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Polymerization of *p*-cresol, formaldehyde, and piperazine and structure of monofunctional benzoxazine-derived oligomers

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ABSTRACT

By using a secondary amine, e g. piperazine, a Mannich base polymer, having similar structure to the traditional polybenzoxazine, is synthesized. Unlike all the reported polybenzoxazines that are colored, the white polymer shows good thermal property that is close to the degradation temperature of the polybenzoxazine derived from difunctional benzoxazine monomers. ^{31}P NMR spectroscopy in combination with facile phosphorus derivatization and previous model compound studies are utilized to clarify the structures of piperazine-based systems as well as the main chain and end group of traditional polybenzoxazines.

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1. Introduction

Polybenzoxazine is known as a polymer with a chemical structure of aza-methylene phenol repeating unit obtained from the cationic ring-opening polymerization of benzoxazine monomer. Benzoxazine monomer can provide linear (Scheme 1a) or cross-linked polymers, depending on the number of benzoxazine rings per molecule and existence of other reactive sites (Scheme 1b). Unusual properties of this polymer have been reported [1–6]. Excellent review articles attest the wide-spread and strong interest in polybenzoxazine research throughout the world [7–13]. In addition to the development of traditional monomeric benzoxazine resins, new classes of polybenzoxazines have been actively studied in the past several years. These classes of materials are polymeric having benzoxazine groups either at the main chain [14–33], side chain [34–41] or chain end [42–44]. These polymeric or oligomeric chains are capable of further cross-linking, showing the advantageous properties of both thermoplastics and thermosetting resins.

Riess *et al.* found that the polymerization of monofunctional benzoxazine (Scheme 1c) proceeded with a limit of four to six repeating units [45]. Moreover, Laobuthee, *et al.* found an unexpected single oxazine ring from the Mannich reaction between benzoxazine dimer, formaldehyde, and amine because one hydroxyl group forms a very stable intramolecular hydrogen bonding and prevents one of the phenolic groups from reacting (Scheme 2) [46]. This product is always produced without any specific conditions or catalyst. The hydrogen bonding deactivates the reactivity of the ortho- position of the ring.

Recently, our group has synthesized a Mannich base compound from *p*-cresol (or *p*-methylanisole, *p*-methoxyphenol, 3,4,5-trimethylphenol), formaldehyde, and piperazine (Scheme 3), which will be reported in this paper. Primary amines, which have two adjacent reactive hydrogen atoms, present a problem in the Mannich reaction because they can react in a number of different ways to give mixtures containing labile or cyclic products such as benzoxazine monomer and dimer [8]. In contrast, secondary amine has only one reactive hydrogen atom and is much less prone to side reaction. The Mannich oligomers obtained from phenol, formaldehyde, and piperazine had previously been synthesized [47–49] and reported as having a good selectivity for copper and mercury ions [50–53]. This class of polymers was also used as a property modifier for epoxy resins [54]. However polymer structures were poorly characterized. Therefore, it will be important to verify what is the final product of this Mannich product. Furthermore, the knowledge obtained from this Mannich product based on the secondary amine will aid in understanding the structure of the Mannich product from polymerization of *p*-cresol and methylamine based benzoxazine (abbreviated as *p*C-m) by simplifying the side reactions. The clarification will be a useful guidance how the

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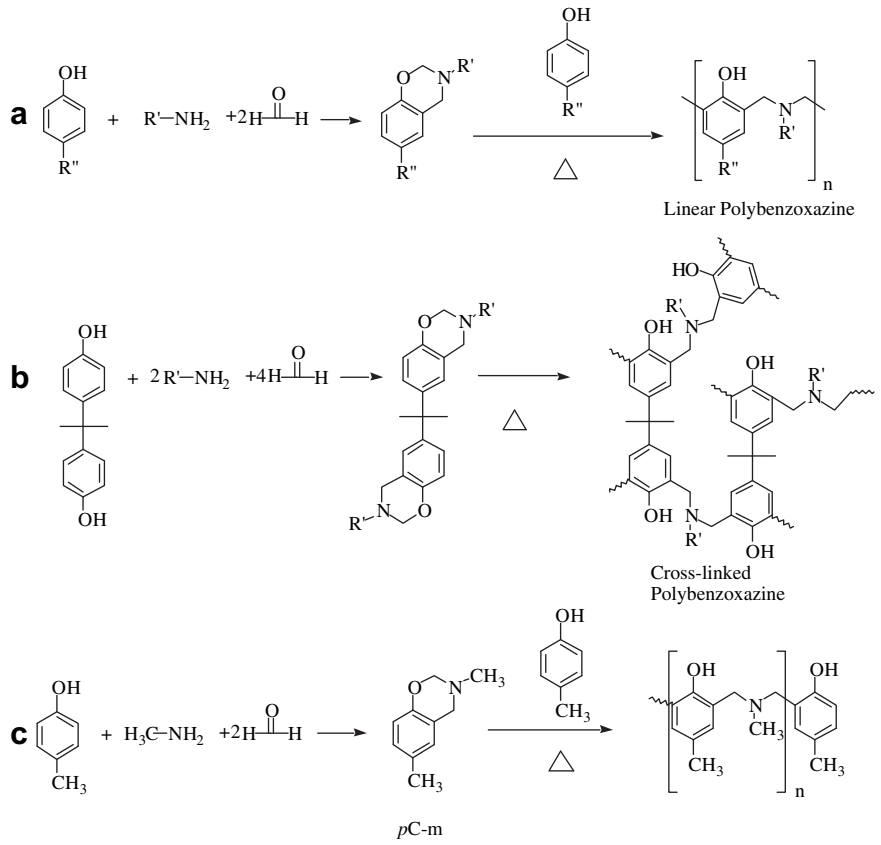
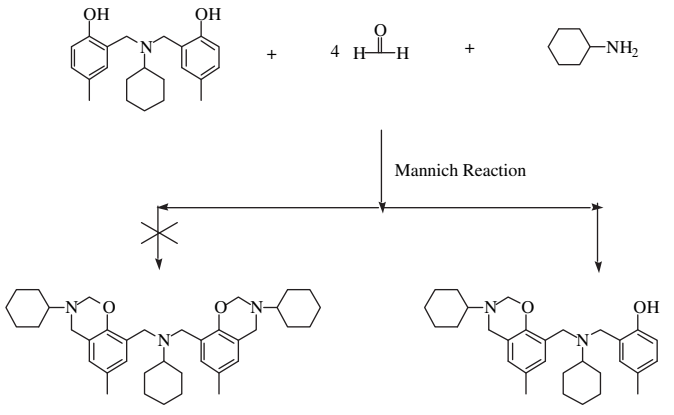


Scheme 1. (a) Synthesis of linear polybenzoxazine (b) synthesis of cross-linked polybenzoxazine (c) *p*-cresol, methylamine based benzoxazine (*p*C-m) synthesis and expected reaction product (R', and R" are substituents).

chain is terminated, and also the answer to whether or not we obtain a desired Mannich bridge structure polymerized in traditional conditions for benzoxazine.

The chemical repeat unit in polybenzoxazine, including terminal and other reaction by-products, contains labile phenolic hydroxyl groups. These functional groups could serve as a means for attaching a nucleus that would give strong and well-separated nuclear magnetic resonance (NMR) signals for the structural identification [55]. The particular nucleus used is phosphorus, because phosphorus has a large range of chemical shift, ~700 ppm, which ensures a good separation of signals of the ^{31}P resonances in different environments. The sensitivity of a ^{31}P NMR experiment is 377 times more than carbon and only about 15 times less than that of a proton NMR experiment [56]. Furthermore, it is well known that derivatization of a phenolic group with phosphorus halides is quantitative and rapid [57–60]. This is very significant in order to ensure reliable results. Recently, our group utilized ^{31}P NMR spectroscopy to examine the structure of benzoxazine by using phenolic and benzoxazine oligomer model compounds [61]. Despite the fact that many papers on benzoxazine-based polymers have been reported, very few papers studied the chain structure of the polymerizing benzoxazine systems. Therefore, it is our interest to further the understanding of the chain structure of the polymerizing benzoxazine systems, in particular, using a Mannich polymer that is made of secondary amine rather than the usual primary amine systems.



Scheme 2. Unexpected product from Mannich reaction between dimer, formaldehyde, and cyclohexylamine.

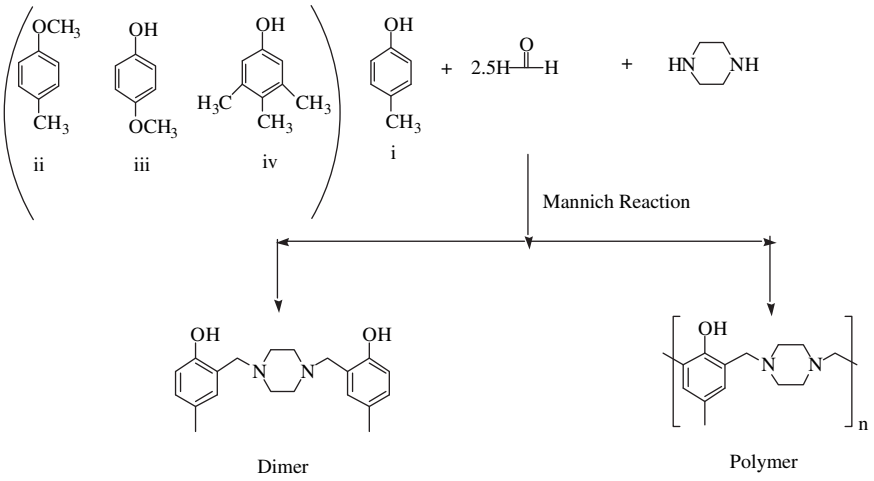
2. Experimental

2.1. Starting materials

All the chemicals were purchased from Aldrich Chemical Company and used as received.

2.2. Polymerization using p-cresol, formaldehyde, and piperazine (Scheme 3)

p-Cresol (10.8 g, 0.10 mol) and piperazine (8.60 g, 0.10 mol) were dissolved in 95% aqueous ethanol (200 ml) and stirred as 0.25 mol of 37% aqueous formaldehyde solution was slowly added at 0 °C. After 4 h at room temperature, the mixture was heated with



Scheme 3. Possible products from Mannich reaction between p-cresol, formaldehyde, and piperazine.

stirring at 115 °C for 48 h. The resulting polymer precipitate was filtered and washed with ethanol at room temperature. The polymer was purified by precipitation from hot toluene with petroleum ether.

2.3. Benzoxazine polymerization (Scheme 1c)

2.3.1. Synthesis of 3,6-dimethyl-2H, 4H-benzo[e]1,3-oxazine (pC-m, Scheme 1C) [1]

The mole ratio of the reagents, amine:formaldehyde:phenol, was 1:2:1 for the synthesis of *p*C-m. A solution of 0.40 mol (32.5 g, 30.0 ml) of formaldehyde in 50 ml of 1,4-dioxane was stirred with 0.2 mol (15.5 g, 17.2 ml) of methylamine solution in 20 ml of 1,4-dioxane while being chilled in an ice bath for 20 min. To this mixture was added 0.20 mol (21.6 g, 19.2 ml) of *p*-cresol in 50 ml of dioxane. The mixture was then heated, stirred, and allowed to reflux for 5 h. After the mixture was allowed to cool to room temperature, the solvent was removed by a rotary evaporator. The resulting yellow oil was dissolved in 200 ml of ethyl ether and washed with 5 × 50 ml of 1.5 N aqueous sodium hydroxide solution to remove unreacted −OH groups. The ethereal solution was dried over anhydrous sodium sulfate overnight. After ether was removed by a rotary evaporator, the benzoxazine monomer was a very pale yellow liquid. With only slight chilling, *p*C-m easily turned to solid and was stable at room temperature. Further purification was done by sublimation, which produced a clear, colorless needle-like crystal. Yield: 70%; ^{1}H NMR (200 MHz, $CDCl_3$, 273 K): δ 2.25 (3H, Ar−CH_3), 2.59 (3H, N−CH_3), 3.92 (2H, Ar−CH_2−N), 4.79 (2H, O−CH_2−N), 6.67–6.79 (3H, Ar−H); ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ 20.0 (1C, Ar−C), 39.1 (1C, N−CH_3), 51.3 (1C, Ar−C−N), 83.1 (1C, O−C−N), 115.4–152.0 (6C, Ar).

2.3.2. Synthesis of 2,6-bis({[(2-hydroxy-3,5-dimethylphenyl) methyl]methylamino} methyl)-4-methylphenol (Methyl-trimer) [62]

The starting monomer, 3,6,8-trimethyl-2H, 4H-benzo[e]1,3-oxazaperhydroine prepared according to the previous literature58 and p-cresol by the ratio of 1:1 were added together and heated at 80 °C for 12 h, resulting in yellow product. Purification was done by recrystallization from hexane. Then, this product was reacted again with an equimolar portion of the 3,6,8-trimethyl-2H, 4H-benzo[e] 1,3-oxazaperhydroine monomer at 80 °C for 48 h. The resulting yellow product was cooled and was subsequently purified by column chromatography with silica gel using hexane/acetone (20:1) as the eluent. White fine crystal; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.22, 2.21 (15H, Ar−CH_3), 2.22 (6H, N−CH_3), 3.68 (8H, Ar−CH_2−N), 6.70, 6.84, 6.86 (6H, Ar−H); ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ 15.8, 20.3 (5C, Ar−CH_3), 41.0 (2C, N−CH_3), 58.8–59.6 (4C, Ar−C−N), 122.1–154.0 (18C, Ar).

2.3.3. Synthesis of 6-({[(2-hydroxy-3,5-dimethylphenyl)methyl] methylamino}methyl)-2-[({[2-hydroxy-3-({[(2-hydroxy-3,5-dimethylphenyl)methyl]methylamino}methyl)-5-methylphenyl] methyl}methylamino)methyl]-4-methylphenol (Methyl-tetramer) [62]

2-({[(2-hydroxy-5-methylphenyl)methyl]methylamino} methyl)-4-methylphenol and 3,6,8-trimethyl-2H, 4H-benzo[e]1,3-oxazaperhydroine monomer (1:2 mol ratio) were refluxed in chloroform for 48 h. After the reaction mixture was cooled to room temperature, chloroform was removed with a rotary evaporator, and the resulting yellow solid was subsequently purified by column chromatography with silica gel using hexane/acetone (20:1) as the eluent. White fine powder; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.22, 2.21 (18H, Ar−CH_3), 2.23 (9H, N−CH_3), 3.63, 3.66 (12H, Ar−CH_2−N), 6.66, 6.84, 6.86 (8H, Ar−H); ^{13}C NMR (200 MHz, $CDCl_3$, 298 K): δ 15.8, 20.3 (6C, Ar−CH_3), 41.0 (3C, N−CH_3), 57.6–59.6 (6C, Ar−C−N), 121.8–153.7 (24C, Ar).

2.3.4. Synthesis of 6-[(2-hydroxy-3,5-dimethylphenyl)methyl]-2,4-dimethylphenol [63]

2,4-Dimethylphenol (3.1 g, 25 mmol) was refluxed with 5 %w/w aqueous sodium hydroxide (25.0 g, 31 mmol) and 37 %w/w aqueous formaldehyde (4.14 g, 51 mmol) for 4 h. The dark brown mixture was cooled and neutralized with glacial acetic acid (3 cm^3). The pale precipitates were washed with water and dried in vacuum to give a mustard yellow powder (4.3 g, 67%). Recrystallization from chloroform/petroleum ether gave a pale yellow product; yield 78%; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.12 (6H, Ar−CH_3), 2.23 (6H, Ar−CH_3), 3.85 (2H, CH_2), 6.02 (2H, OH), 6.80 (2H, Ar−H), 6.94 (2H, Ar−H); ^{3}C NMR (200 MHz, $CDCl_3$, 298 K): δ 16.0, 20.4 (4C, Ar−C), 31.2 (1C, Ar−CH_2), 123.8–148.8 (12C, Ar).

2.3.5. Benzoxazine polymerization

The effect of solvent was avoided by employing a melt polymerization method. The monomer was reacted with an initiator in the melt state. The conditions are stated in Table 1. The polymerization was carried out in a closed system, under nitrogen gas.

Table 1
Benzoxazine Curing Condition.

Exp.	Benzoxazine	Initiator (% by mole)	Temperature	Time
A	*p*C-m	*p*-Cresol (100)	Step 1:140 °C Step 2:160 °C	Step 1: 1 h 30 min Step 2: 30 min
B	*p*C-m	*p*-Cresol (5)	Step 1:140 °C Step 2:160 °C	Step 1:1 h 30 min Step 2: 30 min
C	*p*C-m	2,4-Dimethyl-phenol (5, 10, 15)	145 °C	30 min
D	*p*C-m	2,4-Dimethyl-phenol (5, 10, 15)	160 °C	30 min
E	BA-m (Scheme 1b, R′ = methyl)	–	Step 1:140 °C Step 2:160 °C	Step 1:1 h 30 min Step 2: 30 min

3. Characterization

3.1. Nuclear magnetic resonance spectroscopy (NMR)

3.1.1. ^{1}H and ^{13}C NMR

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were taken using Varian 200 MHz Gemini NMR spectrometer. The proton frequency of 200 MHz and its corresponding carbon frequency were used for the analysis. Deuterated chloroform (internal reference: tetramethysilane) was used as a solvent.

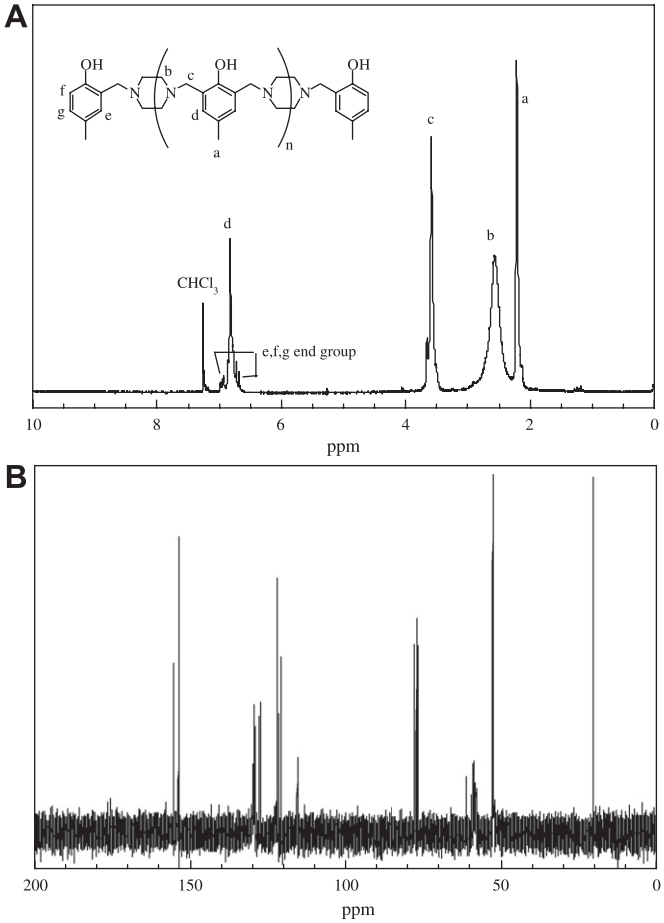


Fig. 1. (A) ^{1}H and (B) ^{13}C NMR of polymer product from polycondensation of *p*-cresol, formaldehyde, and piperazine.

Table 2
Summary of ^{1}H NMR and ^{13}C NMR spectra from Fig. 1.

	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(a) CH_3	2.35	21.5
(b) —N N—	2.50	55.4
(c) Ar—CH_2—N	3.62	51.0
(d) Ar—H	6.49[a], 6.50, 6.69[a], 6.70[a]	115.1, 123.1, 129.6, 129.7, 154.8, 155.3

[a] end group.

3.1.2. ^{31}P derivatization procedure

Samples (20 mg) were dissolved in a 1:1 mixture of $CDCl_3$ acted as a dissolving solvent, and pyridine acted as both a solvent and HCl acceptor in a 5-mm NMR tube. Phosphorination was achieved by adding 50 μl 1,3,2-dioxaphospholanyl chloride (132DOP; Scheme 2). The chloroform prevented the precipitation of the pyridine hydrochloride byproduct. The resulting solution was shaken for 30 min at room temperature prior to analysis.

3.1.3. ^{31}P NMR spectroscopy

The ^{31}P NMR spectra were measured on Varian XL-300 Spectrometer using a 5-mm broad band probe at room temperature. The spectrum was obtained at the phosphorous frequency of 121.44 MHz. The internal lock was provided by $CDCl_3$. All signals were referenced to the external standard, which is 85% H_3PO_4 (0 ppm) and/or the internal standard, which is a reaction product of 132DOP with water (121.34 ppm) [56]. An intensity at signal 121.34 ppm correlated with the moisture content in the sample and it was found that the position of this line was not affected by experimental conditions, and hence was a suitable reference signal. A spectral window was from 120.00 to 145.00 ppm. The acquisition time was 10 min and the number of transients was 256.

3.2. Size exclusion chromatography (SEC)

SEC analysis was performed on a Varian Prostar with a 254 nm fixed wavelength ultraviolet UV detector model 320, and RI detector model 350, equipped with Waters Styragel column (Lichrosphere 5RP18C25, 7.8 × 300 mm). Chromatographic grade tetrahydrofuran was used as an eluent. The purity was examined by Hewlett–Packard 6890 Gas Chromatography-5973 Mass Selective Detector. A molecular weight calibration curve was constructed

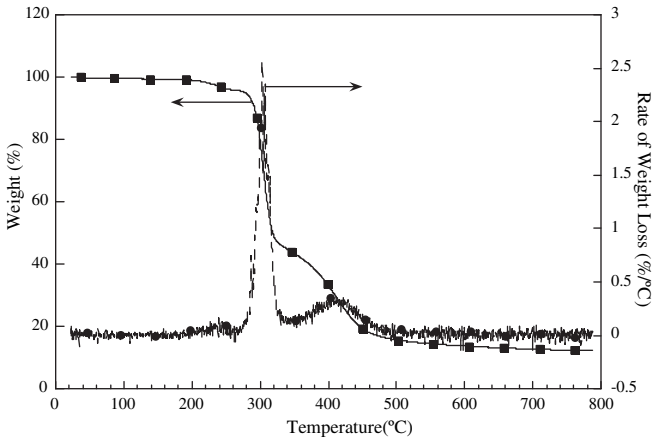


Fig. 2. TGA thermogram and derivative of weight loss of polymer product from polycondensation of *p*-Cresol, formaldehyde, and piperazine.

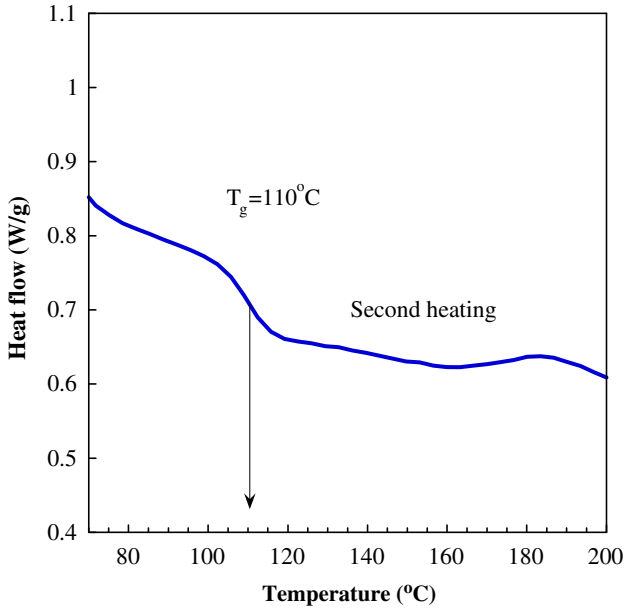


Fig. 3. Second DSC run of the piperazine-based poly(Mannich base).

based on various monodisperse anionic polymerized polystyrene (PDI = 1.02–1.06) from Toyosoda, Japan.

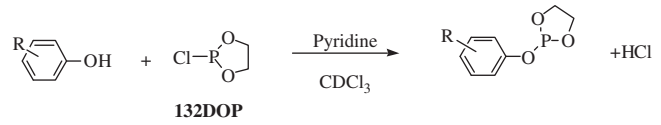
3.3. Themogravimetric analysis (TGA)

A TA Instrument 2950 Thermogravimetric Analyzer Hi-Res model 2950 was used for all TGA experiments that were carried out under nitrogen purge at a flow rate of 90 ml min^{-1}. A heating rate of 10 °C min^{-1} from room temperature to 800 °C was used.

4. Results and discussion

4.1. Polymer obtained from p-cresol, formaldehyde, and piperazine (Scheme 3)

After the polymer synthesis from *p*-cresol, formaldehyde, and piperazine for 48 h, a white solid was precipitated from the solution. The purification was done in hot toluene and petroleum ether. A colorless solid was obtained, which was soluble in chloroform and hot toluene but insoluble in ethanol. The ^{1}H and ^{13}C NMR



132DOP

Scheme 4. The derivatization reaction used throughout this work, i.e., the reaction of 1,3,2-dioxaphospholanyl chloride (132DOP) with active hydrogen compounds; R = substituent group.

spectra are shown in Fig. 1 and the results are summarized in Table 2. The aromatic hydrogen on the symmetrically substituted rings of the polymer structure gave singlet resonance at 6.50 ppm. We hypothesize that the multiple weak resonances around this singlet peak are signals from the terminal groups. However, it is difficult to verify with certainty, even in the ^{13}C NMR spectrum (Fig. 1B). The investigation of the terminal group will be reported later in this paper using ^{31}P NMR spectroscopy.

Fig. 2 shows the TGA thermogram of the Mannich polymer based on *p*-cresol and piperazine. This polymer exhibits high thermal stability. The 5% and 10% weight reduction temperature as abbreviated as T_{d5} and T_{d10} are 260 °C and 300 °C, respectively. These results are comparable to the cross-linked polybenzoxazine derived from bisphenol-A and aniline monomer (abbreviated as BA-a) [6], and also better than compounds from polymerization of monofunctional polybenzoxazine [64]. However, the char yield of this product is 18% at 800 °C, which is lower than the polybenzoxazine derived from BA-a. This difference can be explained by the BA-a based benzoxazine containing more cross-linking units, while there is less possible cross-linking units in piperazine-*p*-cresol based structure. The degradation temperature is quite unexpected because the molecular weight of this product is a modest 3600 by SEC or approximately 10 units.

In order to increase the molecular weight, a different solvent system was used to improve the solubility of the product by using 50:50 by volume of chloroform : ethanol. As expected, instead of observing a solid precipitated within 4 h, it took more than one day for the polymer to precipitate. However, the molecular weight did not increase beyond 3600 and the TGA thermogram showed almost the same result as using 100% ethanol. The reason of this is that chloroform has lower polarity than ethanol. In order to proceed the reaction, the hydrogen bonding has to be deactivated because the hydrogen bonding decreases the nucleophilicity of the ortho-substitution of the aromatic ring. The hydrogen bond in hydrophobic solvent, e g. chloroform, is stronger. Therefore, the reaction is difficult to undergo.

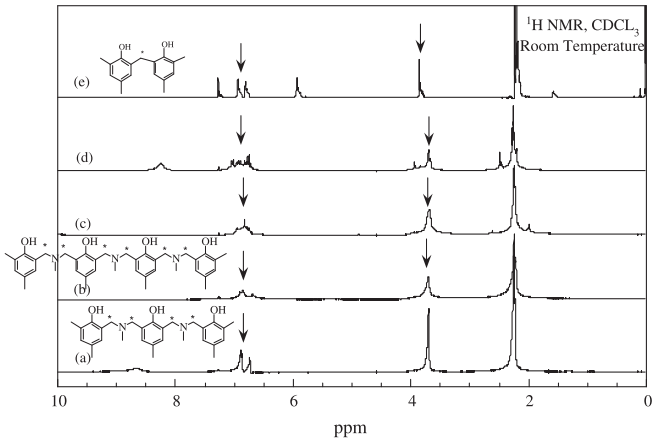


Fig. 4. ^{1}H NMR spectra of (a) trimer; (b) tetramer; (c) product from Exp. B (Table 1); (d) product from Exp. A (Table 1); and (e) 6-[(2-hydroxy-3,5-dimethylphenyl)methyl]-2,4-dimethylphenol.

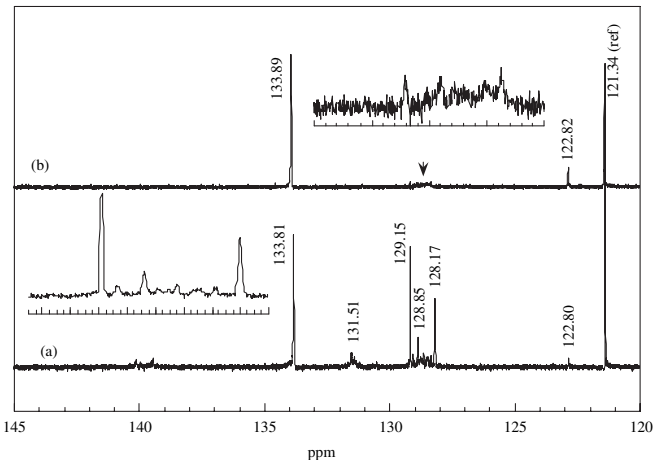
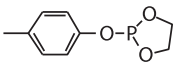
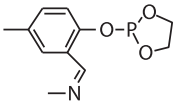
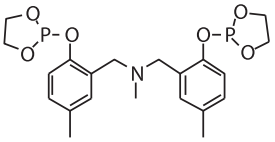
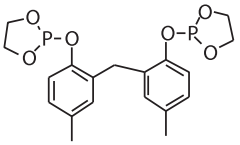
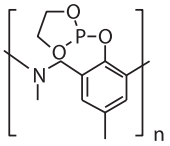


Fig. 5. ^{31}P NMR spectra of (a) product from Exp. A (Table 1); and (b) product from Exp. B (Table 1).

Table 3
Summary of ^{31}P NMR spectra from Fig. 5 (a) and 5(b).

Compound	^{31}P NMR (ppm)	
	5(a)	5(b)
	128.17	–
	128.85	–
	129.15	–
	131.51	–
	133.81	133.89

A high boiling point and high polarity solvent, e.g. dimethylformamide (DMF) was used to minimize the limitation stated above. Unfortunately, the solubility became the limiting factor again, resulting in low molecular weight. 4-Methylanisole, 4-methoxyphenol, and 3,4,5-trimethylphenol (ii, iii, and iv in Scheme 3) were used instead of *p*-cresol. The methyl-blocking group (4-methylanisole) was used to prevent hydrogen bonding. Therefore, electrons from oxygen can de-localize to the aromatic ring and increase the nucleophilicity of 6-substitution, and also increase the solubility. Nevertheless, –OR is less powerful activator than –OH, and only low molecular weight oligomers were obtained. For 3,4,5-trimethylphenol, although the nucleophilicity at the *ortho*- position is higher than other starting phenol, the reaction does not proceed because of the steric hindrance.

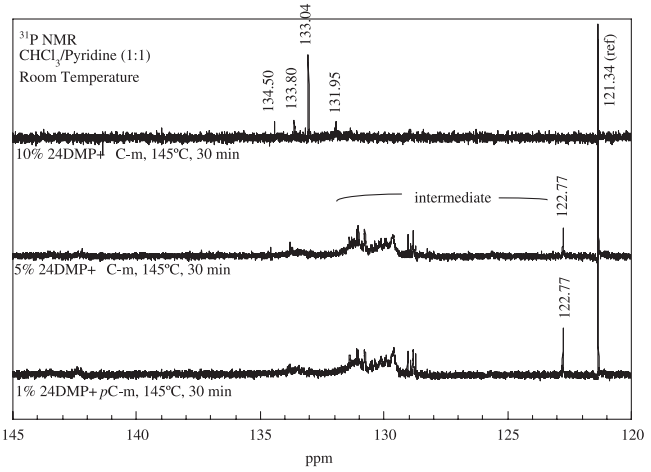


Fig. 6. ^{31}P NMR spectra of product from *p*C-m initiated by 1, 5 and 10 mol% of 2,4-dimethylphenol (24DMP) at 145 °C for 30 min (Exp. C) and derivatized with 132-DOP (Scheme 2) in chloroform and pyridine at room temperature.

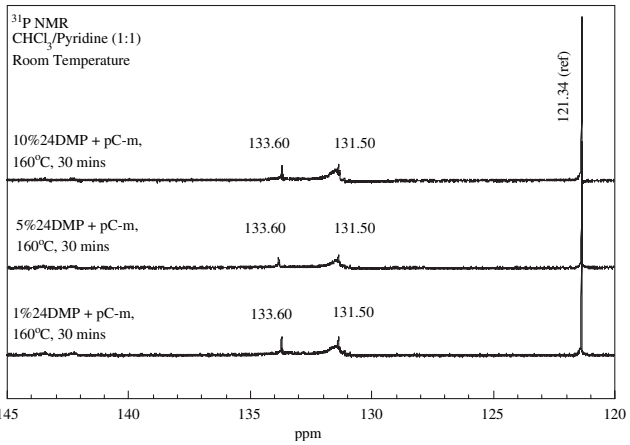


Fig. 7. ^{31}P NMR of product from *p*C-m initiated by 1, 5 and 10% by mole of 2,4-dimethylphenol (24DMP) at 160 °C for 30 min (Exp. D) and derivatized with 132-DOP (Scheme 2) in chloroform and pyridine at room temperature.

Knowing that this polymer is thermally stable at least up to 200 °C, DSC analysis was conducted. Since there are no polymerizable groups present in the polymer, no exotherm peaks would be expected. However, due to the solvent sample preparation, there is an expected thermal history built in the system. Thus, the sample was first heated to 200 °C to eliminate the thermal history. Since more rigid polybenzoxazines derived from bisphenol-A/aniline based monomer (BA-a) shows T_g around 170 °C [1], this choice of 200 °C was thought to be sufficient to be well above the expected T_g considering relatively flexible units. The DSC result of the second heating is shown in Fig. 3 where T_g was observed to be 110 °C. This T_g was somewhat lower than expected from the structure, possibly because of the modest molecular weight of the polymer examined.

4.2. Terminal group studies

4.2.1. Polybenzoxazine (Scheme 1c)

It is important to study the structure of terminal groups in order to obtain the idea of how the molecular weight can be increased. If the spectroscopic data indicates that the end groups still carry protons *ortho* to the phenolic hydroxyl groups, then further chain extension would occur. *p*C-m was reacted with *p*-cresol by the ratio of 1:1 by mole (Exp. A, Table 1). The ^{1}H NMR spectrum of the crude product is shown in Fig. 4d. *p*C-m was also polymerized by using 5 mol % *p*-cresol as an initiator, whose ^{1}H NMR spectrum is shown in Fig. 4c. The proton resonance on the aromatic ring and also methylene groups are in very close proximity as those of Methyl-trimer (Fig. 4a), Methyl-tetramer (Fig. 4b), and 6-[(2-hydroxy-3,5-dimethylphenyl)methyl]-2,4-dimethylphenol (Fig. 4e). It is difficult to identify the end group of this crude product. Hence, a facile technique using ^{31}P NMR has been utilized to provide more detailed structural information. The assignment of this system was previously studied in our group [61]. The crude products were derivertized with 132DOP (Scheme 4), and the ^{31}P NMR spectra are obtained as shown in Fig. 5a and b for Exp. A and Exp. B (Table 1), respectively. The opening of the oxazine ring upon polymerization results in the formation of Mannich bridge structure with the hydroxyl group from the phenolic portion that can be reacted with 132DOP. Therefore, it is possible to observe changes in the ^{31}P NMR spectrum as polymerization proceeds. From Fig. 5a and (b), the observed ^{31}P resonances are summarized in Table 3.

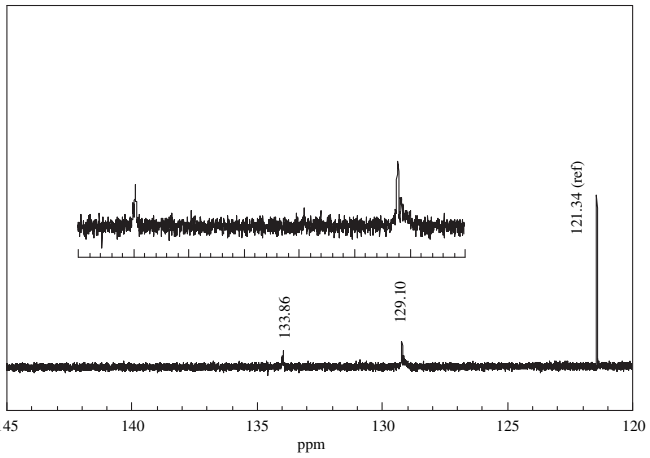


Fig. 8. ^{31}P NMR spectrum of not fully cured (Exp. E, Table 1) bisphenol-A and methylamine based benzoxazine.

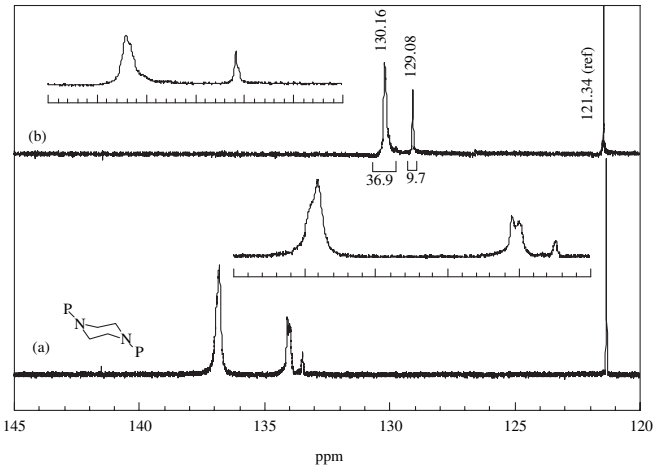


Fig. 10. ^{31}P NMR spectra of (a) piperazine; and (b) product from polymerization of *p*-cresol, formaldehyde, and piperazine (1:2.5:1).

pC-m was polymerized by initiating with 1, 5, and 10 mol % of 2,4-dimethylphenol (24DMP) at 145 °C for 30 min (Exp. C, Table 1), and then derivatized with 132DOP (Scheme 2). The ^{31}P NMR spectra of the derivatized products are shown in Fig. 6. The following observations were made from these spectra: (i) by using 1 and 5% 24DMP, we observed many complicated resonances around 128.00–132.00 ppm indicating that there are many hydroxyl groups from intermediate species which has different structures because the temperature and initiator concentration is not high enough to make completion of the reaction; (ii) when the concentration of the initiator increases to 10%, we can observe the major signal at 133.04 ppm which can be compared to the signal of the main chain in trimer and tetramer model compounds; (iii) the minor signal indicated the intermediate structures at 131.95, 133.80, 134.50 ppm; and (iv) the derivatized hydroxyl group having a resonance at 122.77 ppm decreases in intensity when the percentage of 24DMP increases.

pC-m was also initiated by 1, 5, and 10 mol % of 2,4-dimethylphenol (24DMP) at higher temperature (Exp. D: 160 °C for 30 min). The crude products were derivatized using 132-DOP in chloroform and pyridine, and ^{31}P NMR spectra were obtained as shown in Fig. 7. No changes of ^{31}P NMR chemical shifts between different amounts of 24DMP were observed for this case. The spectra of all three samples are the same because the temperature, time, and concentration of initiator are already high enough to change the monomer to the target product. The peak position at 133.60 ppm indicates derivatized phenolic hydroxyl group in the main chain and 131.50 ppm indicates the derivatized phenolic hydroxyl end group.

Benzoxazine monomer synthesized from bisphenol-A, formaldehyde, and amine (BA-m) was polymerized, using the literature methodology [4]. The product was difficult to dissolve in chloroform. Therefore, the experiment was done in a milder condition (Exp. E: Table 1). The spectra are shown in Fig. 8, which means that bisphenol-A methylamine based benzoxazine (BA-m) chemical repeat unit is Mannich base (133.86 ppm) and the end group is open ortho- position aromatic group (129.10 ppm). No resonance at 131.50 ppm, which corresponds to the methylene bridge linkage, was observed. The polymerization was taken place under stronger condition, and the reaction products were derivatized with 132DPO. The ^{31}P NMR spectra obtained are shown in Fig. 9. There is only the phosphorus derivative of the Mannich base main chain observed at 133.80 ppm.

pC-m was also heated at 160 °C for 30 min without p-cresol. The ^{31}P NMR spectroscopy showed no resonance in the 131.00–133.00 ppm. This means that the oxazine ring was not opened to form a phenol and Mannich base bridge structure.

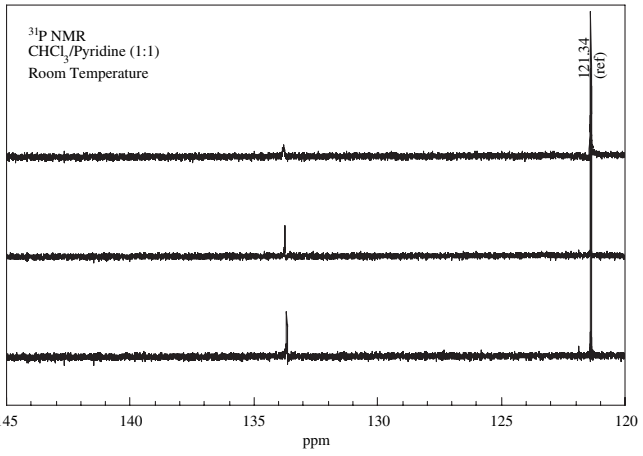
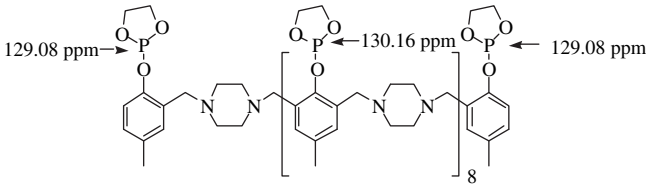


Fig. 9. ^{31}P NMR spectrum of crude products from polymerization of bisphenol methylamine based benzoxazine at 185 °C for 10, 45, and 60 min from lower to upper spectrum.

4.2.2. *Mannich polymer with piperazine (Scheme 3)*

In Fig. 10, ^{31}P NMR spectra of the product from polymerization, shown in Scheme 3 is totally different from the ^{31}P NMR of its starting material. The resonance at 130.16 ppm corresponds to the phosphorus derivative from the main chain and the resonance at 129.08 ppm corresponds to the end group. The integral ratio confirms the results from ^{1}H NMR and SEC that it has 8 units of main chain and two end groups as summarized in Scheme 5.



Scheme 5. ^{31}P NMR resonance of Mannich polymer from the reaction between p-cresol, formaldehyde, and piperazine.

5. Conclusions

A facile ^{31}P NMR technique has been utilized to provide detailed structural information of the benzoxazine product, based on the assignment of the model compounds. We found the evidence of desired Mannich structure from polymerization of benzoxazine only if we have a proper time and temperature. If a large amount of catalyst/initiator was added and also polymerized at too low a temperature, evidence of other compounds was observed. Investigation of the polymer from Mannich polycondensation confirms the possibility of this molecule to undergo longer chain.

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