reported the ring opening of benzoxazine monomer initiated by an intermolecular hydrogen bond with phenol derivatives. Riess *et al*. [5] proposed a mechanism catalyzed by dissociation of phenol. To overcome the termination at dimer, we concentrated on the optimal amount of *p*-cresol and solvent as well as reaction time and temperature.

Regardless of the variation of the molar ratio and solvents, the white precipitate was obtained. The characterization by TLC, HPLC, FTIR, ^{1}H NMR, and EA showed that the product was the dimer **4a**. In addition, it was found that the generation of **4a** is largely dependent on the amount of *p*-cresol (Fig. 4). When the molar ratio of the *p*-cresol increases, the yield of the dimer is increased. Unexpectedly, at 1:1, the yield is highest for all solvents. This implies that the reaction between **1a** and *p*-cresol might possibly be stoichiometric.

If *p*-cresol acts as an initiator in a reverse Mannich reaction, a generated open-ring intermediate should attack at the ortho position of either **1a** or *p*-cresol (see speculated mechanism). Thus, the product obtained should be a mixture of dimer and mono-oxazine compound as detailed in Scheme 3. However, the compound

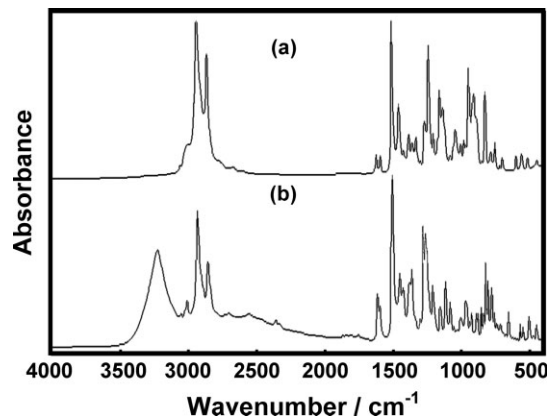


Figure 2. FTIR spectra of (a) **1a** and (b) **4a**.

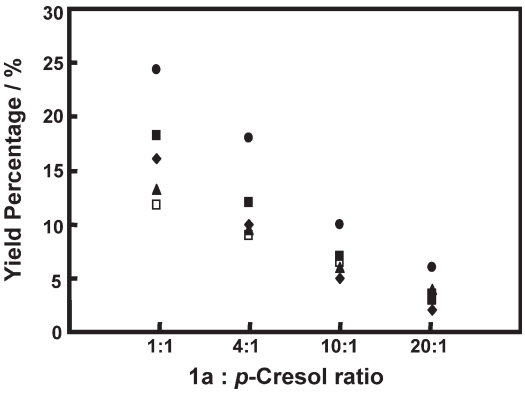
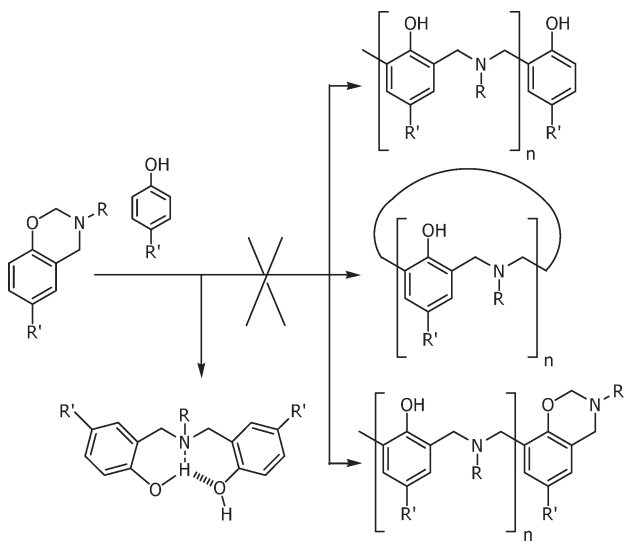


Figure 4. Yields of the product obtained from the reaction of **1a** and *p*-cresol carried out at the boiling point of each solvent; MeOH (♦), iso-PrOH (■), iso-BuOH (▲), cyclohexane (●), and xylene (□).

Scheme 3



obtained is a single component and its characterization does not correspond to the mono-oxazine product [11].

Figure 4 also implies that the yields of **4a** are increased for all molar ratios when the reactions have been carried out at low temperature. The yields from lower reaction temperatures, such as MeOH (bp 65°C) and cyclohexane (bp 80°C) are higher than those from higher reaction temperatures, such as iso-BuOH (bp 110°C) and mixed xylenes (bp 135°C).

Figure 5 implies two important results related to the optimum temperature and polarity effect. As expected, the highest yields are obtained at 65°C for every solvent. Considering the solvent polarity, the nonpolar ones (yield 40–60%) give higher yields than the polar ones (18–35%). This implies that the reaction is preferably carried out with nonpolar solvents (see speculated mechanism).

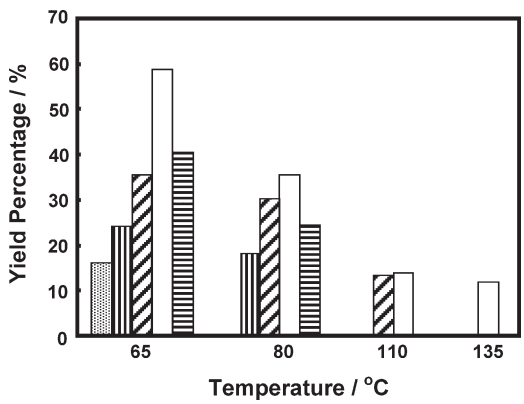


Figure 5. Yields of the product obtained from **1a** and *p*-cresol under various temperatures: 65, 80, 110, and 135°C in various solvents; MeOH ⊡, iso-PrOH ▮, iso-BuOH ◪, xylene □, and cyclohexane ▤.

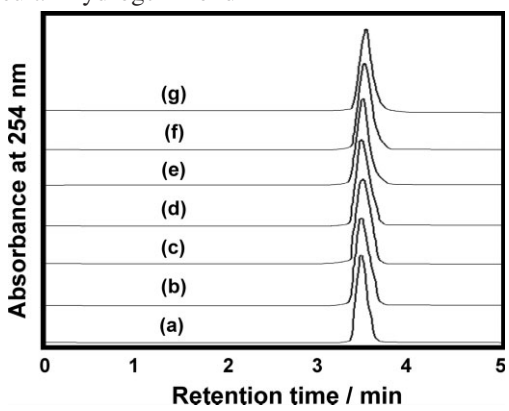


Figure 6. HPLC chromatograms of the product obtained from **1a** and *p*-cresol at 65°C in neat condition with various ratios; (a) 0.5:1, (b) 1:1, (c) 2:1, (d) 3:1, (e) 4:1, (f) 10:1, and (g) 20:1.

Neat liquid state reaction. It can be expected that the polymerization of *p*-substituted phenol-based benzoxazine might be favorable in neat condition. After heating the mixture of **1a** and *p*-cresol in various ratios to the molten state, the white powder precipitated soon after 30 min. Figure 6 shows that each product obtained exhibits only a single component with t_R 3.430 min. The NMR spectra of all products were same as shown in Figure 3, hence, we conclude that all products are **4a**.

Figure 7 shows the comparative studies between neat and solvent (xylene) conditions with a fixed molar ratio of **1a** and *p*-cresol of 1:1. Both reactions give the dimer in high yield (~90%) at 65°C. It is obvious that the neat condition also provides a stoichiometric reaction between **1a** and *p*-cresol. When the reactions are carried out at temperatures either lower or higher than 65°C, the yield is drastically decreased. This supports our speculation about the effect of temperature.

It is important to point out that when the reaction was carried out to satisfy the thermal initiation (above

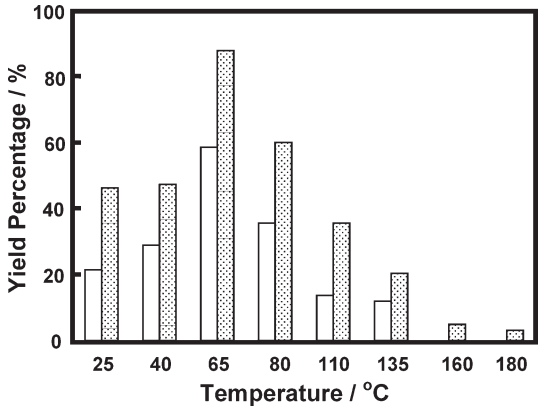


Figure 7. Yields of the product obtained from **1a** and *p*-cresol at various temperatures; 25, 40, 65, 80, 110, 135, 160, and 180°C in □ mixed xylenes and ⊡ neat condition.

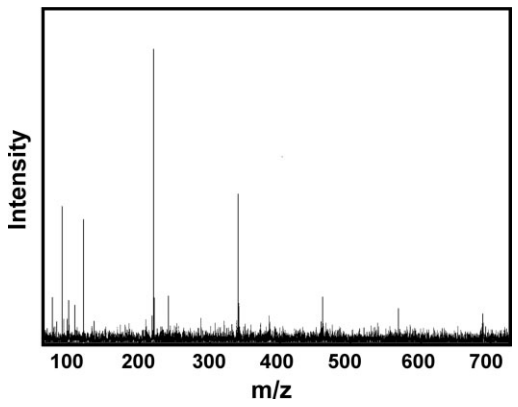


Figure 8. Mass spectrum of the mixture obtained from **1a** and *p*-cresol at 180°C.

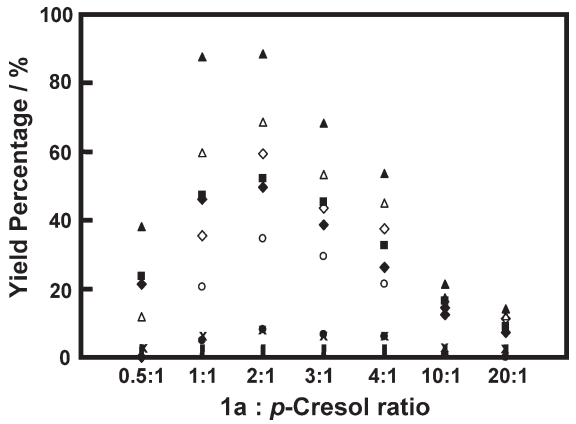


Figure 9. Yields of the product obtained from **1a** and *p*-cresol in various temperatures; 25 (♦), 40 (■), 65 (▲), 80 (△), 110 (◇), 135 (○), 160 (●), and 180°C (×) in neat condition.

140°C) condition as reported by Riess *et al.* [5], the precipitation of dimer **4a** is decreased to 2–3% (Fig. 7). Figure 7 also suggests that the reaction either in solution (mixed xylenes) or neat give maximum yield at the reaction temperature 65°C. At the same time, the neat liquid becomes a dark-brownish highly viscous liquid. A further study by LC-MS indicates the various fragments belonging to the dimer, appearing at m/z = 340, as well as other incomplete structures associated with the starting materials (Fig. 8). The trace fragments (m/z = 570 and 678) of higher molecular weight than dimer is also observed. These fragments could result from dimer aggregation or from trimer and tetramer. This implies that high temperature does not favor the polymerization but brings into play the competition between thermal dissociation of benzoxazine and chain propagation as reported by Riess *et al.* [5]

Reactivity of 1a and *p*-cresol. Figure 9 gives important information about the reactivity of **1a** and *p*-cresol as related to the reaction temperature. Generally, stoichiometric balance gives the highest yield with an equivalent molar ratio between the two reactants.

At high-reaction temperatures such as 110 and 135°C, our results indicate that even a lesser amount (stoichiometric imbalance) of *p*-cresol in the system, such as a molar ratio of **1a** and *p*-cresol of 2:1, 3:1, and 4:1, provides a yield of **4a** higher than that of equivalent molar quantities (stoichiometric balance).

It should be noted that the stoichiometric ratio 1:1 and the effectiveness of this stoichiometric ratio are different due to the reactivity of the reactive species. In this case, the reactive species are deactivated by heat [5]. Thus, the high yield of **4a** might result in the case of stoichiometric imbalance because the reactive species, **1a**, were always present in high concentration in the system.

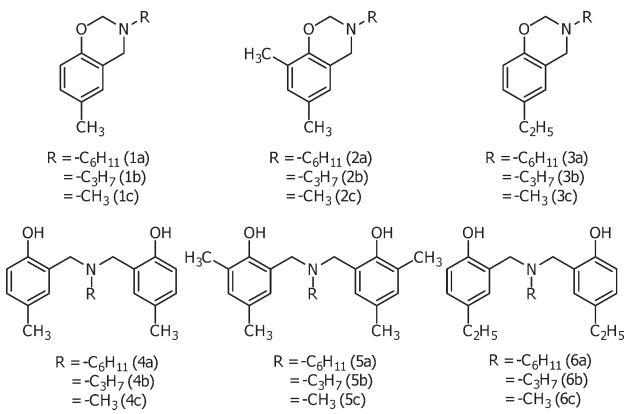
In the case of low temperatures (65°C and 80°C), the yield from the reactant ratios in stoichiometric balance gives the maximum yield when compared with other ratios. This shows that there is no deactivation of **1a** at the low temperature, and the high yield is obtained as expected.

Taking the above discussion into consideration, we speculated that without thermal degradation, the reactivity of *p*-cresol is ~0.8–0.9. This is strongly supported by the results that **4b–4c**, **5a–5c**, and **6a–6c** (Scheme 4) give similar yields (80–90%).

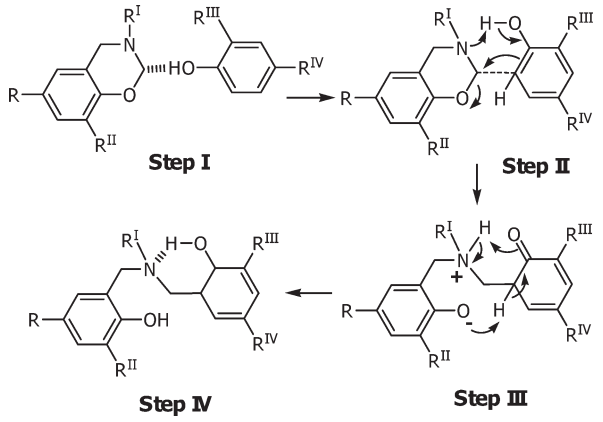
When we consider that there is no deactivation at 65°C, it is natural to expect that all molar ratios should give a yield of **4a** of 90%. However, Figure 9 shows that the yield of **4a** decreases significantly with an excess amount of **1a**. This implies that the reaction of **1a** and *p*-cresol could not proceed effectively. In other words, the ring opening reaction occurs only when the intermediate between **1a** and *p*-cresol is effectively formed.

Since only the dimer is obtained in every case, we conclude that the *p*-substituted phenol in the reaction does not provide a reactive site for another step in ring

Scheme 4



Scheme 5



opening polymerization. In fact, Riess *et al*. [5] reported that the *in situ* ring opening polymerization of *p*-substituted phenol initiated by disubstituted phenol (10%) gave a range of dimers to octamers as evaluated by NMR and vapor pressure methods. Although the structural characterization of the purified product in those cases was not reported in detail, the results support our speculation about some obstructive effects in polymerization.

It is known that the cyclization might be successful in dilute conditions [12]. Thus, an attempt was made to prepare cyclic compounds by using a mixture of **1a** and *p*-cresol (20:1) diluted in mixed xylenes to $5 \times 10^{-3}M$. These systems did not even give a white precipitate as in the previous reactions and the reactants remained in the solution.

Speculated mechanism. To explain why self termination occurs to prevent the polymerization, we combine our results with the mechanisms proposed by Burke *et al*. [4] and Riess *et al*. [5] We speculated that the reaction proceeded as follows. As shown in Scheme 5, intermolecular hydrogen bonding takes place between benzoxazine and the free ortho position in the phenol.

Here, the ring opening of benzoxazine requires some protonation from the phenol derivatives at the nitrogen atom of the oxazine ring to further react with the phenol derivative at ortho position. If the phenol derivative was an initiator, after generating the dimer, the hydroxyl group of one unit of the dimer would further attack another benzoxazine molecule. As a result, a linear polymer chain would be obtained. However, in our case, it is important to note that the reaction terminates as soon as the dimer is formed. This implies that phenol derivatives act as a reactant, not as an initiator, since the reaction does not give products other than dimer.

The effect of temperature and polarity might play an important role (Scheme 5). At this step, an effective ring opening requires thermal degradation, whereas the intermolecular hydrogen bonding between **1a** and *p*-cresol needs lesser thermal motion to maintain stability. Thus, the effect of temperature to drive the reaction provides a dilemma. This might be the reason why we found that the reaction can best proceed at a defined temperature (at 65°C) rather than at a higher or lower temperature (below or higher than 65°C).

In the case of solvent polarity, proton dissociation of phenol results when a polar solvent is used. However, at the same time, the hydrogen bond with the polar solvent will stabilize that proton. In contrast, nonpolar solvents promote the intermolecular hydrogen bonding between the benzoxazine and phenol derivatives. The significant yield of dimer in the nonpolar solvent might result from phenol dissociation rather than intermolecular hydrogen bonding. The effect of intermolecular hydrogen bonding is much enhanced as evidenced from experiments in the neat liquid state.

Stereo structure of dimer: A key factor for obstructive effect in polymerization. Previously, we detailed the unique stereo structure of benzoxazine dimer with strong inter- and intramolecular hydrogen bonds. The stabilization of a symmetrical compound through an intramolecular hydrogen bond inevitably gives us an asymmetric compound [11]. The X-ray structural analyses of dimers (**4a–4c**, **5a–5c**, and **6a–6c**) shows clearly that *p*-substituted based benzoxazines have inter- and intramolecular hydrogen bonds that stabilize the compounds [11,13,14]. Thus, after the single step of ring opening polymerization that produces the dimer, the stability of the network of inter- and intramolecular hydrogen bonding brings about the self termination. It can be concluded that stereo structure of dimer is the key factor to terminate the polymerization.

CONCLUSIONS

Although, in theory, a linear polymer can be obtained from the ring opening polymerization of *p*-substituted phenol-based benzoxazines, this work shows that in practice we will probably never achieve the polymer. Even when the reaction conditions were varied in terms of solvent, neat liquid state, reaction temperature, and concentration, the product was inevitably the dimer. Considering the factors involved in the ring opening reaction, our results show that, in the initial step, the hydrogen bonding between phenol derivatives and benzoxazine is primary when compare with phenol dissociation. Combining this with the previous X-ray structure analyses [11,13,14], we conclude that the obstructive effect of dimer in polymerization might result from the strong intramolecular hydrogen bond between the

hydroxyl group of the phenol ring and the aza methylene group in the dimer.

Thus, the mechanism and the reaction assumed from the formula are not always practical. As shown here, the unique stereo structure of benzoxazine dimer leads to the self termination and obstructs the polymerization as clarified in Scheme 5.

EXPERIMENTAL

Chemicals. Paraformaldehyde was purchased from Sigma (St. Louis, MO). *p*-Cresol, 2,4-dimethylphenol, 4-ethylphenol, methylamine (40% w/v in water), cyclohexylamine, and propylamine, deuterated chloroform ($CDCl_3$), and anhydrous sodium sulfate were purchased from Fluka Chemicals (Buchs, Switzerland). HPLC grade tetrahydrofuran (THF), methanol, propan-2-ol, mixed xylenes, 2-methylpropan-1-ol, cyclohexane, sodium hydroxide, and diethyl ether were the products of Ajax chemicals (Australia). All chemicals were analytical grade and used as received.

Procedures. Benzoxazines, **1a**–**3c**, were prepared by using phenol, formaldehyde, and amine derivatives in the ratio of 1:2:1, respectively. *p*-Cresol was added into solution of cyclohexylamine and *p*-formaldehyde, then refluxed for 6 h. The crude product was washed and solvent was removed to obtain **1a**. Compounds **1b** and **1c** were prepared similarly but using propylamine and methylamine, respectively, instead of cyclohexylamine. In the preparation of **2a**–**2c** and **3a**–**3c**, 2,4-dimethylphenol and 4-ethylphenol were used as phenol derivatives, respectively. The ^1H nuclear magnetic resonance (NMR) spectrometers were a Bruker ACF with a proton frequency of 200 MHz. Fourier transform infrared spectra were measured at a resolution of 4 cm^{-1} by a Bruker Equinox55/S spectrophotometer equipped with deuterated triglycine (DTGS) detector under constant purge with dry air. High-performance liquid chromatography (HPLC) was done with a Hewlett Packard HP1100 HPLC and a diode array detector model G1315A #DE72002547 fixed at 254 nm. The samples were eluted through a Whatman Partisil 5, a silica gel column with an average pore diameter of 8.5 nm, and a surface area > 350 m^2/g by maintaining the flow rate at 1 mL/min throughout the experiment. Liquid chromatography mass spectrometer (LC-MS) was a Bruker Esquire-LC using methanol as a mobile phase. Elemental analysis (EA) was performed by a Perkin Elmer 2400 Series II CHNS/O analyzer with a combustion temperature of 975°C and a reduction temperature of 500°C.

Reaction of 1a and *p*-cresol in various solvents and temperatures. Benzoxazine **1a** (1.6 mmol) and *p*-cresol were reacted in molar ratios of 1:1, 4:1, 10:1, and 20:1 in various solvents (5 mL), methanol (MeOH), propan-2-ol (iso-PrOH), 2-methylpropan-1-ol (iso-BuOH), cyclohexane, and xylene. The mixtures of monomer **1a** and *p*-cresol in each solvent were reacted at room temperature (~25°C), 40, 65, 80, 110, 135, 160, and 180°C. The completion of the reaction was followed by thin layer chromatography (TLC) and the reaction was stopped after 8 h. The solvent was removed and the crude product was washed with diethyl ether several times before drying at 60°C for 6 h.

Reaction in neat liquid state under various temperatures. Mixtures of **1a** and *p*-cresol (0.5:1, 1:1, 2:1, 3:1, 4:1, 10:1, and 20:1) were prepared and stirred at room temperature (~25°C), 40, 65, 80, 110, 135, 160, and 180°C. The mixtures were allowed to react until viscous. The precipitates obtained from the reaction were collected, washed with diethyl ether before drying at 60°C for 6 h.

Similarly, **1b**–**1c**, **2a**–**2c**, and **3a**–**3c** were reacted with *p*-cresol, 2,4-dimethylphenol, and 4-ethylphenol, respectively. The compounds obtained were qualitatively analyzed by FTIR, ^1H NMR, HPLC, LC-MS, and EA. From structural analyses, the compounds obtained are proposed as shown in Scheme 3.

2,2′-[(Cyclohexylimino)di(methylene)]bis(4-methylphenol) (4a). 80% yield; $R_f = 0.30$ (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 181°C; FTIR (KBr, cm^{-1}): 3226 (br, OH), 1500 (vs, C—C), 1449 (m, N—CH), 1249 (s, C—N), 1210 (m, C—N—C), 819 (s, C—N—C); ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (m, 2H, **CH_2**), 1.45 (m, 4H, **CH_2**), 1.82 (m, 4H, **CH_2**), 2.22 (s, 6H, **CH_3**—Ar), 2.70 (m, 1H, **CH**), 3.72 (s, 4H, Ar—**CH_2**—N), 6.68 (d, 2H, Ar—**H**), 6.85 (s, 2H, Ar—**H**), 6.90 (d, 2H, Ar—**H**). Anal. calcd. for $C_{22}H_{29}NO_2$: C, 77.88; H, 8.55; N, 4.13. Found: C, 77.90; H, 8.56; N, 4.16.

2,2′-[(Propylimino)di(methylene)]bis(4-methylphenol) (4b). 80% yield; $R_f = 0.22$ (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 149°C; FTIR (KBr, cm^{-1}): 3251 (br, OH), 1501 (vs, C—C), 1467 (m, N—CH_2), 1276 (s, C—N), 1210 (s, C—N—C), 819 (s, C—N—C); ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.87 (t, 3H, **CH_3**—CH_2—CH_2—N), 1.65 (m, 2H, CH_3—**CH_2**—CH_2—N), 2.22 (s, 6H, **CH_3**—Ar), 2.50 (t, 2H, CH_3—CH_2—**CH_2**—N), 3.70 (s, 4H, Ar—**CH_2**—N), 6.68 (d, 2H, Ar—**H**), 6.85 (s, 2H, Ar-**H**), 6.90 (d, 2H, Ar—**H**). Anal. calcd. for $C_{19}H_{25}NO_2$: C, 76.25; H, 8.36; N, 4.69. Found: C, 76.28; H, 8.31; N, 4.70.

2,2′-[(Methylimino)di(methylene)]bis(4-methylphenol) (4c). 90% yield; $R_f = 0.24$ (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 163°C; FTIR (KBr, cm^{-1}): 3271 (br, OH), 1499 (vs, C—C), 1456 (m, N—CH_3), 1249 (s, C—N), 1209 (m, C—N—C), 815 (vs, C—N—C); ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.23 (s, 6H, Ar—**CH_3**), 2.23 (s, 3H, N—**CH_3**), 3.69 (s, 4H, Ar—**CH_2**—N), 6.70 (d, 2H, Ar—**H**), 6.83 (s, 2H, Ar—**H**), 6.86 (d, 2H, Ar—**H**). Anal. calcd. for $C_{17}H_{21}NO_2$: C, 75.28; H, 7.75; N, 5.17. Found: C, 75.31; H, 7.77; N, 5.19.

2,2′-[(Cyclohexylimino)di(methylene)]bis(4,6-dimethylphenol) (5a). 90% yield; $R_f = 0.38$ (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 152°C; FTIR (KBr, cm^{-1}): 3384 (br, OH), 1484 (vs, C—C), 1451 (m, N—CH), 1245 (m, C—N), 1199 (m, C—N—C), 858 (m, C—N—C); ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (m, 2H, **CH_2**), 1.45 (m, 4H, **CH_2**), 1.82 (m, 4H, **CH_2**), 2.20 (s, 6H, **CH_3**—Ar), 2.22 (s, 6H, **CH_3**—Ar), 2.70 (m, 1H, **CH**), 3.72 (s, 4H, Ar—**CH_2**—N), 6.70 (s, 2H, Ar—**H**), 6.85 (s, 2H, Ar—**H**). Anal. calcd. for $C_{24}H_{33}NO_2$: C, 78.47; H, 8.99; N, 3.82. Found: C, 78.49; H, 8.97; N, 3.85.

2,2′-[(Propylimino)di(methylene)]bis(4,6-dimethylphenol) (5b). 90% yield; $R_f = 0.43$ (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 116°C; FTIR (KBr, cm^{-1}): 3298 (br, OH), 1483 (vs, C—C), 1450 (m, N—CH_2), 1250 (m, C—N), 1199 (vs, C—N—C), 852 (m, C—N—C); ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.85 (t, 3H, **CH_3**—CH_2—CH_2—N), 1.65 (m, 2H, CH_3—**CH_2**—CH_2—N), 2.20 (s, 6H, **CH_3**—Ar), 2.22 (s, 6H, **CH_3**—Ar), 2.50 (t, 2H, CH_3—CH_2—**CH_2**—N), 3.65 (s, 4H,

Ar—**CH_2**—N), 6.70 (s, 2H, Ar—**H**), 6.85 (s, 2H, Ar—**H**). Anal. calcd. for $C_{21}H_{29}NO_2$: C, 77.06; H, 8.87; N, 4.28. Found: C, 77.05; H, 8.86; N, 4.27.

2,2′-[(Methylimino)di(methylene)]bis(4,6-dimethylphenol) (5c). 80% yield; R_f = 0.39 (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 123°C; FTIR (KBr, cm^{-1}): 3399 (br, OH), 1484 (vs, C—C), 1427 (m, N—CH_3), 1243 (m, C—N), 1214 and 1201 (m, C—N—C), 847 (m, C—N—C); ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.22 (s, 12H, Ar—**CH_3**), 2.25 (s, 3H, N—**CH_3**), 3.68 (s, 4H, Ar—**CH_2**—N), 6.72 (s, 2H, Ar—**H**), 6.81 (s, 2H, Ar—**H**). Anal. calcd. for $C_{19}H_{25}NO_2$: C, 76.26; H, 8.36; N, 4.68. Found: C, 76.27; H, 8.34; N, 4.69.

2,2′-[(Cyclohexylimino)di(methylene)]bis(4-ethylphenol) (6a). 80% yield; R_f = 0.21 (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 170°C; FTIR (KBr, cm^{-1}): 3251 (br, OH), 1499 (vs, C—C), 1450 (m, N—CH), 1250 (s, C—N), 1207 (m, C—N—C), 818 (m, C—N—C); ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.15 (t, 6H, **CH_3**—CH_2—Ar), 1.15 (m, 2H, **CH_2**), 1.45 (m, 4H, **CH_2**), 1.82 (m, 4H, **CH_2**), 2.52 (q, 2H, CH_3—**CH_2**—Ar), 2.70 (m, 1H, **CH**), 3.72 (s, 4H, Ar—**CH_2**—N), 6.72 (d, 2H, Ar—**H**), 6.87 (s, 2H, Ar—**H**), 6.94 (d, 2H, Ar—**H**). Anal. calcd. for $C_{24}H_{33}NO_2$: C, 78.47; H, 8.99; N, 3.82. Found: C, 78.51; H, 8.97; N, 3.79.

2,2′-[(Propylimino)di(methylene)]bis(4-ethylphenol) (6b). 80% yield; R_f = 0.28 (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 132°C; FTIR (KBr, cm^{-1}): 3265 (br, OH), 1499 (vs, C—C), 1447 (m, N—CH_2), 1247 (s, C—N), 1205 (m, C—N—C), 819 (s, C—N—C); ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.87 (t, 3H, **CH_3**—CH_2—CH_2—N), 1.18 (t, 3H, **CH_3**—CH_2—Ar), 1.65 (m, 2H, CH_3—**CH_2**—CH_2—N), 2.52 (q, 2H, CH_3—**CH_2**—Ar), 2.52 (t, 2H, CH_3—CH_2—**CH_2**—N), 3.70 (s, 4H, Ar—**CH_2**—N), 6.72 (d, 2H, Ar—**H**), 6.87 (s, 2H, Ar—**H**), 6.94 (d, 2H, Ar—**H**). Anal. calcd. for $C_{21}H_{29}NO_2$: C, 77.06; H, 8.87; N, 4.28. Found: C, 77.08; H, 8.89; N, 4.31.

2,2′-[(Methylimino)di(methylene)]bis(4-ethylphenol) (6c). 90% yield; R_f = 0.34 (5% MeOH in $CHCl_3$); clear and colorless solid; mp = 130°C; FTIR (KBr, cm^{-1}): 3301 (br, OH), 1499 (vs, C—C), 1460 (m, N—CH_3), 1251 (s, C—N), 1207 (m, C—N—C), 821 (s, C—N—C); ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.17 (t, 6H, Ar—CH_2—**CH_3**), 2.25 (s, 3H, N—**CH_3**), 2.54 (q, 4H, Ar—**CH_2**—CH_3), 3.72 (s, 4H, Ar—**CH_2**—N), 6.73 (d, 2H, Ar—**H**), 6.87 (s, 2H, Ar—**H**), 6.94 (d, 2H, Ar—**H**). Anal. calcd. for $C_{19}H_{25}NO_2$: C, 76.26; H, 8.36; N, 4.68. Found: C, 76.24; H, 8.35; N, 4.65.

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