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KINETIC MODELING OF MAIN-CHAIN BENZOXAZINE POLYMER SYNTHESIS STUDIED USING POLYMATH: CASE STUDY

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ABSTRACT

This study reports kinetics of benzoxazine synthesis of main chain type benzoxazine polymer (MCBP(BA-a)), which was derived using Mannich condensation reaction of bisphenol-A with formaldehyde and aniline. The chemical structural of MCBP(BA-a) was confirmed by Fourier-transform infrared (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Kinetics of benzoxazine (BZ) synthesis was theoretically studied using Polymath Software. The synthesis of BZ precursors consist of two main reactions. Reaction of amine with formaldehyde, and then followed by the reaction of phenolic compound with the intermediate component of the first reaction. Therefore, the effect of the reaction constant ratio (k_2/k_1) was investigated. In addition, the initial concentration of phenolic compound on the product also was evaluated. The results indicated that the best ratio of k_2/k_1 was found to be 2. The increase in the initial concentration of bisphenol-A an increase in the production BZ was observed. The results indicated that this theoretical study has good agreement with the experimental conditions for synthesis of main chain type benzoxazine.

***Keywords**:*
Bisphenol-A. Benzoxazine synthesis.
Kinetic modeling.
Polymerization.

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1 INTRODUCTION

Polybenzoxazines (PBZs) are thermosetting polymers that have received tremendous attention as an important class of polymeric materials in multidisciplinary applications due to their

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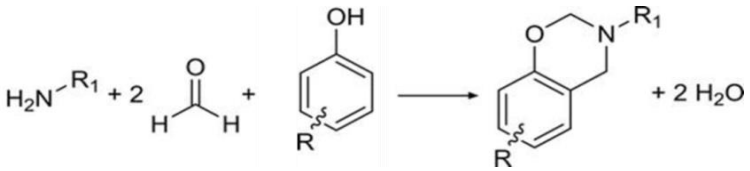
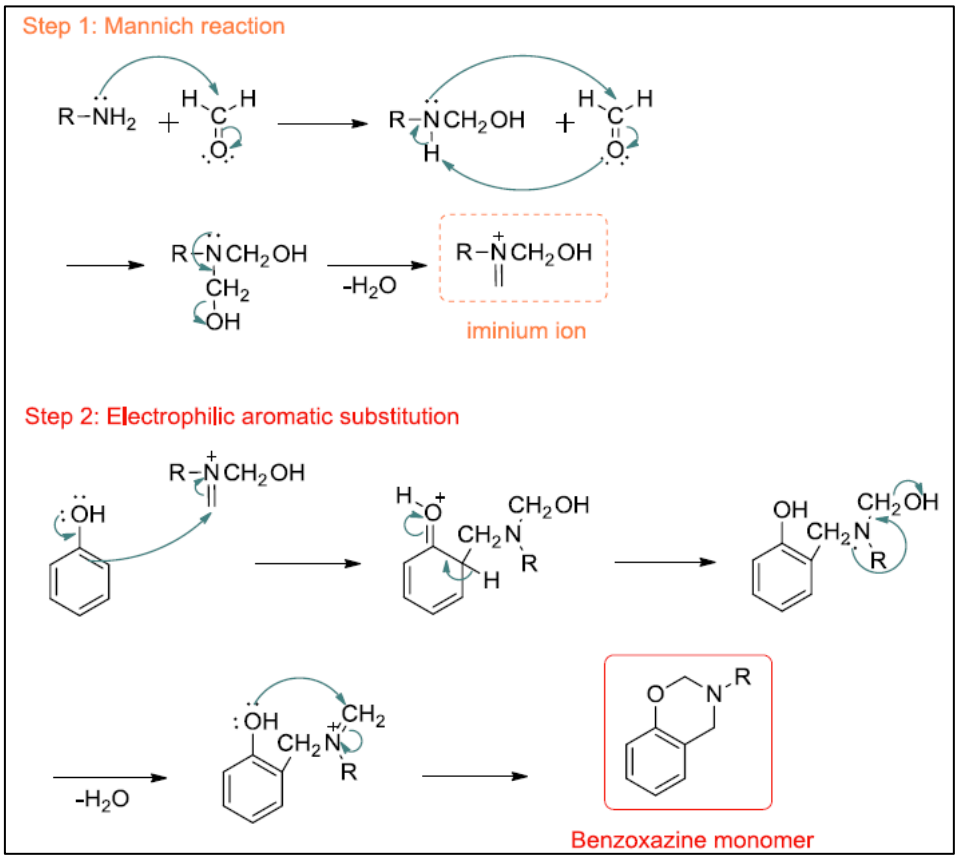
excellent properties including dimensional stability, chemical resistance, and improved thermal and physical properties [1,2].

BZ monomer is a molecule where an oxazine ring is attached to a benzene ring, which was discovered in 1944 by Holly and Cope [3]. BZs have been synthesized using Mannich condensation reaction of the starting materials (phenolic compounds, amines and formaldehyde) as seen in Scheme 1. Currently, there are various experimental types have been developed to synthesize BZ precursors, which can be classified into solvent Mannich condensation reaction and solventless reaction. Solventless method has two positive points: Eco-friendly material because there are no solvents that used and the reaction can be completed in short time. Evan though solventless is more favourable in industrial processes, the Mannich condensation of phenol and a primary amine with formaldehyde in presence of solvents is considered to be the more public method [2].



Scheme 1. The synthesis reaction of benzoxazine monomers; Adopted from Reference [1].

Previously, it was proposed that BZ synthesis occurs in two steps as seen in Scheme 2 [1]. In the first step, a fast chemical reaction of amine with formaldehyde leads to formation of an iminium ion. The second step is an electrophilic aromatic substitution followed by a ring-closure via dehydration reaction of the product, leading to the final BZ precursors. Therefore, the resultant of reaction of formaldehyde and amine is known as the intermediates [4]. Benzoxazines (BZs) precursors can be polymerized to form (PBZs) without any catalysts. It well known that BZs precursors are transformed to PBZs structure by thermally ring-opening polymerization of BZ monomers [5,6]. Due to the unique features of PBZs, development new BZs recourses has received considerable attention [1,5]. Therefore, PBZs-based materials have been attached in many applications due to their positive characteristics including volumetric stability during polymerization, high glass transition temperature, excellent mechanical integrity, high thermal stability, high char yield, good dielectric properties, and low flammability [1]. These good features are due to the outstanding molecular structure of BZ monomers and their polymerization behaviors. The more crosslinking density of PBZs, the more excellent properties that have been achieved [1,2]. Hence, it is necessary to understand the synthesis kinetics of BZ. Evan though many researchers investigated the polymerization kinetics of BZ precursors [7], only limited studies have been reported for synthesis kinetics of BZs [4].



Scheme 2. Classical approach for the synthesis of mono-functional BZ; Adopted from Reference [1].

As seen in Scheme 2, the kinetic parameters of BZ formation is depends on two step reaction. In point of view the kinetics, the controlling step of the reaction is very important to increase the productivity. Therefore, in BZ chemistry, it is possible that starting materials or intermediates play the key for the synthesis of BZ. It is well known that the formaldehyde, amine, and phenolic compound are the starting materials; however, formaldehyde and amine only are involving in the reaction for synthesis of the intermediate component. Therefore, the first reaction is more to be the controlling step reaction. Additionally, concentration of phenolic compound plays an important role in the BZ formation due to its reaction with the intermediate. Zhang and his co-worker [4] experimentally investigated the kinetics for BZ derivation from n-propylamine, phenol, and formaldehyde solution as starting materials at different conditions (i.e., concentrations of the stating materials, reaction temperature, and time). They found that phenol played an important role in the preparation of BZ and the key starting material. The reaction of starting materials produce mono-benzoxazine monomer; however, main-chain benzoxazine polymer (MCBP) showed better properties. To the best of our knowledge, there is no study has been reported for investigation of the synthesis kinetics

of the MCBP. In the present study, the kinetics for BZ synthesis from aniline, bisphenol A, and formaldehyde was theoretically investigated. The models for the concentration changes of the chemicals with time were derived. In addition, the kinetic parameters for formation of main-chain benzoxazine polymer were studied using *polymath* software. Finally, the effect of bisphenol A concentration in the BZ production was also investigated.

2 MATERIALS AND METHOD

2.1 Materials

Bisphenol-A (97%), para-formaldehyde (97%), and aniline (99%) were purchased from Sigma-Aldrich. The solvents, chloroform, 1,4-dioxan, and ethanol were purchased from Fisher Scientific. All chemicals were used as received without any further purification.

Table 1 Represents the abbreviations and purity of the starting materials.

Chemical	Abbreviation	Denotes in the rxn Eq.	Purity	Melting Point
Aniline	a	A	97%	-6.3
Formaldehyde	-	B	97%	-
Bisphenol A	BA	C	99%	158
Main-chain benzoxazine polymer	MCBP(BA-a)	D	--	110

2.2 Characterizations

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker NMR spectrometer (300 MHz). FTIR spectra for the composites were recorded from 4000 to 400 cm^{-1} on an Agilent Cary 630 FTIR spectrometer instrument. Differential scanning calorimetry (DSC) Model 2920 was used with a temperature ramp rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests of DSC study [8].

2.3 Synthesis of MCBP(BA-a)

The main chain benzoxazine polymer MCBP(BA-a) was synthesized according to the procedure reported elsewhere [9]. Stoichiometric amounts of bisphenol-A (0.05369 mol), paraformaldehyde (0.21475 mol), and aniline (0.10737 mol) were mixed together at room temperature, and then placed in a three-necked flask equipped with a condenser setup in order to collect the water evolved during the condensation reaction. The mixture of reactants was

heated at a constant temperature of 110 °C for 30 min with continuous constant stirring until the product became yellowish color. The resultant product was dissolved in 1,4-dioxan and washed three times with NaOH aqueous solution and twice with distilled water and finally with copious amount of distilled water followed by vacuum drying to give light-yellow crystal as seen in Figure 1.

2.4 Polymerization of Benzoxazine MCBP(BA-a)

Polymerization of the obtained BZ precursor was a part of this study. Figure 1 shows the transformation of the resultant MCBP(BA-a) precursor into a film form. A specific amount of the collected MCBP(BA-a) was grained into a powder, and then it dissolved in a 1,4-dioxan as a solvent to produce a homogeneous MCBP(BA-a) solution. The obtained solution was casted over a clean glass plate, and then it was dried at atmosphere for 24 h. The polymerization behavior of the produced MCBP(BA-a) monomer was a also evaluated. The study was performed based on thermally stepwise polymerization of the thin-film of MCBP(BA-a) up to 200 ^{o}C /2 h in an air circular oven. As seen in Figure 1, the change in the color of the film from yellowish to brown color is ascribed to the change in the chemical structure of MCBP(BA-a) precursor due to the ring-opening polymerization. Similar tendency was widely observed [9-12].

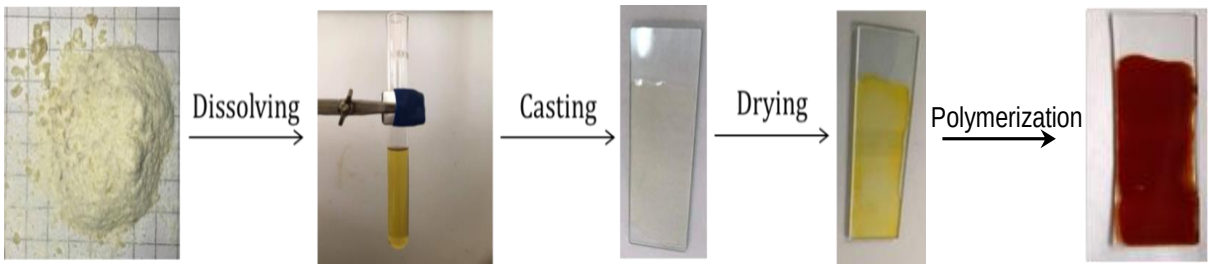


Figure 1 Preparation steps of MCPB(BA-a) thin film.

3 THEORY AND CALCULATION

3.1 Kinetic Modeling of MCBP(BA-a) synthesis

Previously, it has been reported that the production of BZ precursors via Mannich condensation reaction consists of two steps as given in Eqs. (1) and (2) [1,4]: In the first step, aniline (A) reacts with paraformaldehyde (B) to produce an iminium ion as an intermediate material (C). In the second step, an iminium ion (C) reacts with bisphenol-A (D) to produce BZ (E).

$$A + 2B \overset{k_1}{\rightarrow} C \quad (1)$$

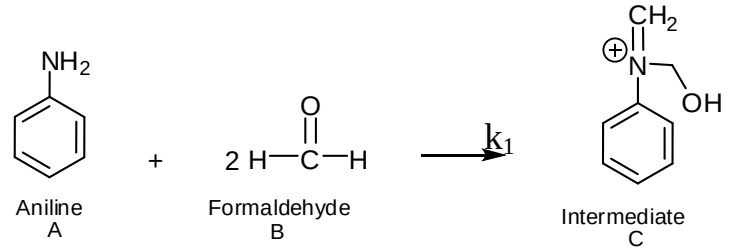
$$2C + D \overset{k_2}{\rightarrow} E \quad (2)$$

According to the proposed synthesis equations, the reaction in Scheme 1 for BZ production is considered a non-elementary reaction due to the formation intermediate products. These products from the reaction of amine and formaldehyde will react with phenol and form BZ as the final product.

The rate equations for chemical reactions are differential equation forms that describe the change of concentration of the component with time. In the present work, the reaction rate equations of amine, formaldehyde, phenol, and the produced BZ were developed. Therefore, the changes in the concentrations of these components were investigated. *Polymath* software was used to solve the derived differential equations. Also, the effect of initial concentration of starting reactant (bisphenol-A) and effect of reaction rate constants ratio are studied.

3.1.1 First reaction: Mannich reaction

In the present study, the synthesis kinetics of the main-chain type BZ polymer MCBP(BA-a) depends on the concentrations of aniline, formaldehyde, and bisphenol A as the starting materials with initial mole ratio of 2:4:1. According, in the first reaction, each one mole of aniline as the source of primary amine reacts with two moles of formaldehyde to form intermediate product as given in Scheme 3.



Scheme 3 Formation of an iminium ion as intermediate product from the first reaction.

According to the reaction in Scheme 3, each 1 mol of aniline (A) reacts with 2 moles of formaldehyde (B) to form an iminium ion (C), which has defined in Eq. 1 as the first reaction for BZ formation. Therefore, the changes in the concentrations of the starting materials with time can be written as:

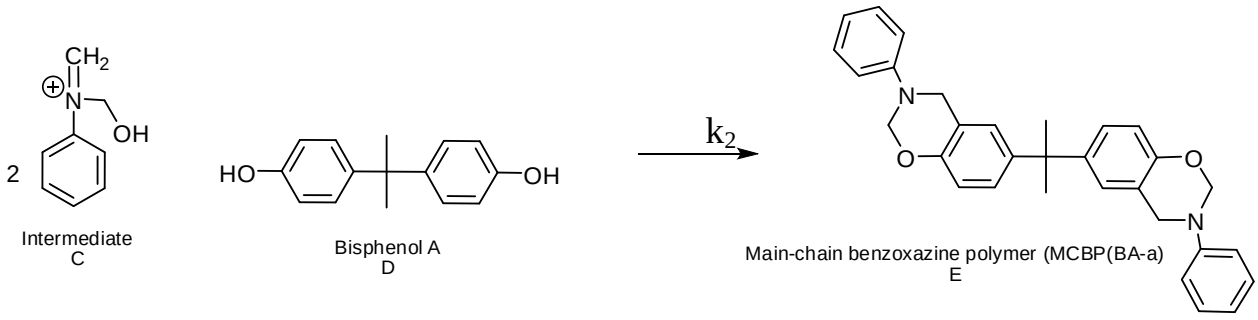
$$\frac{dC_A}{dt} = -k_1 C_A C_B^2 \quad (3)$$

$$\frac{dC_B}{dt} = -2 k_1 C_A C_B^2 \quad (4)$$

Where: C_A is the concentration of aniline (A), mol/L; C_B is the concentration of the formaldehyde (B), mol/L; k_1 is the reaction rate constant for first reaction, $L^2/mol^2.h$; and t is the reaction time, h.

3.1.2 Second reaction: Electrophilic aromatic substation

The poduced iminium ion as intermediate product from the first reaction is attractive and favrable to react with the third starting material, bisphenol A, via electrophilic aromatic substation. In this reaction, the main-chan benzoxazine polymer as the final product of reaction of 2 mole of the iminium ion with one mole of besiphenol A as shown in Scheme 4.



Scheme 4 *Formation of main-chain benzoxazine polymer (MCBP(BA-a)) as final product.*

According to the first and the second reactions that given in Eqs 1 and 2, the change in the concentration of the reactants and products in Scheme 4 can be expressed as:

$$\frac{dC_C}{dt} = k_1\, C_A C_B^2 - k_2 C_C^2 C_D \qquad (5)$$

$$\frac{dC_D}{dt} = -\frac{1}{2} k_2\, C_C^2 C_D \qquad (6)$$

$$\frac{dC_E}{dt} = \frac{1}{2} k_2\, C_C^2 C_D \qquad (7)$$

Where C_A is the concentration of aniline (A), mol/L; C_B is the concentration of paraformaldehyde (B), mol/L; $C_C$is the concentration of intermediate material (C), mol/L; C_D is the concentration of bisphenol-A (D), mol/L; C_E is the concentration of BZ (E), mol/L; k_1 is the reaction rate constant for first reaction, L^2/ mol^2.h; k_2 is the reaction rate constant for second reaction, L^2/ mol^2.h; t is the operating time, h.

4 RESULTS AND DISCUSSION

4.1 Confirmation of Chemical Structural of Benzoxazine

The structure of the MCBP(BA-a) confirmed using ^{1}H NMR and FT-IR. Figure 2 shows the ^{1}H NMR spectra recorded for the MCBP(BA-a). The single at 1.56 ppm was related to the protons of methyl group (–CH_3). The single protons at 6.00 and 4.61 ppm are ascribed to (–O–CH_2–N–) and (Ar–CH_2– N–), respectively, which are the characteristic protons of oxazine ring. The multiple bands in the range of 6.78–7.21 ppm is may due to the protons of benzene rings [6,9].

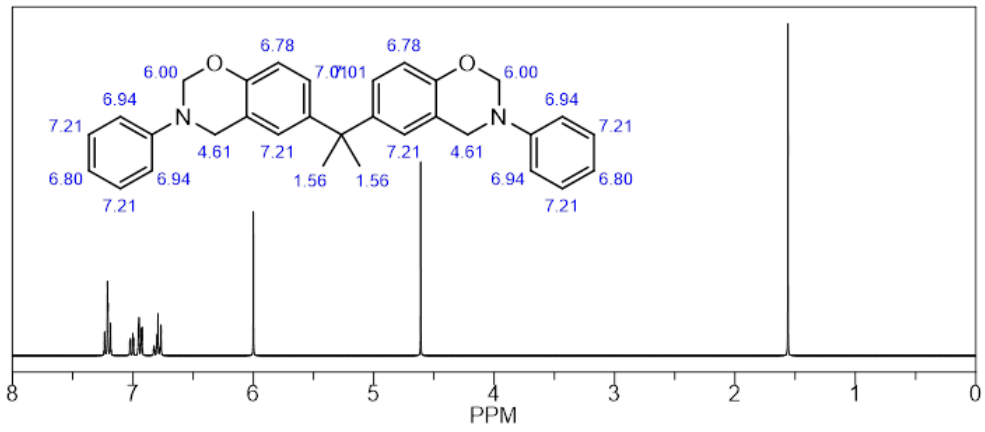


Figure 2. ^{1}H NMR spectrum of Bisphenol-A benzoxazine monomer.

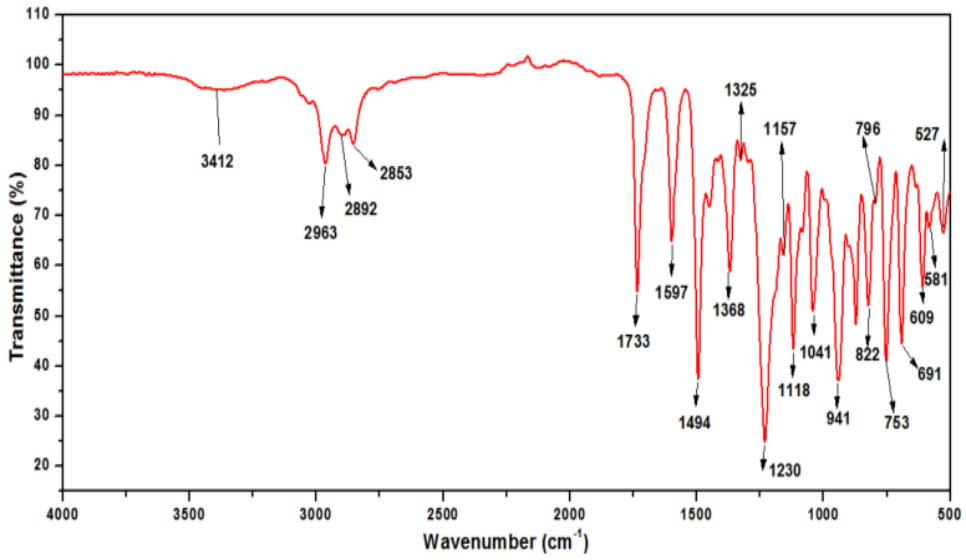


Figure 3. FTIR of Bisphenol-A aniline-based benzoxazine monomer.

Figure 3 represents FT-IR spectrum of the obtained main-chain benzoxazine polymer (MCBP(BA-a)). The characteristic absorption peak at 941 cm^{-1} indicates the oxazine ring. Also, 1230 cm^{-1} indicates the C–O–C symmetric and asymmetric stretching of C–O–C located at 1041 cm^{-1}. C–N–C asymmetric and symmetric stretching vibration observed at 1118–1157 cm^{-1} and around 822 cm^{-1} confirmed the structure of the BZ ring. The sharp and very strong bands at 1494 cm^{-1} and the bands with medium intensity at 1597 cm^{-1} correspond to the tri-substituted structure of the benzene ring with in-plane as well as the out-of-plane bending mode of C-H. There is an OH peak at 3412 cm^{-1} and it may due to ring-opening benzoxazine monomer structure in smaller quantity [6-9].

4.2 Differential Scanning Calorimetry (DSC)

DSC has been widely used to study the polymerization behavior of BZ monomer. The research group of the Professor Ishida [13] has been reported the DSC thermograms of high purity MCBP(BA-a) as given in Figure 4. The thermogram shows a sharp endothermic peak at 110 °C, thus supporting the notion of high purity of monomer. However, the results shows a typical exothermic behavior at high temperature 265 °C, which is ascribed to the ring-opening polymerization of benzoxazine [6,9,13,14]. The enthalpy of the endothermic or exothermic event is determined by the integration of the area under the DSC peak.

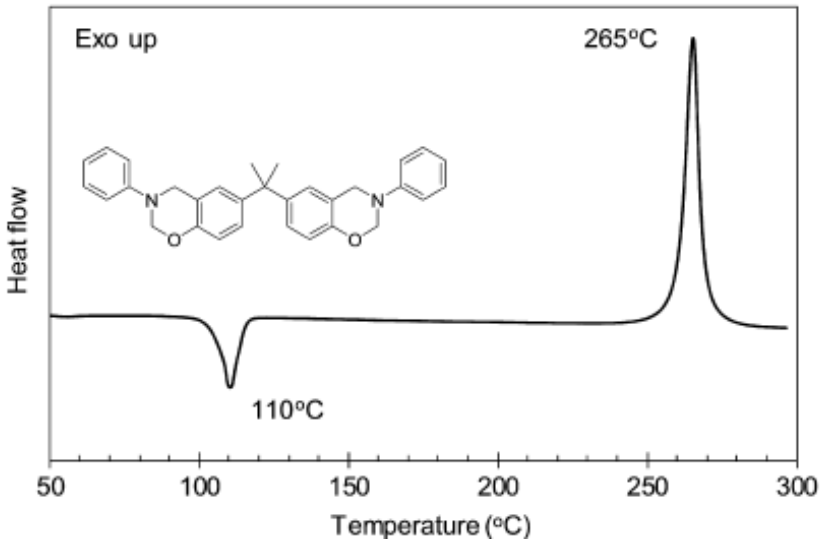


Figure 4. DSC curve for bisphenol-A benzoxazine monomer; Adopted from Reference [12].

4.3 Kinetic Analysis of Synthesis of the Benzoxazine Monomer

Figure 5 shows the kinetics of the reactants, intermediate components, and products. These changes in concentrations with time were determined theoretically using *Polymath* software as described in Section 3. The results indicated that the initial concentrations of aniline (A), formaldehyde (B) and bisphenol-A (D) decrease with an increase in the reaction time, however, resultant BZ (E) increases with time. For example, with an increase in time from 0 to 3 min the concentration of aniline, formaldehyde, and bisphenol-A were decreased from 3.84 to 0.84, 7.68 to 1.68, and 1.92 to 1.18 mol/L, respectively. The decrease in the concentrations of the starting materials is in general due to the consumption of these reactants and contributes for formation of BZ monomer (E). Also, the results indicated that the intermediate product (C) was sharply increased with time in the first 3 min, and then it was gradually decreased until reached a minimum value after about 60 min. For example, the initial concentration of intermediate product (C) was increased from 0 to 1.7 mol/L with an

increase in time from 0 to ~2.7 min. However, it was decreases from 1.7 to ~0.3 mol/L with an increase in time from ~2.7 min to 120 min. this behavior of change in the concentration has been considered in many series reactions [4]. The fast increase in the concentration of the intermediate at beginning of reaction can be explained that the accumulation of this component was increased due to the generation from the first reaction without consumption; however, the decline in the intermediate composition in the mixture was reduced is ascribed to its consumption after starting the second reaction [4].

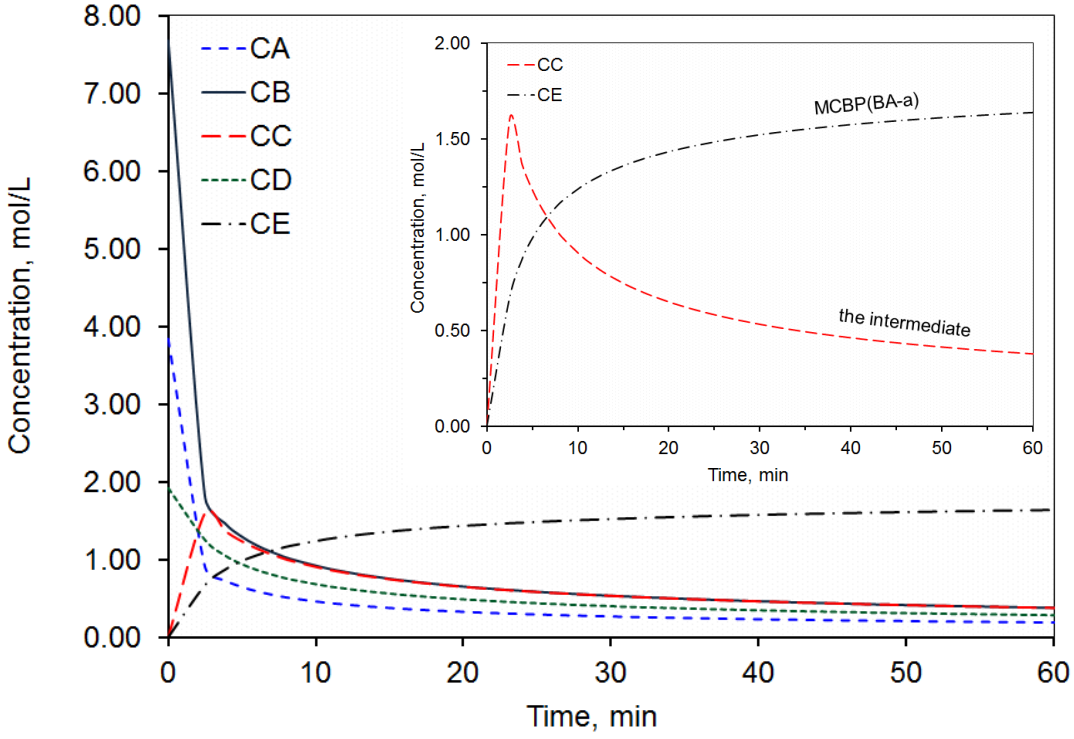


Figure 5. Concentration profiles of reactants and product.

4.3.1 *Effect of Initial Concentration of Starting Materials*

Figure 6a displays the change in MCBP(BA-a) concentration (C_E) with time at different initial concentrations of bisphenol-A (C_{Do}) and the equilibrium values are shown in Figure 6b. The results indicated that the concentration of MCBP(BA-a) is directly proportional with the initial concentration of bisphenol-A, as the concentration value of bisphenol-A increases, an increases in the productivity of MCBP(BA-a) was observed. For example, when the initial concentration of bisphenol-A (C_{Do}) was increased from 1.3 to 1.7 mol/L, the concentration of BZ (C_E) was increased from 1.19 to 1.37 mol/L during an increase in the time from 0 to 20 min. The results also showed that the concentration of MCBP(BA-a) reaches the equilibrium values at low bisphenol-A concentrations faster than at high concentrations. For instance, the equilibrium concentration of MCBP(BA-a) was achieved after only 20 min reaction time for

using C_{Do} was 1 mol/L; however, initial concentration (C_{Do}) of 1.5 mol/L showed an equilibrium after 75 min. these finding are in good agreement with literature [4].

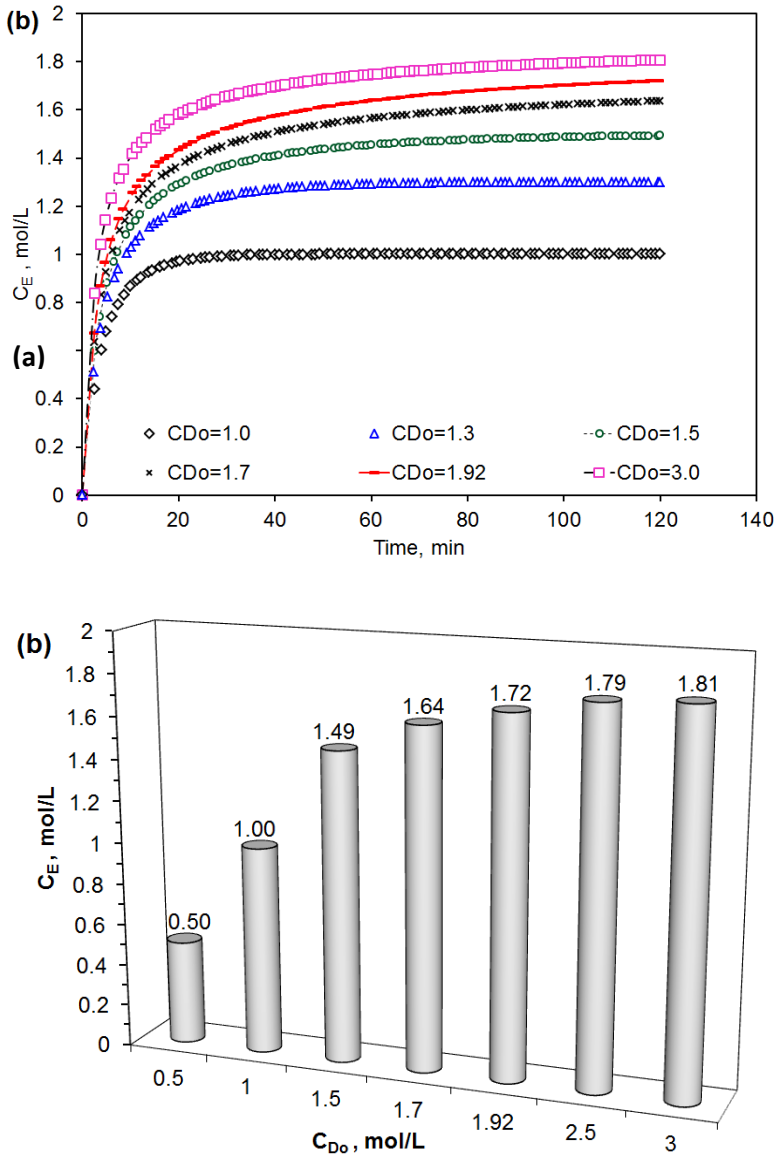


Figure 6 Effect of the initial concentration of bispheneol A on the productivity of BZ: (a) function of time, and (b) at equilibrium concentration.

As seen in Figure 6b, the optimum initial concentration of bisphenol A as the phenolic compound of the starting materials is 1.92 mol/L. Therefore, the change in of the concentrations of bisphenol A and the produced BZ was investigated and the results are given in Figure 7. It is clear that the productivity of BZ was fast at the first 17 min, and then it was gradually increased to reach equilibrium. The results indicated that the concentration of

bisphenol A was reduced from 1.92 to 0.18 mol/L after 1 h. According to initial and final concentrations of bisphenol A as starting material, its conversion was estimated as given in Eq. 8. Therefore, the conversion of bisphenol A was found to be 90.5% after 1h.

$$x_A = \left(1 - \frac{C_A}{C_{Ao}}\right) \times 100 \qquad (8)$$

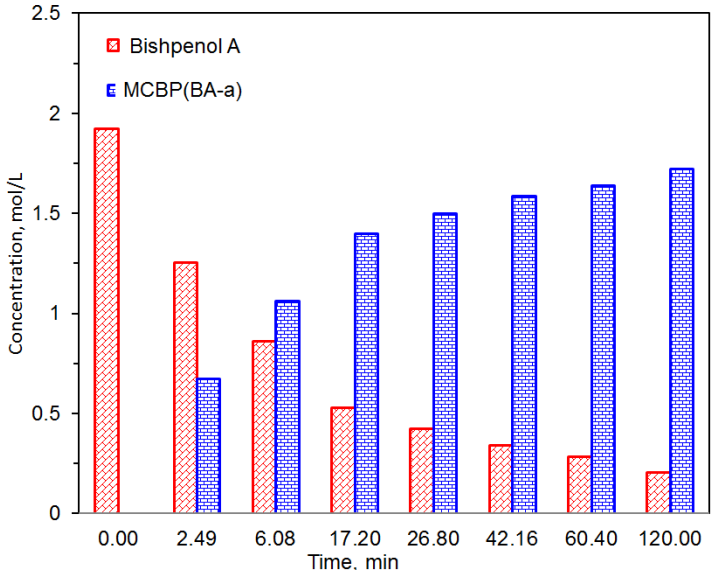


Figure 7 The productivity of BZ using 1.92 mol/L initial concentration of basiphenol A as a function on the reaction time.

4.3.2 Effect of (k_2/k_1) ratio

According to Eqs. 1 and 2, the value of k_1 is defined as the reaction constant of aniline (A) with formaldehyde (B) to produce intermediate product (c) and the value of k_2 is defined as the reaction constant of the intermediate with the phenol (D) to produce (E) as the final product, MCBP(BA-a). Figure 8 shows the concentration of the intermediate product C_E as a function of time (t) at various reaction constants ratios k_2/k_1. The results indicated that the concentration of the final product MCBP(BA-a) is to be directly proportional to the k_2/k_1 ratio as it increases with increase in k_2/k_1. It obvious that the MCBP(BA-a) concentration reaches the equilibrium of 1.5 mol/L at k_2/k_1 = 1; however, when k_2/k_1 = 2 the it reaches the equilibrium at 3 mol/L. This means that the k_2/k_1 ratio must be kept high to get the highest concentration of MCBP(BA-a), whereas increase the second reaction (see Schemes 1 and 2). Accordingly, the first reaction, which involves the reaction of aniline with formaldehyde, is to be the controlling step.

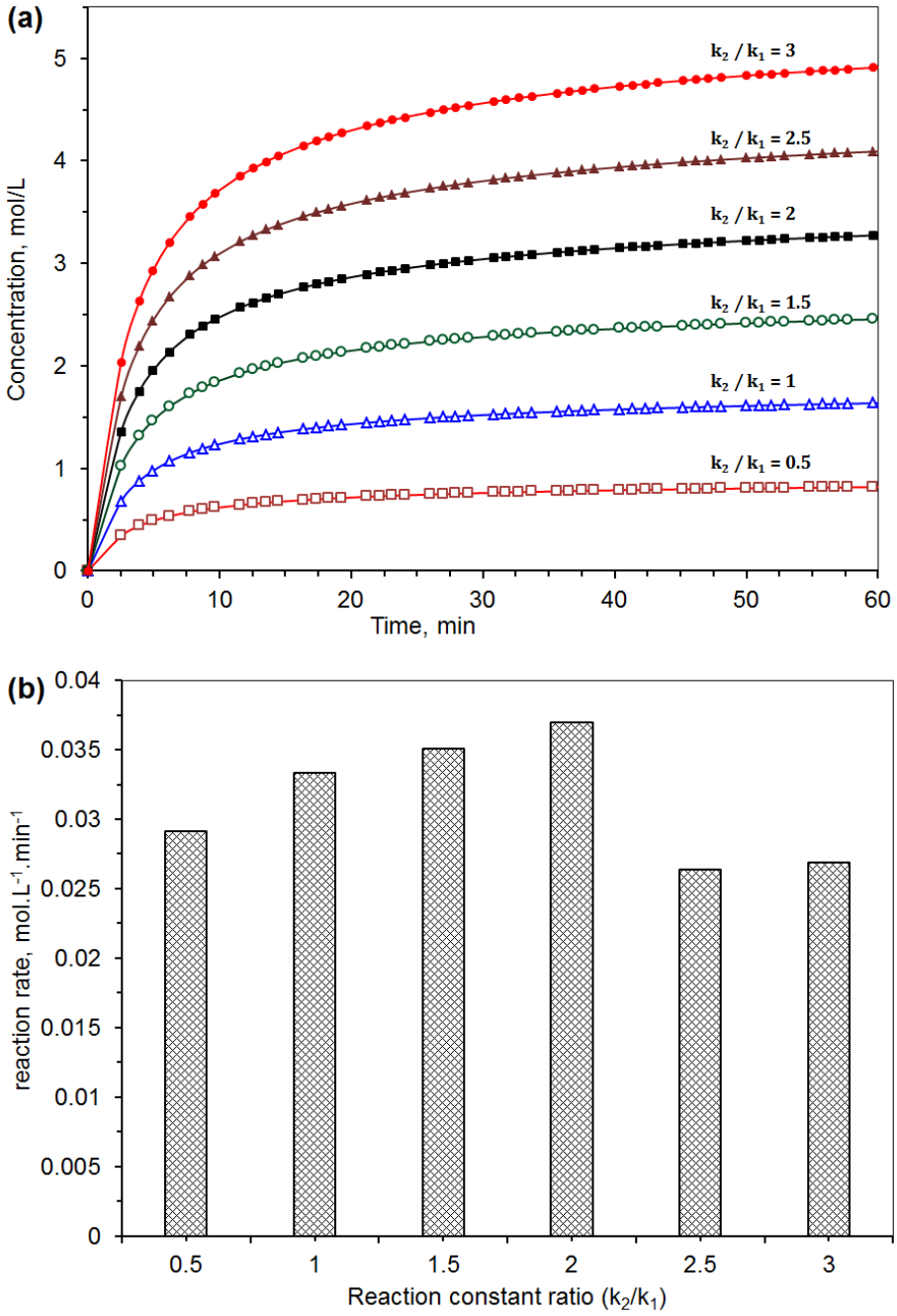


Figure 8 Effect of reaction constant ratio on: (a) Concentration profile of bisphenol-A at different k_2/k_1 ratio. (b) Reaction rate for MCBP(BA-a) production at different k_2/k_1 ratio.

The previous studies indicated that BZ synthesis is endothermic reaction [1,2,6]. Therefore, these reactions are favorable with temperature. This require the operating at a high temperature and that is not possible due to polymerization issue of the monomer at high

temperatures. The results also indicated that the MCBP(BA-a) concentration (C_E) reaches the equilibrium at high k_2/k_1 ratios faster that at lower values of reactions constants ratios. For example, when k_2/k_1 = 0.5, CE at 10 min is approximately equal to C_E at 30 min which is almost equal 0.7 mol/L. Table 4.1 shows the equilibrium concentration and reaction rate of (E). The reaction rate constant is important to determine the time which the reaction to finish.

5 CONCLUSIONS

In this study, the synthesis BZ monomer that derived from the reaction of bisphenol-A, aniline, and paraformaldehyde was experimentally prepared using the solventless method and kinetics of this reaction was also theoretically investigated. The effect of reaction constants ratio on the concentration of the resultant BZ monomer in the mixture was investigated. The results showed that the formation of BZ monomer has proportional relation with the ratio of the reaction constants as k_2/k_1. In addition, to achieve a maximum conversion, the second reaction rate constant (k_2) should be kept a double of the first reaction rate constant (k_1) (i.e. k_2=2 k_1). Furthermore, the results indicated that the initial concentration of bisphenol-A has considerable effect on the production of BZ monomer. The amount of the produced BZ increases with an increase in the initial concentration of phenolic compounds.

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نمذجة حركية تحضير البوليمر بنزوكسازين ذو السلسلة الرئيسية بإستخدام البولي- ماث (POLYMATH): دراسة حالة

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الملخص

في هذا البحث تمت دراسة تأثير وجود أيون الثيوكبريتات على التأكل النقري لسبائك الفولاذ المقاوم للصدأ في تراكيز مختلفة من محاليل كلوريد الصوديوم. كل التجارب أجريت عند 50 درجة مئوية. الطريقة المستخدمة في هذه الدراسة تسمى طريقة الجهد المتغير. تم اختبار نسب مختلفة من ثيوكبريتات /كلوريد (نسب 0، 0.01، 0.03، 0.075، 0.1، 0.2، 0.3) و تشير هذه الدراسة إلى حركية تحضير البنزوكسازين من نوع السلسلة الرئيسية الذي يرمز بالرمز (MCBP(BA-a))، والذي تم اشتقاقه باستخدام تفاعل مانك التكثيف (Mannich condensation reaction) لمركب (bisphenol-A) مع الفورمالديهايد (formaldehyde) والأنيلين (aniline). تم تأكيد التركيب الكيميائي للمادة الناتجة (MCBP(BA-a)) بواسطة جهاز الأشعة تحت الحمراء (FTIR) والتحليل الطيفي بالرنين المغناطيسي النووي (H NMR1). تمت دراسة حركية تحضير البنزوكسازين نظريًا باستخدام برنامج البولي مات (Polymath). يتكون تحضير البنزوكسازين من تفاعلين رئيسيين. تفاعل الأمين مع الفورمالديهايد يحدث أولاً، ثم يليه تفاعل مركب (bisphenol-A) مع الناتج الوسيط للتفاعل الأول. لذلك، تم فحص تأثير النسبة بين ثابتي التفاعل لتكوين المادة الوسطية الذي يمثله التفاعل الثاني وتكون الناتج النهائي الذي يمثله التفاعل الأول (k_2/k_1) على إنتاجية البنزوكسازين. بالإضافة إلى ذلك، التحقق من دور وتأثير التركيز لمركب (bisphenol-A) كمادة أولية على إنتاجية البنزوكسازين من ضمن هذه الدراسة. ولقد أشارت النتائج بأن أفضل نسبة k_2/k_1 لإنتاج البنزوكسازين ذو السلسلة الرئيسية (MCBP(BA-a)) كانت 2.0. وكذلك أفادت النتائج بأن الزيادة في التركيز الأولي لمركب (bisphenol-A) وزيادة في إنتاج البنزوكسازين (MCBP(BA-a)). أشارت النتائج إلى أن هذه الدراسة النظرية تتفق بشكل جيد مع الشروط التجريبية لتصنيع نوع البنزوكسازين ذو السلسلة الرئيسية.

الكلمات الدالة:
البنزوكسازين ذو السلسلة الرئيسية.
تحضير البنزوكسازين.
نمذجة حركية التفاعل.
البلمرة.

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