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Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide

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Abstract

Three phosphorus-containing bisphenol compounds, bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO), bis(4-hydroxyphenoxyphenyl)phenylphosphine oxide (BPPPO), and bis(4-hydroxyphenoxy)phenylphosphine oxide (BPHPPO) have been synthesized as starting materials for the synthesis of benzoxazine monomers. Benzoxazine monomers containing phenylphosphine oxide have been prepared and subsequently characterized by FT-IR and ^{1}H NMR. The monomers are thermally initiated and polymerized via ring-opening polymerization. Thermogravimetric analysis indicates that phosphorylation can have a profound effect on increasing char yield and on thermal degradation temperatures.

Keywords: Benzoxazine; Phosphorous; Phenylphosphine oxide; Thermogravimetric analysis

1. Introduction

Polybenzoxazines have been developed as a class of ring-opening phenolic resins. The chemistry for the synthesis of the benzoxazine monomer deals with the Mannich reaction involving the condensation of phenol, formaldehyde, and primary amine [1–5]. The traditional phenolic polymers have advantages including high temperature resistance, flame retardance, inherent hardness, and dielectric insulation properties [6]. Nonetheless, a number of disadvantages also exist. They are brittle, release small molecules upon curing, require use of strong acids as catalysts, have poor shelf life, and lack of molecular design flexibility. Unlike traditional phenolic resins, polybenzoxazines, derived from their precursors via the ring-opening polymerization process, overcome those shortcomings while maintaining the desirable properties. Synthesis, kinetics, characterization, as well as final properties of benzoxazine monomers and related polymers have been investigated in our laboratory [7–13]. The monomer structure of benzoxazine can be designed by changing the starting material used; phenol and primary amine. Benzoxazine monomers synthesized from bisphenol-A, formaldehyde, and methylamine (3-methyl-6-[1-methyl-1-(3-methyl(2*H*,4*H*-benzo[3,4-*e*]1,3-oxazaperhydroin-6-yl))ethyl]-2*H*,4*H*-benzo[*e*]1,3-oxazine, abbreviated as BA-m) and bisphenol-A, formaldehyde, and aniline (6-[1-methyl-1-(3-phenyl(2*H*,4*H*-benzo-[3,4-*e*]1,3-oxazaperhydroin-6-yl))ethyl]-3-phenyl-2*H*,4*H*-benzo[*e*]1,3-oxazine, abbreviated as BA-a) have been

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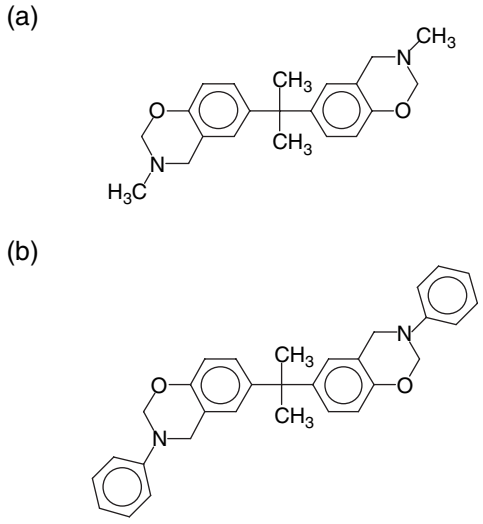


Fig. 1. Structure of BA-m (a) and BA-a (b) benzoxazine monomers.

studied extensively and therefore are used as reference materials in this study (Fig. 1).

It is well known that phosphorus compounds are excellent candidates for thermally stable materials. Organophosphorus compounds have been used as flame retardants for decades [14]. The presence of the phosphorus compound plays an important role in the high performance of thermally stable materials due to its ability to inhibit ignition and promote char formation. The phosphorus-containing polymers, therefore, have been extensively synthesized and characterized to investigate the improvement of thermal properties [15–22]. Therefore, incorporating a phosphorus-containing group into the benzoxazine monomer was thought to increase the char yield of polybenzoxazine. In this study, three different types of phosphorus compounds were incorporated into the structure of polybenzoxazine in the form of phenylphosphine oxide functional group and the structural relationship between those three phosphorus compounds and three different kinds of amines is investigated.

2. Experimental

2.1. Materials

All chemicals were used as received. Magnesium turnings (99+%) and phenylphosphonic dichloride (97%) were received from Lancaster Synthesis Inc. 4-(Benzyloxy)phenol (98%) was received from Acros Chemical Company. 1-Bromo-4-fluorobenzene (99%), *p*-formaldehyde (95%), methylamine (40 wt% solution in water), aniline (99%), and palladium (5 wt% (dry basis) on activated carbon), were obtained from Aldrich Chemical Company. 3-Ethynylaniline (95+%) was received from TCI America Chemical Company and used as received. Celite 521 was received from Acros Chemical Company. Sodium carbonate (anhydrous), magnesium sulfate (anhydrous), dichloromethane (A.C.S. grade), tetrahydrofuran (A.C.S. grade), pyridine (A.C.S. grade), and ethanol (95%) were obtained from Fisher Scientific Inc. Tetrahydrofuran was distilled over sodium with benzophenone (99%). Dichloromethane was refluxed over CaH_2 and distilled before use.

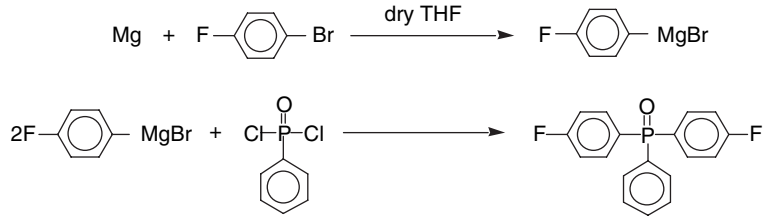
2.2. Synthesis of bis(4-fluorophenyl)phenylphosphine oxide (BFPPO)

BFPPO was synthesized according to a literature procedure [23] via Grignard reaction except for the purification procedure (Scheme 1). To a 1000-ml three neck round-bottom flask equipped with mechanical stirrer, addition funnel, condenser, and N_2 inlet/outlet, magnesium turnings (16.8 g, 0.69 mol) were dissolved in dry THF (300 ml) as much as possible. The mixture was cooled in ice-water bath. 1-Bromo-4-fluorobenzene (120 g, 0.69 mol) was diluted with dry THF (200 ml) and transferred to an addition funnel. Maintaining temperature of the ice-water bath around 0 °C, the mixture was added to the dilute 1-bomo-fluorobenzene mixture over 3 h. After the addition, the mixture was stirred for an additional 3 h at room temperature until a cloudy gray solution was obtained. To this solution mixture, phenylphosphonic dichloride (70 g, 345 mmol) diluted in dry THF was added through an addition funnel. During the addition, bubbles started to appear and the cloudy gray solution became a clear dark brown solution. Stirring was continued overnight at room temperature.

Ten percent aqueous sulfuric acid was added to acidify the mixture and 300 ml of water was added. Diethyl ether was added in order to separate the solution into organic and aqueous phases. The organic layer was collected by extraction and the aqueous layer was extracted with diethyl ether and THF solvent mixture. The collected organic phase was dried over $MgSO_4$, filtered, and rotary evaporated to give a gel like wet crude product. Column chromatography was employed to avoid repetitive literature work-up procedure, eluting with ethyl acetate–hexane (1:1). The final product was a white crystal with a yield of 72%.

2.3. Synthesis of bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO)

BHPPO was synthesized from the hydrolysis of BFPPO [24,25] (Scheme 2). To a 1000-ml three neck round-bottom flask equipped with a mechanical stirrer, refluxing condenser, and N_2 inlet/outlet, BFPPO (40 g, 127 mmol), 8 N aqueous KOH (57 g, 1.02 mol), and distilled DMSO (140 ml) were added. The reaction



Scheme 1. Synthesis of bis(4-fluorophenyl)phenylphosphine oxide (BFPPO).

mixture was refluxed at 100 °C for 48 h. During the reaction, color of the mixture was changed from white to clear, then from clear to pink, and finally to clear yellow. After the reaction mixture was cooled, the mixture was precipitated into dilute HCl (20%) using an additional funnel with slow addition rate. The white precipitate was filtered through a glass filter under vacuum and dried overnight. The product was white in color with 80% yield.

2.4. Synthesis of (3-methyl(2H,4H-benzo[3,4-e]1,3-oxazaperhydroin-6-yl))(3-methyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl))phenylphosphino-1-one (BHPPO-m)

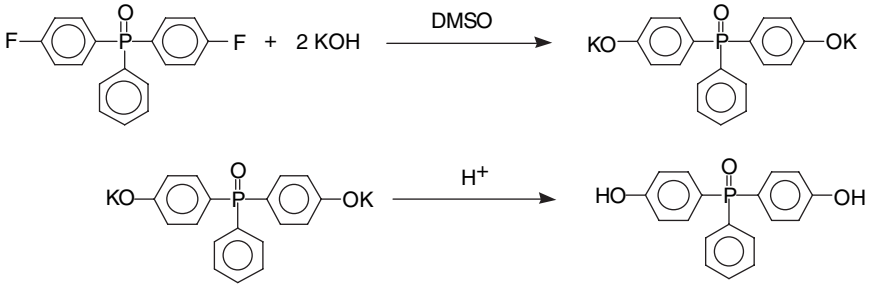
To a 25-ml three neck round-bottom flask equipped with a refluxing condenser, formaldehyde (0.44 g, 14 mmol) and methylamine (0.55 g, 7.1 mmol) were dissolved in 15 ml of chloroform and the mixture was heated to 70 °C. Upon obtaining a clear solution mixture after 15 min, BHPPO (1 g, 3.22 mmol) was added to the clear reaction mixture and stirred for 33 h. After the mixture was cooled, it was washed three times with 3 N NaOH and further washed twice with deionized water. The washed mixture was extracted with chloroform and the extracted organic layer was dried over $MgSO_4$, filtered, and rotary evaporated. The crude product was further purified by column chromatography eluting with ethyl acetate–hexane (3:1) gradually increasing the ratio of ethyl acetate and finally ethyl acetate only to give a final product as a glassy solid (56%) (Scheme 3).

2.5. Synthesis of phenyl(3-phenyl(2H,4H-benzo[3,4-e]1,3-oxazaperhydroin-6-yl))(3-phenyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl))phosphino-1-one (BHPPO-a)

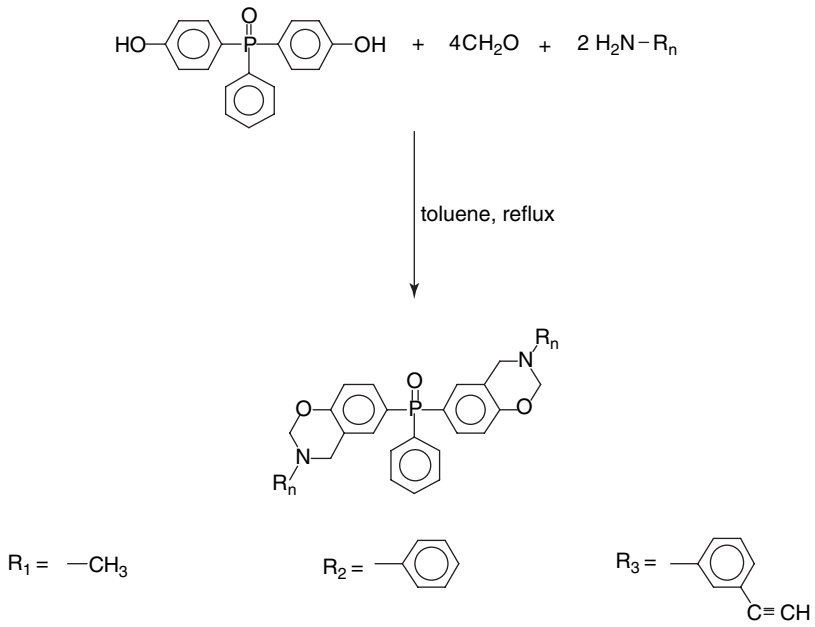
BHPPO-a benzoxazine monomer was synthesized by the same procedure as BHPPO-m. Formaldehyde (0.44 g, 14 mmol) and aniline (0.66 g, 7.1 mmol) were mixed and dissolved in 15 ml of toluene at 70 °C. After a clear solution mixture was obtained, BHPPO (1 g, 3.22 mmol) was added to the clear reaction mixture and was stirred for 18 h. After the mixture was cooled, the mixture was base washed three times with 3 N NaOH and further washed twice with deionized water. The washed mixture was extracted with chloroform and the extracted organic layer was dried over $MgSO_4$, filtered, and rotary evaporated. The crude product was further purified by column chromatography eluting with ethyl acetate–hexane (3:1) gradually increasing the ethyl acetate ratio to give a final product as a slightly yellowish glassy solid (60%) (Scheme 3).

2.6. Synthesis of [3-(3-ethynylphenyl)(2H,4H-benzo[3,4-e]1,3-oxazaperhydroin-6-yl)][3-(3-ethynylphenyl)(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl)]phenylphosphino-1-one (BHPPO-ea)

Typical solvent method for synthesizing benzoxazine monomer was proceeded by using stoichiometric amount of BHPPO (300 mg, 0.97 mmol), formaldehyde (140 mg, 4.3 mmol), and 3-ethynylaniline (250 mg, 2.1 mmol). The reaction completed after 22 h in toluene. The same purification procedure as the previous two



Scheme 2. Synthesis of bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPO).



Scheme 3. Synthesis of BHPPO-based benzoxazine monomers (R_1, R_2, and R_3 represent methyl, phenyl, and 3-ethynylphenyl, respectively, corresponds to BHPPO-m, BHPPO-a, and BHPPO-ea, respectively).

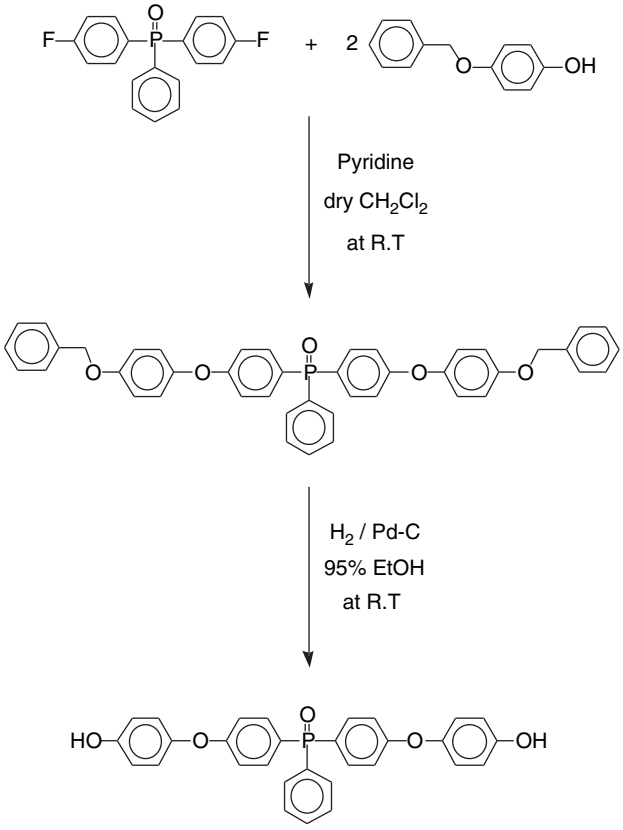
methylamines and aniline-based benzoxazine monomer was performed to give a yellowish glassy solid (65%) (Scheme 3).

2.7. Synthesis of bis(4-benzyloxyphenoxy-4′-phenyl)phenylphosphine oxide (BBPPO)

BBPPO was prepared from the etherification of BFPPO (Scheme 4). To a 250-ml three neck round-bottom flask equipped N_2 inlet and outlet, bis(4-fluorophenyl)phenylphosphine oxide (BFPPO) (10 g, 32 mmol) was dissolved in dry methylenechloride and 4-(benzyloxy)phenol (14 g, 70 mmol) was added to this mixture. The mixture was stirred for 5 min and dry pyridine (10.1 g, 128 mmol) was added dropwise. The mixture became transparent while it was stirred overnight. After the reaction was completed, the crude product was washed with 1 N Na_2CO_3 solution and further washed with deionized water two times to eliminate the pyridine. After extraction, the organic layer was dried over $MgSO_4$ and filtered. The filtrate was rotary evaporated and dried in a vacuum oven. After drying, the product was recrystallized in acetonitrile and a slightly brownish crystal was collected with a yield of 94%.

2.8. Synthesis of bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (BPPPO)

BPPPO was obtained by deprotection of benzyl group in BBPPO through hydrogenation (Scheme 4).



Scheme 4. Synthesis of bis(4-benzyloxyphenoxy-4′-phenyl)phenylphosphine oxide (BBPPO) and bis(4-hydroxyphenoxy-4′-phenyl)phenylphosphine oxide (BPPPO).

In a 500-ml one neck round-bottom flask, BBPPO (23 g, 34 mmol) was dissolved in 95% ethanol with dry palladium (5 wt% (dry basis) on activated carbon, 10 g). Before sealing the flask with a rubber stopper, inside of the round-bottom flask was substituted with hydrogen gas. The mixture was stirred for 54 h under an H_2 environment. The reaction was terminated, after confirming the disappearance of the benzyl peak in the ^1H NMR spectrum. The products were filtered through glass filter with celite. The filtrate was rotary evaporated and dried in a vacuum oven at room temperature.

2.9. Synthesis of bis[4-(3-methyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yloxy))phenyl] phenylphosphino-1-one (BPPPO-m)

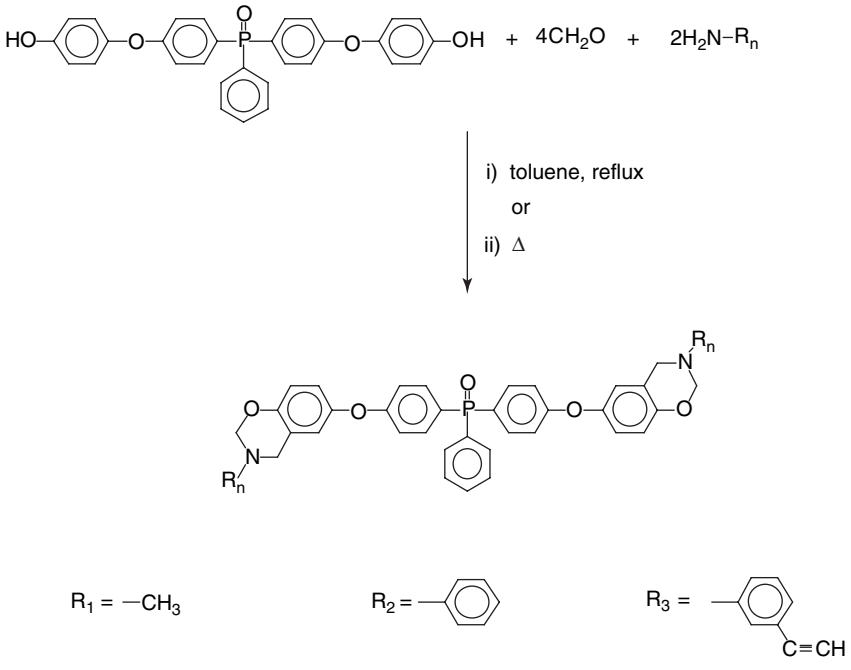
BPPPO-m benzoxazine monomer (Scheme 5) was synthesized by the same synthetic procedure as BHPPO-m through typical solvent method in toluene developed in our laboratory [8]. Compared to BHPPO-m, reaction was completed in much shorter time, due to the screening effect resulting from the introduction of the ether linkage between the two benzene rings. Stoichiometric amount of BPPPO (1 g, 2.0 mmol), formaldehyde (0.28 g, 8.8 mmol), and methylamine (0.34 g, 4.4 mmol) were used in the ring formation reaction and the same purification procedures done in BHPPO-m were proceeded to give glassy solids (68%).

2.10. Synthesis of bis[4-(3-phenyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yloxy))phenyl] phenylphosphino-1-one (BPPPO-a)

Unlike BHPPO-a, the BPPPO-a benzoxazine monomer (Scheme 5) was synthesized by the typical solventless method [9] developed in our laboratory. Stoichiometric amount of BPPPO (600 mg, 1.2 mmol), formaldehyde (168 mg, 5.3 mmol), and aniline (240 mg, 2.6 mmol) were used in corresponding benzoxazine monomer synthesis. In a 5-ml one neck RB flask, formaldehyde and aniline were added and mixed at 60 °C. After stirring for 5 min, BPPPO was added to the mixture and the temperature was raised to 100 °C. After 50 min, stirring was stopped and the mixture cooled to room temperature. Like other benzoxazine monomers, the crude benzoxazine monomer was base washed and further purified by column chromatography eluting with ethyl acetate:hexane (1:3 to 5:1) gradually increasing the ratio of ethyl acetate to give a final product. The product was a slightly yellowish glassy solid with a yield of 64%.

2.11. Synthesis of bis{4-[3-(3-ethynylphenyl)(2H,4H-benzo[3,4-e]1,3-oxazin-6-yloxy)]phenyl} phenylphosphino-1-one (BPPPO-ea)

The BPPPO-ea benzoxazine monomer (Scheme 5) was synthesized by the same procedure used in BPPPO-a. Stoichiometric amount of BPPPO (300 mg, 0.6 mmol),

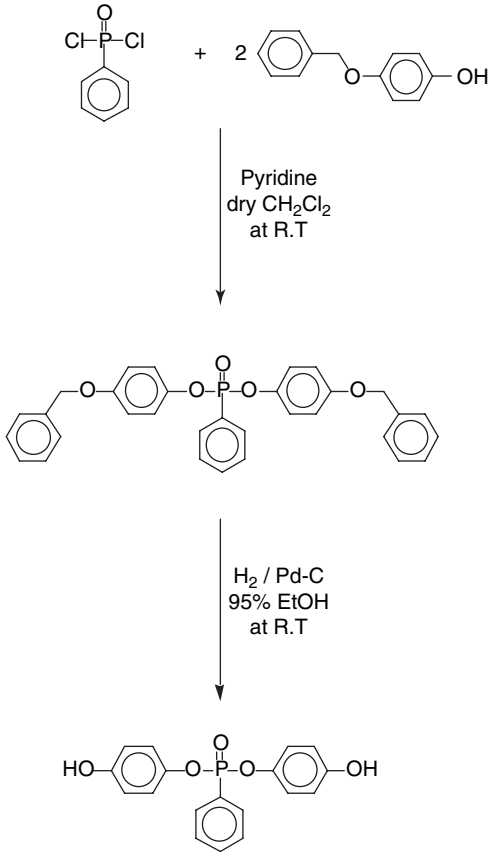


Scheme 5. Synthesis of BPPPO-based benzoxazine monomers (R_1, R_2, and R_3 represent methyl, phenyl, and 3-ethynylphenyl, respectively, corresponds to BPPPO-m, BPPPO-a, and BPPPO-ea, respectively).

formaldehyde (84 mg, 2.7 mmol), and 3-ethynylaniline (160 mg, 1.3 mmol) were used. The same purification procedures, including base washing and column chromatography, were proceeded to give a slightly yellowish glassy solid with a yield of 70%.

2.12. Synthesis of bis(4-benzyloxyphenoxy)phenylphosphine oxide (BBHPPO)

BBHPPO (Scheme 6) was prepared by etherification between phenylphosphonic dichloride and 4-(benzyloxy)-phenol (Scheme 5). In a 250-ml three neck round-bottom flask equipped with an N_2 inlet and outlet, phenylphosphonic dichloride (5 g, 25.6 mmol) was dissolved in dry methylenechloride and 4-(benzyloxy)-phenol (11.3 g, 56.3 mmol) was added to the mixture. The mixture was stirred at room temperature for 5 min and dry pyridine (8.1 g, 102 mmol) was added dropwise. During the reaction, the mixture became transparent and the salt precipitated after 30 min. Stirring was continued overnight. After the reaction was completed, the crude product was washed with 1 N Na_2CO_3 solution and further washed with deionized water two times to eliminate the pyridine. After the extraction, the organic layer was dried over $MgSO_4$ and filtered. The filtrate was rotary evaporated and dried in a vacuum oven. The dried product was used without further purification and had a yield of 86%.



Scheme 6. Synthesis of bis(4-benzyloxyphenoxy)phenylphosphine oxide (BBHPPO) and bis(4-hydroxyphenoxy)phenylphosphine oxide (BPHPPO).

2.13. Synthesis of bis(4-hydroxyphenoxy)phenylphosphine oxide (BPHPPO)

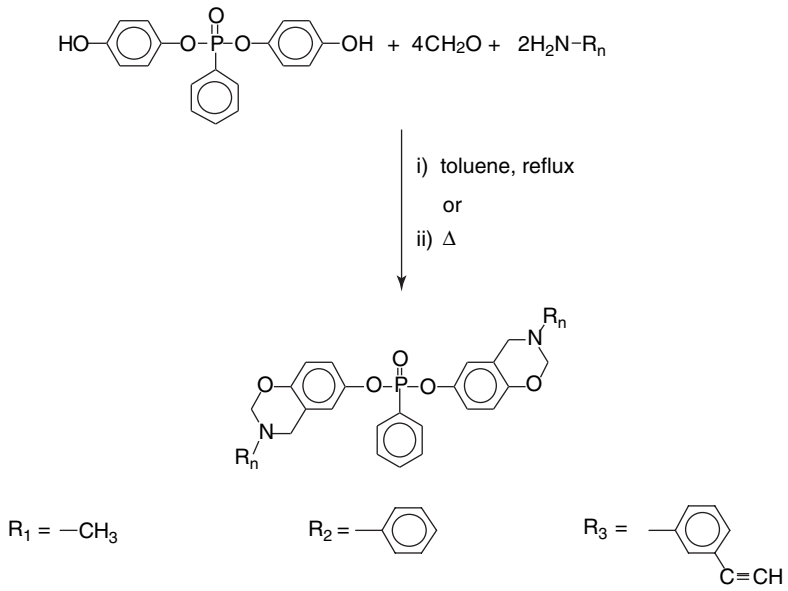
BPHPPO (Scheme 6) was synthesized through hydrogenation by deprotecting the benzyl group in BBHPPO (Scheme 5). In a 500-ml one neck round-bottom flask, BBPPO (5.5 g, 10.5 mmol) was dissolved in 95% ethanol and dry palladium (5 wt% (dry basis) on activated carbon, 10 g) was added. Before sealing the flask with a rubber stopper, the inside of the flask was substituted with hydrogen gas. After sealing, the reaction proceeded for 42 h under H_2. After confirming the disappearance of all benzyl peak, the reaction was stopped and filtered through a glass filter with celite. The filtrate was rotary evaporated and dried in vacuum oven at room temperature. The final product was a light brownish white crystal and was used without further purification (92%).

2.14. Synthesis of bis(3-methyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl)oxy)phenylphosphino-1-one (BPHPPO-m)

BPHPPO-m benzoxazine monomer (Scheme 7) was synthesized by the same solvent method as BHPPO-m or BPPPO-m. Stoichiometric amount of BPHPPO (300 mg, 0.88 mmol), formaldehyde (120 mg, 3.9 mmol), and methylamine (148 mg, 1.9 mmol) were used for the synthesis of the BPHPPO-m benzoxazine monomer. Reaction was finished after 5 h and the crude product was base washed and further purified by column chromatography, eluting with ethyl acetate:hexane (1:3 to 3:1) and gradually increasing the ethyl acetate ratio to give a final product as a light brownish glassy solid with a yield of 48%.

2.15. Synthesis of bis(3-phenyl(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl)oxy)phenylphosphino-1-one (BPHPPO-a)

BPHPPO-a benzoxazine monomer (Scheme 7) was synthesized by the solventless method [9] used in BPPPO-a or BPPPO-ea with BPHPPO (800 mg, 2.3 mmol), formaldehyde (326 mg, 10.3 mmol), and aniline (479 mg, 5.1 mmol). Reaction was completed after 50 min and the crude product was base washed and further purified by column chromatography eluting with ethyl acetate:hexane (1:3 to 1:1) gradually increasing the ethyl acetate ratio to give a final product as a light yellowish glassy solid (73%).



Scheme 7. Synthesis of BPHPPO-based benzoxazine monomers (R_1, R_2, and R_3 represent methyl, phenyl, and 3-ethynylphenyl, respectively, corresponds to BPHPPO-m, BPHPPO-a, and BPHPPO-ea, respectively).

2.16. Synthesis of bis[3-(3-ethynylphenyl)(2H,4H-benzo[3,4-e]1,3-oxazin-6-yl)oxy]phenylphosphino-1-one (BPHPPO-ea)

BPHPPO-ea benzoxazine monomer (Scheme 7) was also synthesized via the solventless method [9] using BPHPPO (300 mg, 0.88 mmol), formaldehyde (120 mg, 3.9 mmol), and 3-ethynylaniline (220 mg, 1.9 mmol). Benzoxazine ring formation reaction was finished within 50 min and then, the crude product was base washed. Column chromatography was proceeded for the increasing ethyl acetate ratio to give a final product as a light yellowish glassy solid (78%).

2.16.1. Instrumentation

The purity of three different starting materials (BHPPO, BPPPO, and BPHPPO) and corresponding benzoxazine monomers with various combinations of amines were checked using a Varian XL 200 nuclear magnetic resonance spectrometer (^{1}H NMR) at a proton frequency of 200 MHz. Deuterated chloroform with 0.05% tetramethylsilane as the internal standard, acetone, and dimethyl sulfoxide were used as NMR solvents. Coaddition of 128 transients yielded a good signal-to-noise ratio spectrum. Relaxation time (D1) of 10 s was used to obtain integration results.

The infrared spectra were taken on a Fourier transform infrared spectrometer (Bomem Michelson MB). One hundred coadded scans were taken with a resolution of 4 cm^{-1} using a liquid nitrogen cooled, mercury–cadmium–telluride (MCT) detector with a specific detectivity; D^* of 1×10^{10} cm $Hz^{1/2}$ W^{-1}, after 20 min purge with nitrogen. The bisphenol solid samples were pressed into KBr pellets. The spectra of benzoxazine monomers were taken by dissolving them in chloroform and casting the solution onto a KBr plate.

The thermal stability of phosphorus-containing benzoxazine monomers were investigated by thermogravimetric analysis (TGA) performed on a TA Instruments High Resolution 2950 thermogravimetric analyzer. Nitrogen was used as a purge gas for all testing. A heating rate of 10 °C/min with a flow rate of 90 ml/min was used for all tests.

3. Results and discussion

The benzoxazine monomer containing BHPPO was synthesized according to a standard procedure shown in reaction Scheme 3 by condensation of BHPPO, formaldehyde and primary amine (methylamine, aniline and 3-ethynylaniline) in toluene at its reflux temperature [5]. The reactivity of BHPPO was expected to be different from bisphenol-A, which was used in this study as a reference starting compound. Therefore, the benzoxazine ring formation reaction was monitored by ^{1}H NMR as a function of reaction time over 15 h for the BHPPO-a benzoxazine monomer and 33 h for the BHPPO-m benzoxazine monomer, respectively (Figs. 2 and 3). The samples were taken directly from the toluene solution every hour and filtered through sodium sulfate to remove remnant water, which was generated during the condensation reaction. The filtrate was dried by air and dissolved in $CDCl_3$ with 0.05% of trimethylsilane as an internal standard for further NMR examination. The region of 0.00–10.00 ppm was chosen for kinetic study. The spectra shown in

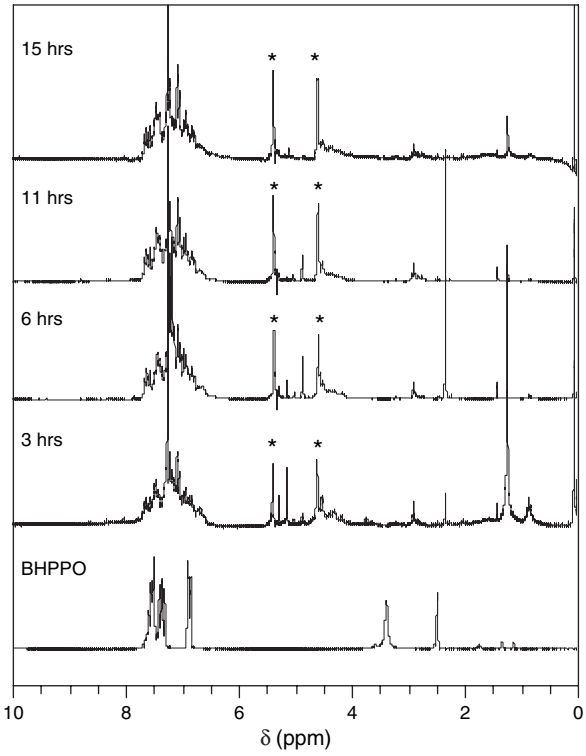


Fig. 2. In situ ^{1}H NMR monitoring of BHPPO-a benzoxazine monomer.

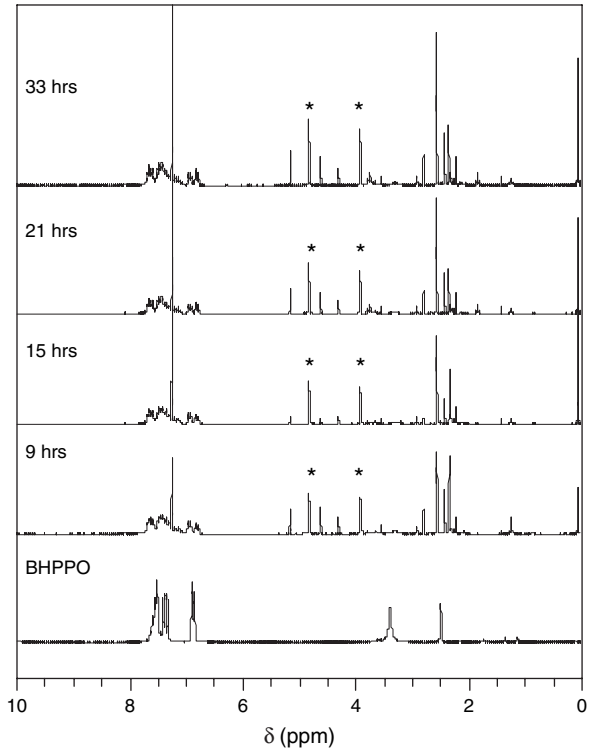
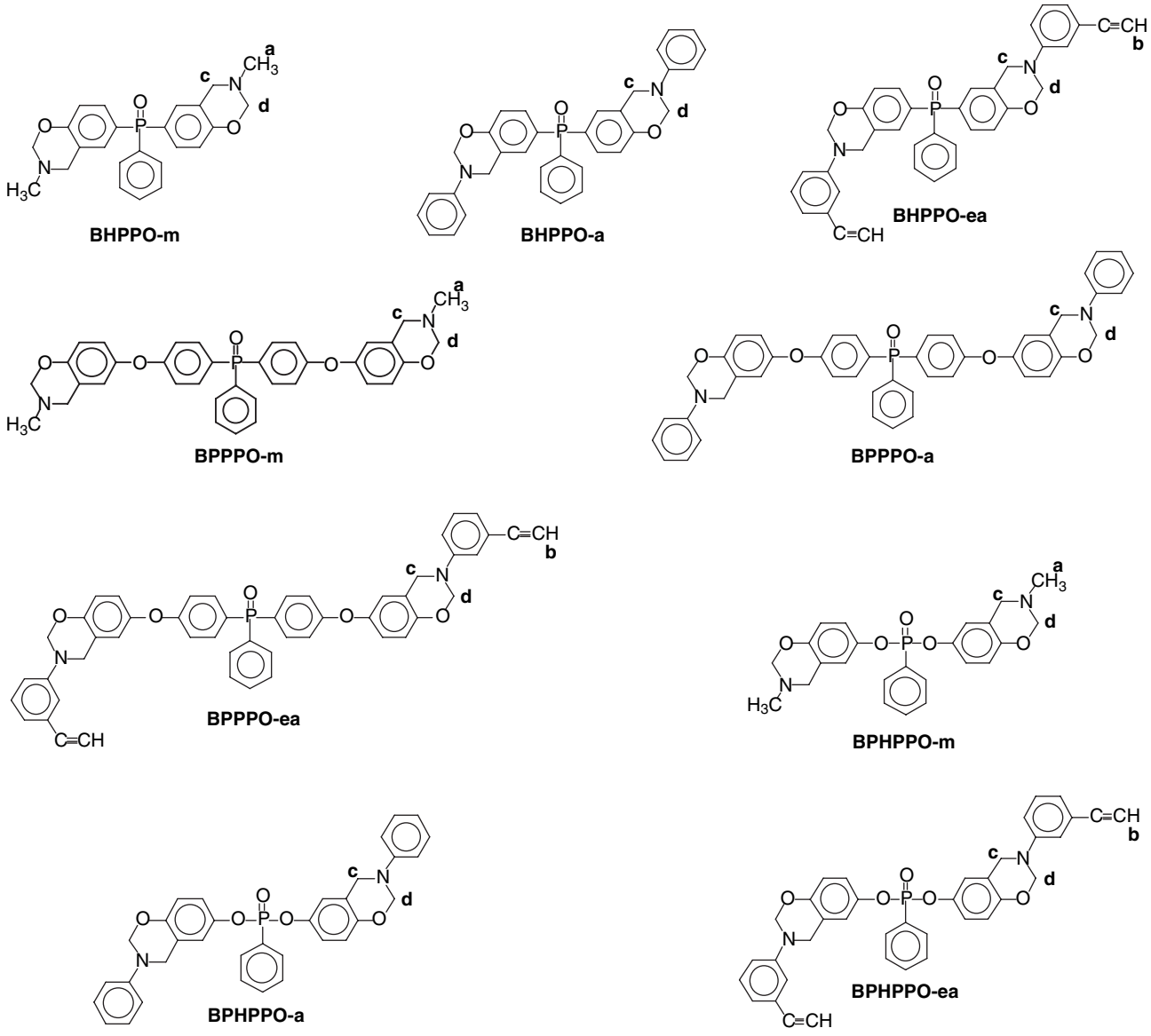


Fig. 3. In situ ^{1}H NMR monitoring of BHPPO-m benzoxazine monomer.

these figures are the representative of samples, which were collected at 1 h time intervals. In case of the BHPPO-a benzoxazine monomer, the intensity of the peak at 5.42 ppm for the methylene protons between the nitrogen atom and oxygen atom in the benzoxazine ring, and peak at 4.64 ppm for the methylene protons between the nitrogen atom and benzene ring in benzoxazine ring both increase with reaction time (designated by the asterisks). Also, the peaks of triazine intermediates between the two representative benzoxazine ring peaks decrease with reaction time. Compared to the BA-a benzoxazine monomer which showed its benzoxazine ring peaks at 5.34 and 4.59 ppm for each methylene proton, the corresponding ring peaks of the BHPPO-a benzoxazine monomer were shifted down field because of strong electron withdrawing character of the phenylphosphonic group. The ring formation reaction of the BHPPO-m benzoxazine monomer was also monitored by the same method mentioned above using ^{1}H NMR as a function of reaction time over 33 h. The relative intensity of the two representative benzoxazine ring peaks at 4.85 and 3.94 ppm and the peak of methyl group attached to the nitrogen atom at 2.59 ppm increases with reaction time compared to that of the aromatic region as a function of reaction time. Generally, in case of the bisphenol-A based benzoxazine monomers (BA-m and BA-a), methylamine showed better reactivity for benzoxazine ring formation compared to aniline because methylamine has higher basicity ($pK_b = 3.38$) than aniline ($pK_b = 9.37$) [30] and, therefore, reaction towards benzoxazine ring occurs relatively fast involving side reactions, such as Schiff base production, especially at a longer reaction time. On the other hand, the BHPPO-based benzoxazine monomers showed opposite trend to the bisphenol-A based ones. Also, each corresponding peak was shifted to lower field compared to the BA-m benzoxazine monomer which showed peak positions at 4.76 and 3.90 ppm while the methyl peak was virtually unchanged at 2.59 ppm. However, in case of the BPPPO and BPHPPO-based benzoxazine monomers (Schemes 5 and 7), they showed almost the same reaction time and reactivity with a various amine combination as reference compounds (BA-m and BA-a). This is mainly due to the screening effect of ether linkage for each compound regardless of the position of ether linkage. Therefore, strong electron withdrawing character of the phenylphosphine oxide group was decreased by adding an ether linkage to the main structure.

Valence-shell electron pair repulsion theory (VSEPR) [28] of phosphorus compounds considers compounds of the formula $X_3P{=}O$ as tetra-coordinated phosphorus compounds even if they are formally pentavalent due to strong dipole of the phosphoryl bond, P=O. Therefore, phenylphosphine oxide group on the phenolic ring is considered a strongly electron withdrawing substituent,

Table 1
^{1}H NMR assignment for aliphatic protons of benzoxazine monomers



Benzoxazine	Proton a (ppm)	Proton b (ppm)	Proton c (ppm)	Proton d (ppm)
BHPPO-m	2.59	–	3.94	4.85
BHPPO-a	–	–	4.64	5.42
BHPPO-ea	–	3.07	4.63	5.40
BPPPO-m	2.58	–	3.85	4.71
BPPPO-a	–	–	4.48	5.27
BPPPO-ea	–	3.06	4.52	5.28
BPHPPO-m	2.58	–	3.90	4.76
BPHPPO-a	–	–	4.54	5.30
BPHPPO-ea	–	3.07	4.58	5.30

which makes substitution reactions on the protons in hydroxyl groups and protons in *ortho* position on benzene ring more difficult. The synthesis of benzoxazine monomers with halogen as an electron withdrawing substituent on the phenolic ring has been studied in our laboratory [29]. The reaction time required for high yield of halogenated benzoxazine monomers has been found significantly longer than for any other benzoxazine

monomers with electron donating substituent on phenolic ring, such as bisphenol-A or *p*-cresol.

The ^{1}H NMR spectral assignments for aliphatic protons of benzoxazine monomers are all tabulated in Table 1. Unlike the BHPPO-based benzoxazine monomers, the BPPPO and BPHPPO-based benzoxazine monomers showed their corresponding chemical shifts similar to the reference materials [26] in spite of the different chemical structure. This fact further supports the screening effect of the ether linkage in the main structure.

Figs. 4–6 show the FT-IR spectra of BHPPO, BPPPO, and BPHPPO starting compounds and the benzoxazine monomers obtained. The band at 1120 cm^{-1} is assigned to the P=O stretching while the band at 1436 cm^{-1} is assigned to the phenyl-P stretching which is used as an internal standard. The phosphorus–carbon stretching frequencies normally occur in the 800–600 cm^{-1} region; however, they have been found very difficult to assign. The bands at 1489, 1236, and 916 cm^{-1} (designated by the asterisks) were assigned to the characteristic modes related to the benzoxazine ring, based on the previous work done in our laboratory [26]. The 1489 cm^{-1} band is assigned to a trisubstituted benzene ring (the C=C in-plane stretching vibration, benzene mode 19b according to Wilson) [27]. The 1236 cm^{-1} band is assigned to the antisymmetric C–O–C stretch. The radial skeletal vibration of the trisubstituted benzene ring gives rise to the band at 916 cm^{-1} (benzene mode 7b [27]). The benzene modes 19b and 7b are expected to be substituent sensitive. Therefore, the peak positions of these benzene modes in the spectra of the benzoxazine monomers containing phenylphosphonic group were compared with the spectrum of the bisphenol-A-based benzoxazine. The bands, which are assigned to the benzene modes 19b and 7b, were shifted to lower frequencies by about 10–20 cm^{-1} due to the presence of the heavier substituent, phenylphosphonic group, compared to the isopropyl group present in bisphenol-A. The amount of shifting also

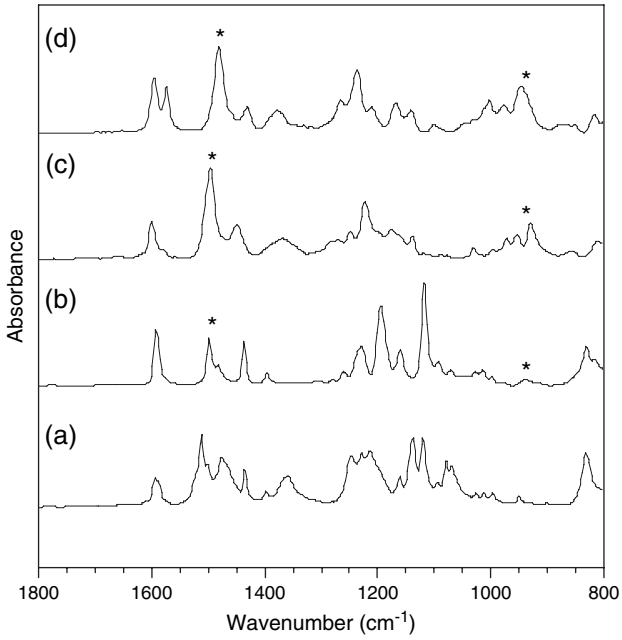


Fig. 5. FT-IR spectra of BPPPO (a), BPPPO-m benzoxazine monomer (b), BPPPO-a benzoxazine monomer (c), and BPPPO-ea benzoxazine monomer (d).

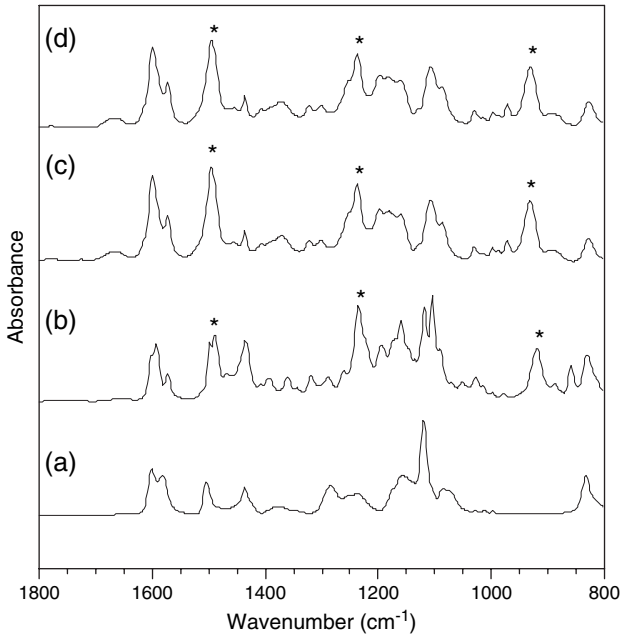


Fig. 4. FT-IR spectra of BHPPO (a), BHPPO-m benzoxazine monomer (b), BHPPO-a benzoxazine monomer (c), and BHPPO-ea benzoxazine monomer (d).

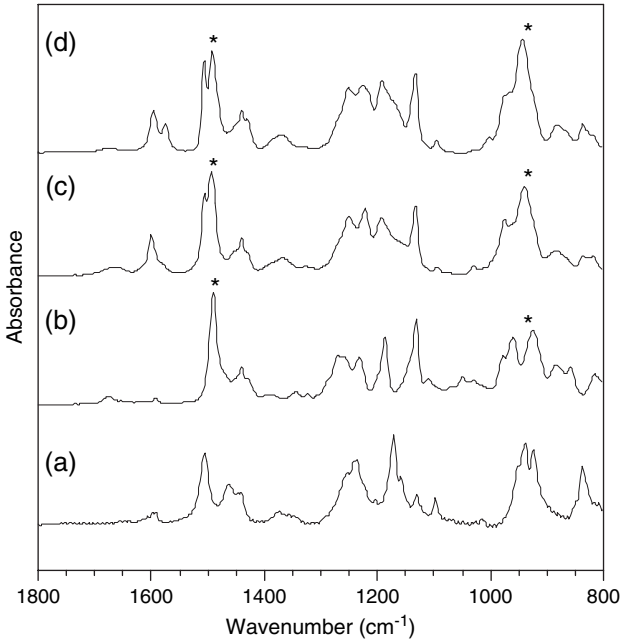


Fig. 6. FT-IR spectra of BPHPPO (a), BPHPPO-m benzoxazine monomer (b), BPHPPO-a benzoxazine monomer (c), and BPHPPO-ea benzoxazine monomer (d).

depended on the amount of shielding effect of the phenyl and ether groups between the phosphonic group and benzoxazine ring. The 1236 cm^{-1} band, which is assigned to the antisymmetric C–O–C stretch, absorbs in the same region for almost all monofunctional and bifunctional benzoxazine monomers.

On the other hand, the intensity of the bands at 832 and 1503 cm^{-1}, which are characteristic of the structure of the bisphenol as a starting compound, decreased after the reaction. The band at 832 cm^{-1} is assigned to the disubstituted benzene C–H out-of-plane deformation (vibration 17b) and the band at 1503 cm^{-1} is assigned to the C=C in-plane stretch (vibration 19a). It is the vibrational assignment for the *para*-substituted benzene ring. The benzene ring in bisphenol structure undergoes substitution from di- to tri-substituted benzene ring, which indicates the formation of benzene ring.

After the synthesis and characterization, the monomers were polymerized via ring-opening polymerization. The polymerization was initiated by thermal activation and cured at 185 °C for 4 h. The thermal decomposition characteristics of nine different polybenzoxazines are listed in Table 2, including the phosphorus content, the temperature of weight loss at different stages, and the char yield of the polymers under nitrogen determined at 800 °C.

Fig. 7 represents the TGA thermograms of polybenzoxazines derived from BA-m and BA-a. Bisphenol-A is one of the phenolic compounds often used as the starting material for the synthesis of polybenzoxazines. Therefore, polybenzoxazines synthesized from bisphenol-A are referred to as ordinary polybenzoxazines in this study. BA-m began to lose weight at 254 °C and then a two-stage weight loss process was observed, one at 272 °C and another at 422 °C. The study [31] using FT-IR–TGA interface shows that the first step of degradation is due to Mannich base cleavage (the cleavage of the C–N bond), resulting in the release of Schiff base (C=N) and various amines. The same study indicates that the second step degradation is due to the release of various substituted phenols after the cleavage of the isopropyl link in the central portion of the bisphenol. At 800 °C, the char yield of this polymer from BA-m under nitrogen is 34%. For BA-a, weight loss started at approximately 276 °C, and a marked decomposition occurred at 398 °C. Unlike BA-m, BA-a did not show significant degradation below 300 °C. This can be explained by the fact that electron delocalization between nitrogen and benzene ring makes it more difficult to break the C–N bond between the nitrogen and phenyl group. Therefore, it is more difficult to lose the phenyl group in BA-a at a higher temperature. The char yield of the polymer derived from BA-a was 29% at 800 °C, under nitrogen. The loss of two methyl groups in BA-m contributes only about 9% to the weight loss, while the loss of two phenyl groups in BA-a contributes approximately 17%, which does not correspond to fact that BA-m has higher char yield than BA-a. The mechanism of degradation of polymers depends on various factors and cannot be correlated at this point.

The thermal decomposition characteristics of nine different polybenzoxazines are listed in Table 2, including the phosphorus content, the temperature of weight loss at different stages, and the char yield of the polymers under nitrogen determined at 800 °C. The TGA thermograms of the polymers derived from BHPPO are shown in Fig. 8. BHPPO weight loss started at 230 °C, and showed similar two-stage weight loss as BA-m. The decomposition temperature of the first stage of weight loss is 250 °C, which was similar to BA-m. However, the temperature of the second stage of weight loss for BHPPO-m is 538 °C, which is 110 °C higher than that of BA-m. The shift of second stage degradation to higher temperature indicates that phorphorus incorporation has a significant effect on improving thermal stability of polybenzoxazines. At 800 °C, a char yield of 48% was achieved by BHPPO-m. This result shows the effect of phosphorylation on increasing char yield of polybenzoxazines. BHPPO-a showed lower char yield but a similar two-stage degradation pattern; however, the 3-ethynylaniline based BHPPO showed significant improvement in char yield due to crosslinking which was made possible by the acetylene functional group. BHPPO-ea showed

Table 2
Thermal decomposition characteristics of polybenzoxazines

Polymers	Phosphorous content (%)	Temperature of 1% wt loss	Temperature of 5% wt loss	Temperature of rapid wt loss	Char yield (%)
BA-m	0	254	264	272, 422	34
BA-a	0	276	330	398	28
BHPPO-m	7.37	233	250	250, 538	48
BHPPO-a	5.69	256	302	295, 456	41
BHPPO-ea	5.23	307	405	469	64
BPPPO-m	5.12	200	212	234, 402	30
BPPPO-a	4.25	364	259	260, 431	51
BPPPO-ea	3.99	350	403	465	76
BPHPPO-m	6.85	239	279	254, 533	34
BPHPPO-a	5.37	271	315	315, 405	52
BPHPPO-ea	4.96	313	351	417	63

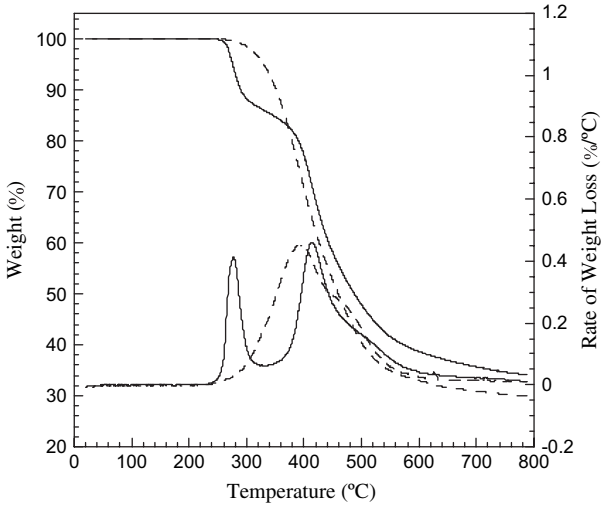


Fig. 7. TG and DTG analyses of BA-m (solid) and BA-a (dashed).

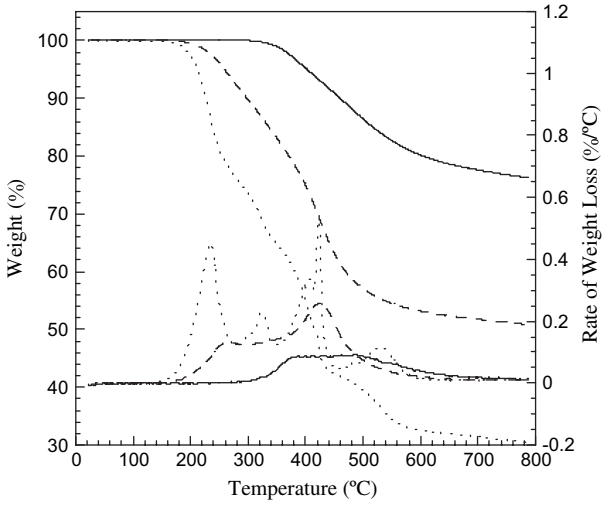


Fig. 9. TG and DTG analyses of BPPPO-m (dotted), BPPPO-a (dashed), and BPPPO-ea (solid).

a much less distinct two-stage degradation pattern than the aniline and methylamine-based polymers.

In Figs. 9 and 10, the TGA thermograms of polymers derived from BPPPO and BPHPPO are shown. The degradation patterns were found to be similar for the BHPPO-based, the BPPPO-based and the BPHPPO-based benzoxazine polymers with the methylamine and aniline-based polymers showing a distinct two-stage degradation pattern while the acetylene functionalized polymers showed a one-stage degradation pattern. In BPPPO and BPHPPO, the aniline-based polymers showed significant improvement of thermal stability (51% char yield) relative to the methylamine-based polymers (31% char yield). Similarly in the BPHPPO system, the char yield improved by 18% when comparing BPHPPO-a and BPHPPO-m. On the other hand, moderate changes in the opposite direction were observed when comparing char yields for BHPPO-m (48%) and BHPPO-a (41%). Thus, for the char yield of corresponding methylamine and amine based materials, there is no trend. This might be due to the change in chain scission mechanism. However, if the bond between the Mannich base chain and the side group, such as phenyl and methyl is broken, the methylamine-based compound will have higher char yield. In addition, for the acetylene functionalized polymers, the weight remained stable at temperatures 70–150 °C higher than the methylamine-based polymers which started to degrade around 230 °C. This is due to the effective crosslinking of the acetylene group. The char yield of BPPPO-ea was 76% while char yield of BPHPPO-ea was 63%. There was significant improvement of thermal stability of BPPPO-ea compared to the other two acetylene functionalized polymers. In addition to the phenylphosphine oxide functional group seen in BHPPO and BPHPPO, BPPPO has ether linkages.

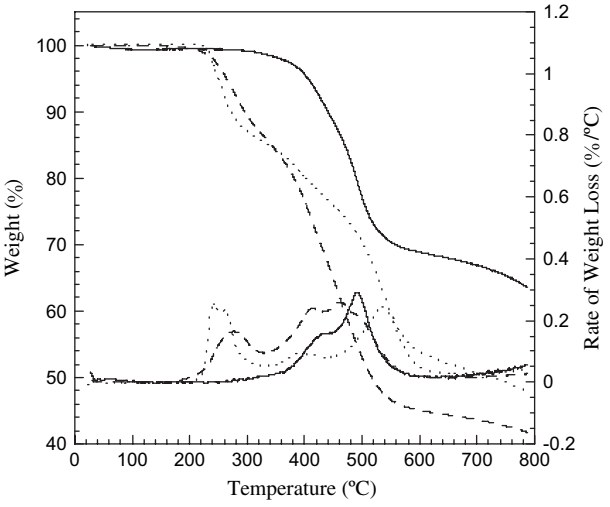


Fig. 8. TG and DTG analyses of BHPPO-m (dotted), BHPPO-a (dashed), and BHPPO-ea (solid).

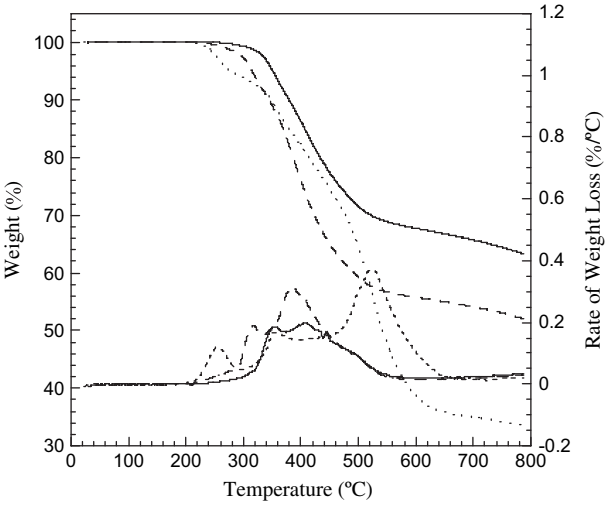


Fig. 10. TG and DTG analyses of BPHPPO-m (dotted), BPHPPO-a (dashed), and BPHPPO-ea (solid).

In our laboratory, it has been observed that polybenzoxazine synthesized from the bisphenol containing ether linkage decomposes at higher temperatures than normal benzoxazines. The explanation was proposed that upon degradation, the acetylene functional group undergoes further crosslinking, which results in more thermally stable structure and degrades at higher temperature. This may explain the high thermal stability of the BHPPO-ea, BPPPO-ea, and BPHPPO-ea.

4. Conclusion

Phosphorus-containing group was introduced into polybenzoxazine via monomer modification. Benzoxazine monomers containing phenylphosphine oxide were synthesized and subsequently polymerized via ring-opening polymerization by thermal initiation. The presence of phenylphosphine oxide group has shown an improvement in the thermal stability of polybenzoxazines except for the combination with methylamine. In case of introducing methylamine to three different types of phenylphosphine oxide structures, only BHPPO showed 14% improvement in char yield. However, the combination with BPPPO backbone and acetylene functional group on the aniline has shown a profound effect on improving the thermal stability of polybenzoxazine, demonstrated by the char yield as high as 76%.

Acknowledgment

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