CHAPTER II

SELF TERMINATION OF BENZOXAZINE DIMER: AN OBSTRUCTIVE EFFECT ON POLYMERIZATION OF *p*-SUBSTITUTED PHENOL-BASED BENZOXAZINE MONOMERS

Abstract

The ring opening polymerization 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 how the stereo structure of the compound controls the reaction and prevents the polymerization that would be expected from the mechanism.

Introduction

3,4-Dihydro-1,3-2H-benzoxazines are known as heterocyclic compounds made 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 a ring opening reaction to obtain a polymer chain with methylene-amine-Mannich bridges at both the ortho and para positions, [-Ph(OH)-CH_2-NR-CH_2-][2-6] (eq 1, Scheme I). Ishida et al.[6-7] proposed that bifunctional phenol-based polybenzoxazines are novel phenolic resins with superb physical and mechanical properties (eq 2, Scheme I).

Since the repeat unit of benzoxazine resembles that of calixarenes, it might be assumed that benzoxazines have a supramolecular structure like calixarenes (Scheme II). For the past few years, our group has paid attention to molecular design of monofunctional phenol-based benzoxazines to achieve a controlled structure namely azamethylene phenol derivatives. It is important to note that, although the reaction and mechanism of ring-opening benzoxazines have been studied since 1952[2], *p*-substituted phenol-based benzoxazines and azamethylene phenols are rarely reported. Based on the reverse Mannich reaction,[8] *p*-substituted phenol, in theory, can produce a high molecular weight linear polymer (eq 3, Scheme I), since the aza-methylene linkage is generated at only the ortho positions in the structure. We attempted to prepare the linear or cyclic aza methylene phenol by using a series of *p*-substituted phenols. However, the polymerization of *p*-substituted phenol based benzoxazines does not proceed as expected. The many reaction conditions we have studied allows us to conclude that the ring opening of *p*-substituted phenols provide neither linear oligomer nor polymer, but only the dimer product.

The present article, thus, are to clarify (i) if indeed we never obtain 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 expectation but also to design a synthesis pathway considering the factors involved at the monomer level.

Results and Discussion

Benzoxazine Dimerization. Carboxylic acids and phenol derivatives are known as acid catalysts for the ring opening reaction of benzoxazine.[5,10] Ishida et al. reported that the ring opening is preferable in high dielectric constant solvents, such as MeOH.

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 suggests that only the starting materials were present in the solution. 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, while those for **1a** and *p*-cresol are found at t_R 3.344 and 3.418 min, respectively.

From FTIR data (Figure 2), the white product gives rise to the band at 3226 cm^{-1} and also a broad band at 3100-2600 cm^{-1}. Daimay et al.[11] reported a broad band at 3200-2600 cm^{-1} corresponding to the strong OH---N bond. A detailed band assignment of benzoxazine OH groups has been reported.[12] Thus, we conclude 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 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 ^1H NMR spectrum of **1a** shows two singlet peaks at δ_H = 4.07 and 4.95 ppm while that of the white precipitate (Figure 3) shows a singlet resonance at δ_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 resonances of aromatic protons could be observed; however, only three resonances 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. Reiss et al.[5] proposed a mechanism catalyzed by dissociation of phenol. In order to overcome the dimerization, we concentrated on finding the optimal amount of *p*-cresol and solvent as well as reaction time and temperature.

Regardless of the variation of the molar ratio and type of solvents, to our surprise, only 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, the generation of **4a** is largely dependent on the amount of *p*-cresol (Figure 4). When the molar ratio of **1a** : *p*-cresol increases, the yield of the dimer also increases. 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 III. However the compound obtained is a single component and its characterization does not correspond to the mono-oxazine we reported previously.[12]

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 non-polar ones (yield 40-60%) give higher yields than the polar ones (18-35%). This implies that the reaction is preferably carried out with non-polar solvents (see the speculated mechanism).

Neat Liquid State Reaction. In order to focus on the effect of the reaction temperature free of the solvent effect, the reactions were carried out in neat molten state. After heating the mixture of **1a** and *p*-cresol in various ratios, 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 and this corresponds to dimer **4a** (Figure 3).

Figure 7 shows the comparative studies between neat and solvent (xylene) conditions with a fixed molar ratio of **1a** and *p*-cresol at 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 140°C) condition as reported by Reiss et al.,[5] the precipitation of dimer **4a** is decreased to 2-3% (Figure 7). At the same time the neat liquid became a dark-brownish highly viscous liquid. A further study by LC-MS indicates the various fragments belonging to the dimer as well as other incomplete structures associated with the starting materials (Figure 8). A trace fragment of higher molecular weight than dimer is also observed. This fragment 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°C and 135°C, our results indicate that even a lesser amount (stoichimetric 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 active species are deactivated by heat.[5] Thus, the high yield of 4a in the case of stoichiometric imbalance might result because the reactive species, 1a, was 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 as compared to 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 approximately 0.8-0.9. Our speculation is strongly supported by the results that **4b-4c**, **5a-5c**, and **6a-6c** (Scheme IV) 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 opening polymerization. In fact, Reiss 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. Though the structural characterization of the purified product in those cases were not reported in detail, the results support our speculation about the self termination of dimer.

It is known that the cyclization might be successful in dilute conditions.[13] 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 $5x10^{-3}$ M. These systems did not even give a white precipitate as in the previous reactions and the reactants remained in the solution.

Speculated Mechanism. Combining 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 V, in the initiation step, 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 oxygen atom of the oxazine ring to form an iminium that further reacts with the phenol derivative. If the phenol derivative were 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 in the initial step (Scheme V). At this step, an effective ring opening requires thermal activation while the hydrogen bonding 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 certain temperature (at 65°C) rather than a monotonous trend.

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, non-polar solvents promote the hydrogen bonding between the benzoxazine and phenol derivatives. The significant yield of dimer in the non-polar 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.

Effect of Stereo Structure of Dimer. 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.[12] The X-ray structural analyses of dimers (**4a-4c**, **5a-5c**, and **6a-6c**)[14] shows that *p*-substituted based benzoxazines have inter- and intramolecular hydrogen bonds that stabilize the compounds. 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.

Experimental Section

Chemicals. Paraformaldehyde was purchased from Sigma (U.S.A.). *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, isopropanol, mixed xylenes, isobutanol, 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 as reported elsewhere (Scheme IV).[9] The ^1H nuclear magnetic resonance (NMR) spectrometer was 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 sulfate (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), isopropanol (iso-PrOH), isobutanol (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 (Scheme IV) were qualitatively analyzed by FTIR, ^{1}H NMR, HPLC, LC-MS, and EA.

***N,N*-Bis(2-hydroxy-5-methylbenzyl)cyclohexylamine, 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); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (2H, m, **CH$_2$**), 1.45 (4H, m, **CH$_2$**), 1.82 (4H, m, **CH$_2$**), 2.22 (6H, s, **CH$_3$**-Ar), 2.70 (1H, m, **CH**), 3.72 (4H, s, Ar-**CH$_2$**-N), 6.68 (2H, d, Ar-**H**), 6.85 (2H, s, Ar-**H**), 6.90 (2H, d, Ar-**H**). Anal. calcd for $C_{22}H_{29}NO_2$: C, 77.88; H, 8.55; and N, 4.13. Found: C, 77.90; H, 8.56; and N, 4.16.

***N,N*-Bis(2-hydroxy-5-methylbenzyl)propylamine, 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); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.87 (3H, t, **CH_3**-CH_2-CH_2-N), 1.65 (2H, m, CH_3-**CH_2**-CH_2-N), 2.22 (6H, s, **CH_3**-Ar), 2.50 (2H, t, CH_3-CH_2-**CH_2**-N), 3.70 (4H, s, Ar-**CH_2**-N), 6.68 (2H, d, Ar-**H**), 6.85 (2H, s, Ar-**H**), 6.90 (2H, d, Ar-**H**). Anal. calcd for $C_{19}H_{25}NO_2$: C, 76.25; H, 8.36; and N, 4.69. Found: C, 76.28; H, 8.31; and N, 4.70.

***N,N*-Bis(2-hydroxy-5-methyl benzyl)methylamine, 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); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.23 (6H, s, Ar-**CH_3**), 2.23 (3H, s, N-**CH_3**), 3.69 (4H, s, Ar-**CH_2**-N), 6.70 (2H, d, Ar-**H**), 6.83 (2H, s, Ar-**H**), 6.86 (2H, d, Ar-**H**). Anal. calcd for $C_{17}H_{21}NO_2$: C, 75.28; H, 7.75; and N, 5.17. Found: C, 75.31; H, 7.77; and N, 5.19.

***N,N*-Bis(2-hydroxy-3,5-dimethylbenzyl)cyclohexylamine, 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); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (2H, m, **CH_2**), 1.45 (4H, m, **CH_2**), 1.82 (4H, m, **CH_2**), 2.20 (6H, s, **CH_3**-Ar), 2.22 (6H, s, **CH_3**-Ar), 2.70 (1H, m, **CH**), 3.72 (4H, s, Ar-**CH_2**-N), 6.70 (2H, s, Ar-**H**), 6.85 (2H, s, Ar-**H**). Anal. calcd for $C_{24}H_{33}NO_2$: C, 78.47; H, 8.99; and N, 3.82. Found: C, 78.49; H, 8.97; and N, 3.85.

***N,N*-Bis(2-hydroxy-3,5-dimethylbenzyl)propylamine, 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); ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.85 (3H, t, **CH_3**-CH_2-CH_2-N), 1.65 (2H, m, CH_3-**CH_2**-CH_2-N), 2.20 (6H, s, **CH_3**-Ar), 2.22 (6H, s, **CH_3**-

Ar), 2.50 (2H, t, CH_3-CH_2-**CH_2**-N), 3.65 (4H, s, Ar-**CH_2**-N), 6.70 (2H, s, Ar-**H**), 6.85 (2H, s, Ar-**H**). Anal. calcd for $C_{21}H_{29}NO_2$: C, 77.06; H, 8.87; and N, 4.28. Found: C, 77.05; H, 8.86; and N, 4.27.

***N,N*-Bis(2-hydroxy-3,5-dimethylbenzyl)methylamine, 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 (200MHz, $CDCl_3$, ppm): δ_H 2.22 (12H, s, Ar-**CH_3**), 2.25 (3H, s, N-**CH_3**), 3.68 (4H, s, Ar-**CH_2**-N), 6.72 (2H, s, Ar-**H**), 6.81 (2H, s, Ar-**H**). Anal. calcd for $C_{19}H_{25}NO_2$: C, 76.26; H, 8.36; and N, 4.68. Found: C, 76.27; H, 8.34; and N, 4.69.

***N,N*-Bis(2-hydroxy-5-ethyl benzyl)cyclohexylamine, 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 (3H, t, **CH_3**-CH_2-CH_2-N), 1.15 (2H, m, **CH_2**), 1.45 (4H, m, **CH_2**), 1.82 (4H, m, **CH_2**), 2.52 (2H, q, CH_3-**CH_2**-Ar), 2.70 (1H, m, **CH**), 3.72 (4H, s, Ar-**CH_2**-N), 6.72 (2H, d, Ar-**H**), 6.87 (2H, s, Ar-**H**), 6.94 (2H, d, Ar-**H**). Anal. calcd for $C_{24}H_{33}NO_2$: C, 78.47; H, 8.99; and N, 3.82. Found: C, 78.51; H, 8.97; and N, 3.79.

***N,N*-Bis(2-hydroxy-5-ethylbenzyl)propylamine, 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 (3H, t, **CH_3**-CH_2-CH_2-N), 1.18 (3H, t, **CH_3**-CH_2-Ar), 1.65 (2H, m, CH_3-**CH_2**-CH_2-N), 2.52 (2H, q, CH_3-**CH_2**-Ar), 2.52 (2H, t, CH_3-CH_2-**CH_2**-N), 3.70 (4H, s, Ar-**CH_2**-N), 6.72 (2H, d, Ar-**H**), 6.87 (2H, s, Ar-**H**), 6.94 (2H, d, Ar-**H**). Anal. calcd for $C_{21}H_{29}NO_2$: C, 77.06; H, 8.87; and N, 4.28. Found: C, 77.08; H, 8.89; and N, 4.31.

***N,N*-Bis(2-hydroxy-5-ethylbenzyl)methylamine, 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 (6H, t, Ar-CH_2-**CH_3**), 2.25 (3H, s, N-**CH_3**), 2.54 (4H, q, Ar-**CH_2**-CH_3), 3.72 (4H, s, Ar-**CH_2**-N), 6.73 (2H, d, Ar-**H**), 6.87 (2H, s, Ar-**H**), 6.94 (2H, d, Ar-**H**). Anal. calcd for $C_{19}H_{25}NO_2$: C, 76.26; H, 8.36; and N, 4.68. Found: C, 76.24; H, 8.35; and N, 4.65.

Conclusions

Although, in theory, a linear polymer can be obtained from the ring opening polymerization of *p*-substituted phenol-based benzoxazines, the present work shows that in practice it will be difficult to achieve the polymer using a phenolic derivative as an initiator. 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 as compared to phenol dissociation. Combining this with our previous X-ray structure analyses, we conclude that the obstructive effect of dimer in polymerization might result from the stable 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 (Scheme III) 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 III.

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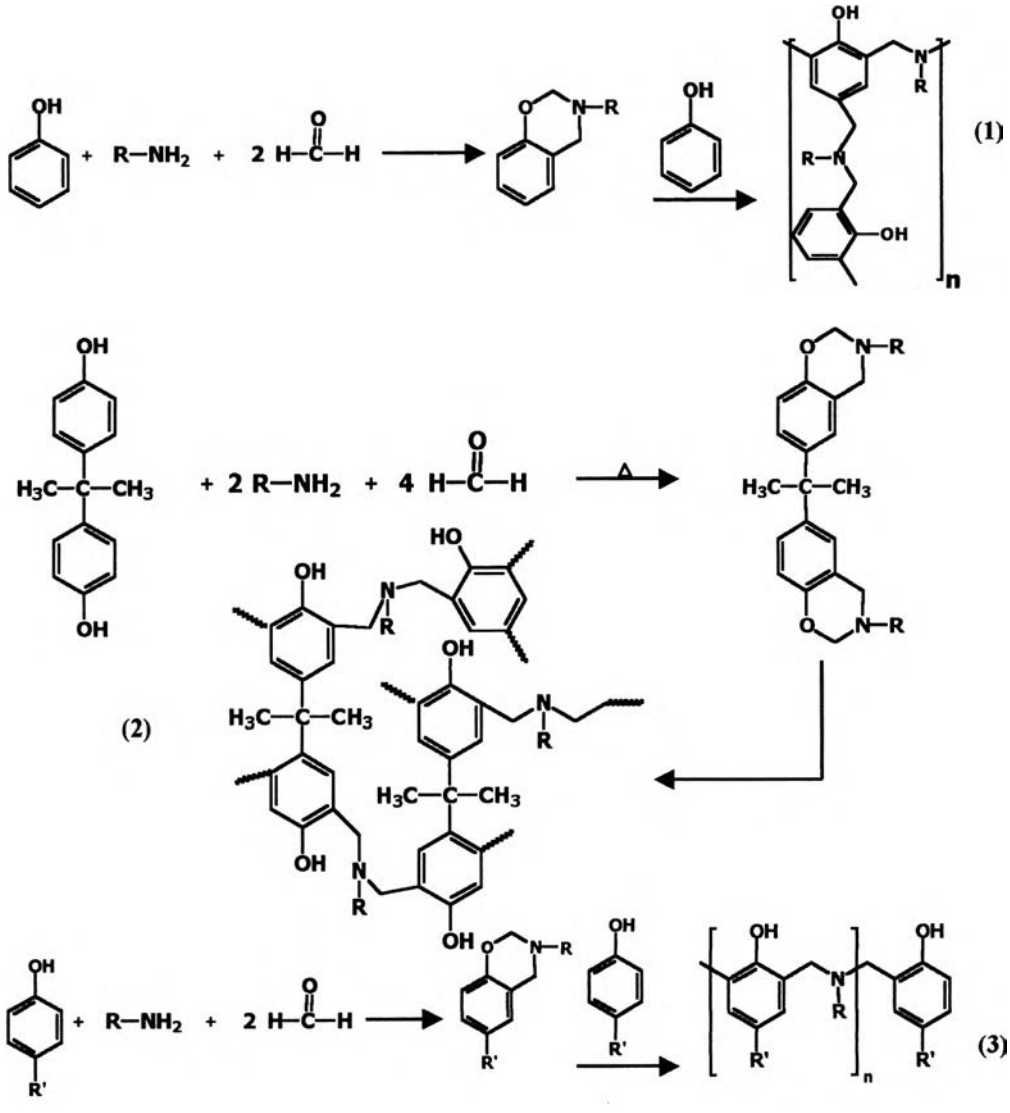
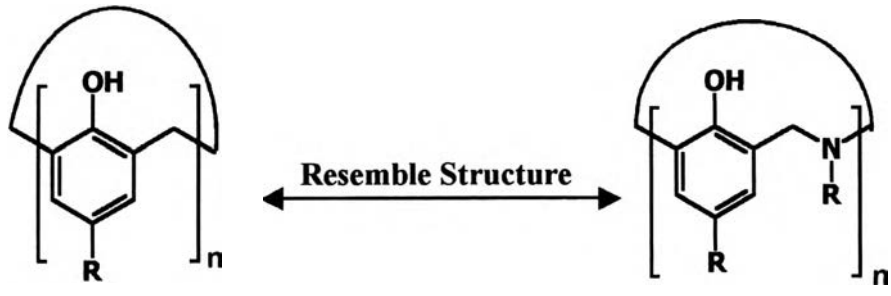
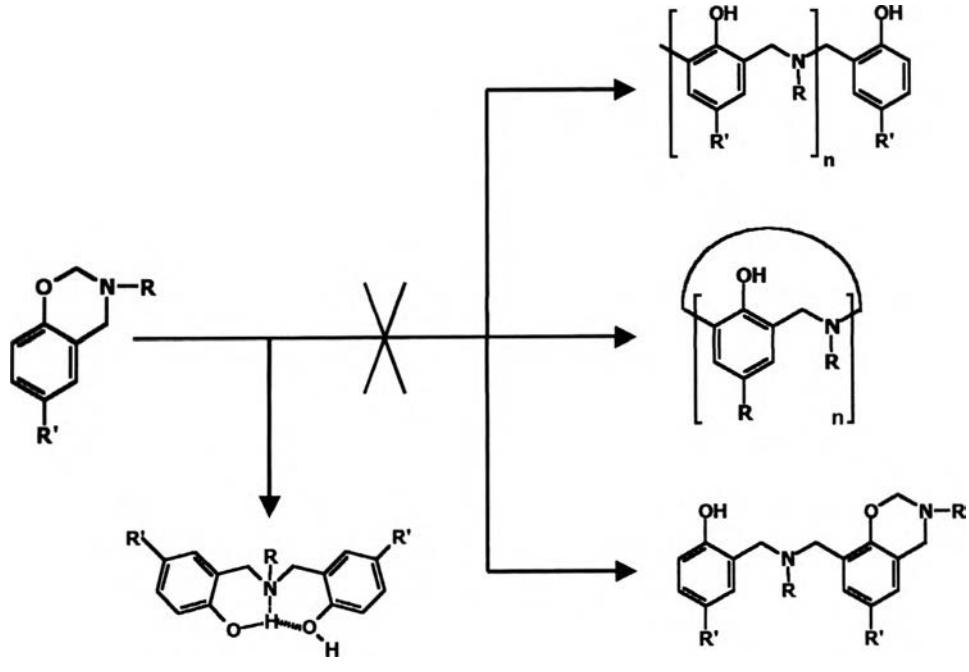


Scheme I. (Apirat et al.)

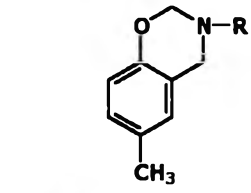


Calixarenes **Pseudocyclic / Cyclic Benzoxazine**

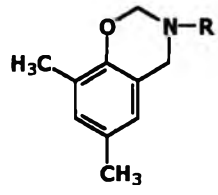
Scheme II. (Apirat et al.)



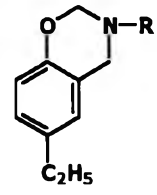
Scheme III. (Apirat et al.)



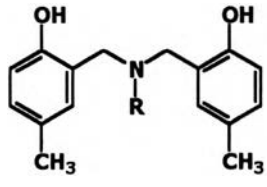
R = -C_6H_{11}(1a)
= -C_3H_7 (1b)
= -CH_3 (1c)



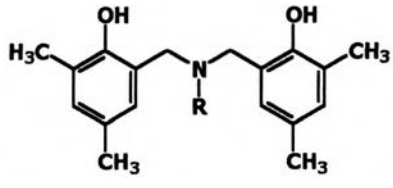
R = -C_6H_{11}(2a)
= -C_3H_7 (2b)
= -CH_3 (2c)



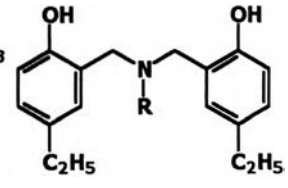
R = -C_6H_{11}(3a)
= -C_3H_7 (3b)
= -CH_3 (3c)



R = -C_6H_{11}(4a)
= -C_3H_7 (4b)
= -CH_3 (4c)

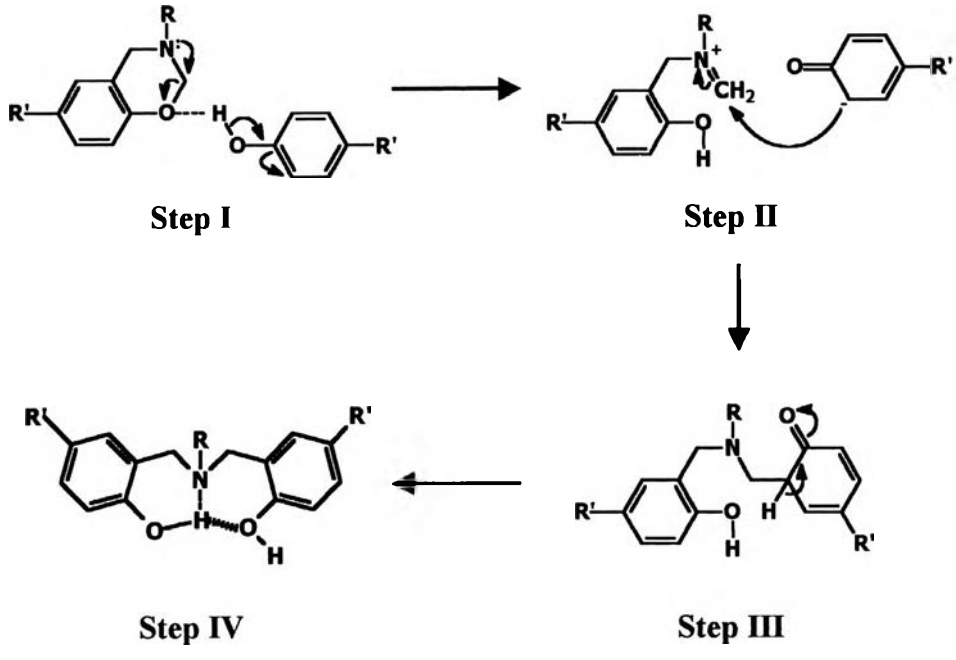


R = -C_6H_{11}(5a)
= -C_3H_7 (5b)
= -CH_3 (5c)



R = -C_6H_{11}(6a)
= -C_3H_7 (6b)
= -CH_3 (6c)

Scheme IV. (Apirat et al.)



Scheme V. (Apirat et al.)

Figure Captions

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

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

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

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.

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 (X)180°C in neat condition.

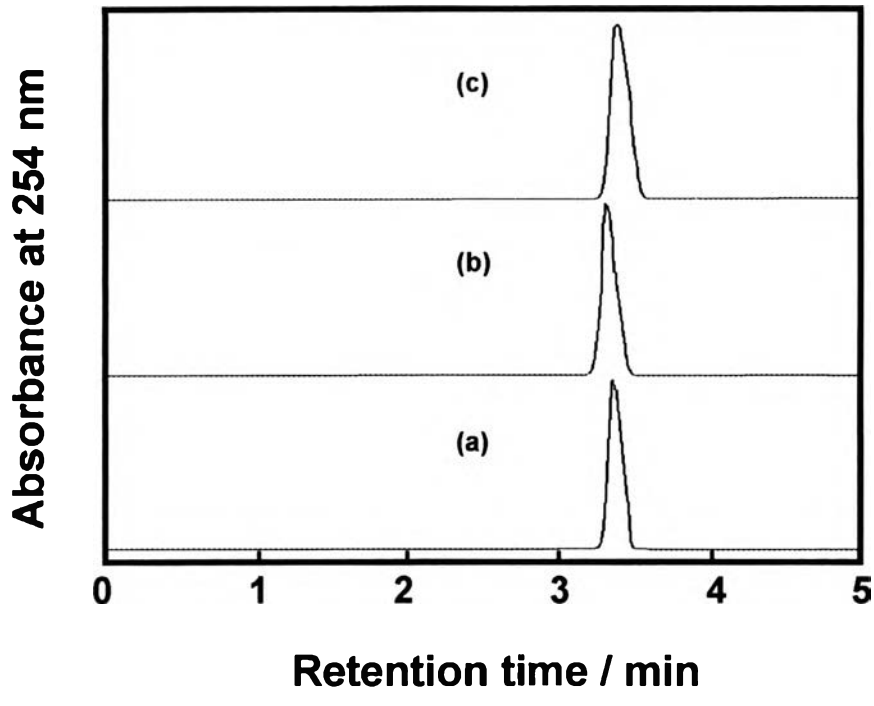


Figure 1. (Apirat et al.)

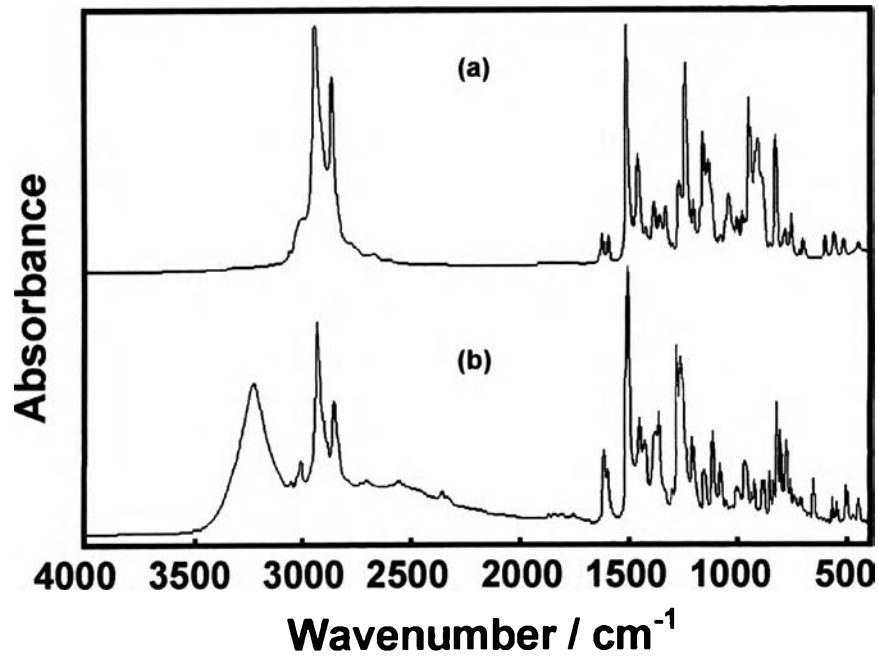


Figure 2. (Apirat et al.)

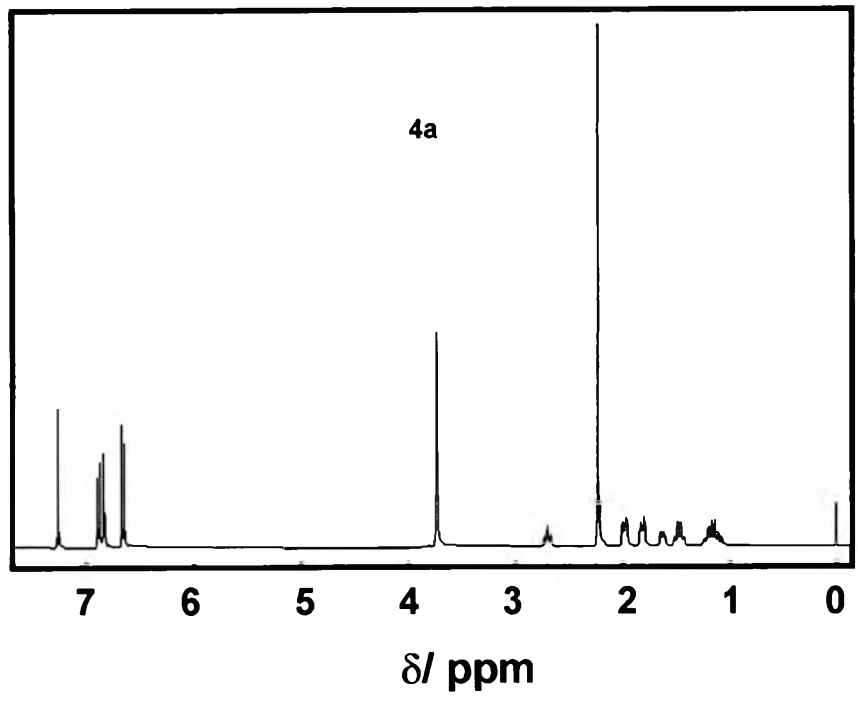


Figure 3. (Apirat et al.)

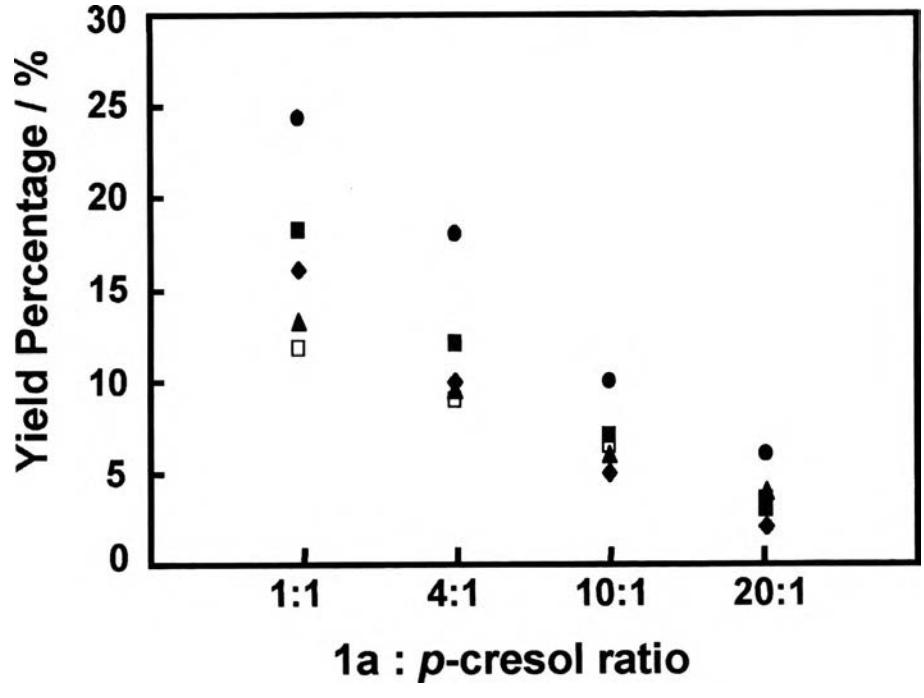


Figure 4. (Apirat et al.)

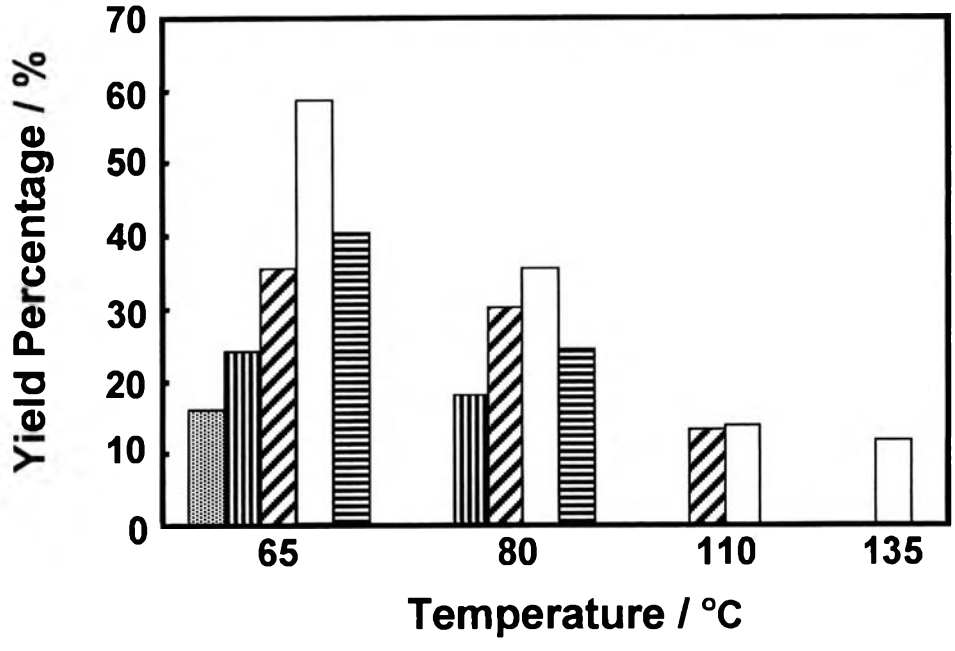


Figure 5. (Apirat et al.)

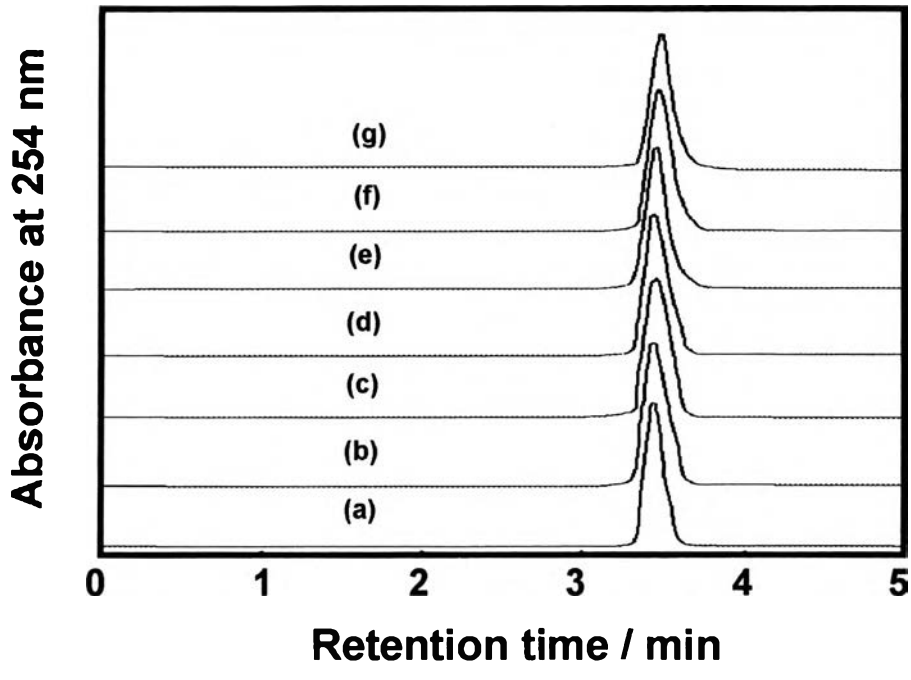


Figure 6. (Apirat et al.)

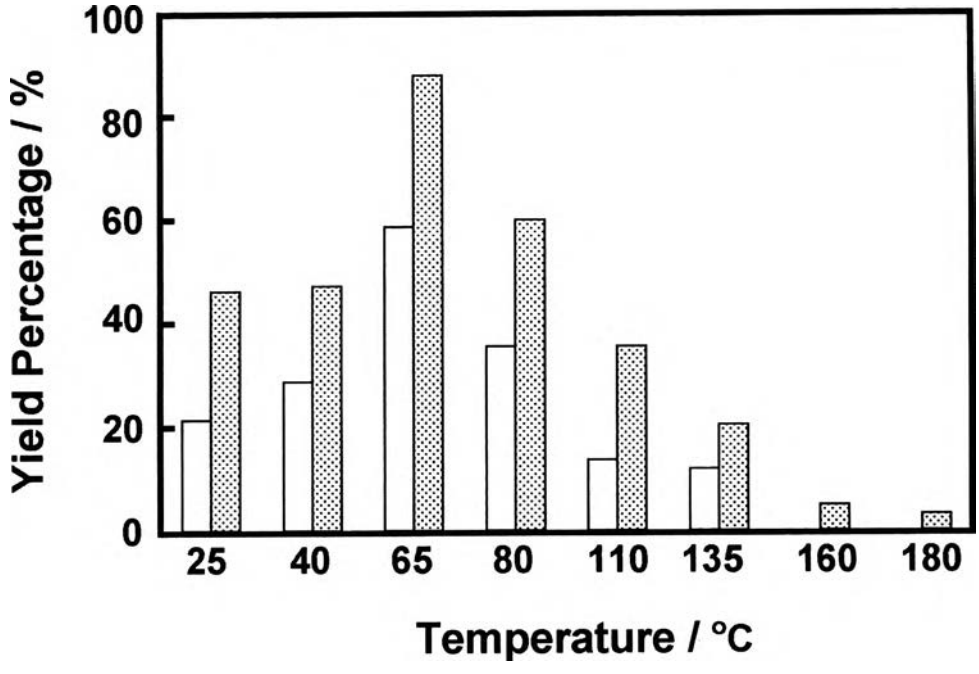


Figure 7. (Apirat et al.)

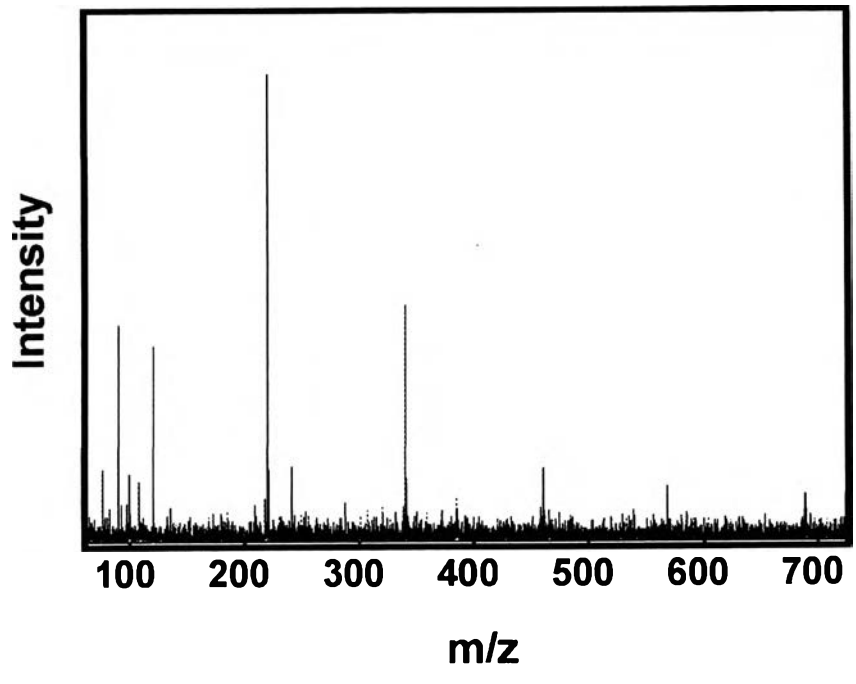


Figure 8. (Apirat et al.)

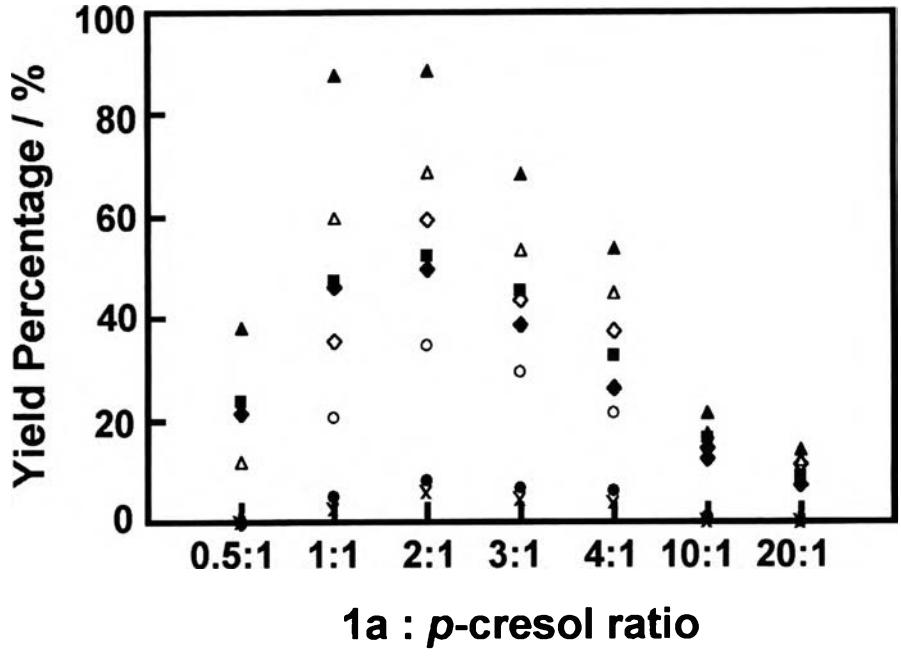


Figure 9. (Apirat et al.)