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Thermally	stable	polybenzoxazines	via
tetrahydrophtha	limide-functional	monobenzoxazines:	Synthesis,
characterization	and thermally activ	vated polymerization kin	netics

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### Highlights

- 1. Two tetrahydrophthalimide-functional benzoxazines were successfully synthesized.
- 2. Polymerization behavior and thermal properties were investigated.
- 3. Polymerization activation energy was calculated by Kissinger and Starink methods.
- 4. The predicated autocatalytic models were in excellent agreement with experimental results.

**ABSTRACT:** Two benzoxazine monomers with attached tetrahydrophthalimide at *para* and *ortho* position have been synthesized via Mannich condensation. The chemical structures of obtained monomers have been confirmed by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FT-IR). The ring-opening polymerization has been examined by differential scanning calorimetry (DSC) analysis, which reveals that the *ortho*-tetrahydrophthalimide benzoxazine monomer exhibits lower polymerization temperature compared with its *para*-counterpart. Besides, the kinetic parameters have been determined by non-isothermal DSC at various

The heating rates. apparent activation energy values of paraand ortho-tetrahydrophthalimide functional benzoxazine monomers are determined to be 107.12 and 91.00 kJ/mol, respectively, according to the Starink method. In addition, the polymerization processes of both monomers can be well described by autocatalytic kinetic models. The predicted curves based on the developed models from this study fit well with the experimental DSC thermograms. Moreover, the thermal properties of polybenzoxazines have also been evaluated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

**Keyword:** Benzoxazine; tetrahydrophthalimide; polymerization kinetics; thermal stability.

#### 1. Introduction

Benzoxazine resin is a relatively new thermoset which can be synthesized by Mannich condensation from phenols, amines, and formaldehyde [1,2]. The corresponding polymerized derivative of benzoxazine resin, namely polybenzoxazine, has been extensively reviewed due to its outstanding advantages [3-6]. The major advantages of polybenzoxazine include their low water absorption [7], high char yield [8], near-zero shrinkage upon polymerization [9], low surface free energy [10,11], and excellent mechanical and thermal properties [12,13]. These various characteristics of this class of polymers are mainly attributed to the existence of inter/intra molecular hydrogen bonding in the cross-linked network.

The molecular design flexibility offers myriad of modification in the structures simply by replacing functionalized phenols or amines to achieve polybenzoxazines with desired properties. To further improve the thermal stability of polybenzoxazines, benzoxazine monomers with different functionalities have been synthesized. These various preparations include the incorporation of functional groups such as maleimide [14], norbornene [15], benzoxazole [16], phthalonitrile [17], allyloxy [18] and amide [19] into the benzoxazine structures. In particular, polybenzoxazines derived from benzoxazines consisting of phthalimide components have been shown to possess significant advantages over the traditional benzoxazine resins [20-22]. However, the trade-off generally exists between the thermal resistance and processability. The rigidity, originating from the combination of imide structure with an aromatic structure, results in polybenzoxazines with a very high glass transition temperature ( $T_g$ ). Meanwhile, the high rigid chemical structure also brings the difficulties in material processing due to the high melting temperature and the narrow processing window [21]. Thus, developing new approaches to improve the processability of imide functional benzoxazines is highly desired.

In this study, two benzoxazine monomers with tetrahydrophthalimide functionality have been synthesized via Mannich condensation. The tetrahydrophthalimide

functionality is in the *para* and *ortho* position with respect to the oxygen group in the oxazine ring of benzoxazines. As a hydrogenated product of phthalimide group, tetrahydrophthalimide can significantly reduce the rigidity of benzene end-cap in phthalimide benzoxazines, resulting in the easy synthesis and processability of benzoxazine resins without sacrificing too much in thermal properties of the polybenzoxazines. polymerization corresponding Besides, the kinetics of tetrahydrophthalimide functional benzoxazines have been systematically investigated via the non-isothermal DSC technique. As one of the most utilized methods to determine the polymerization kinetic parameters, non-isothermal DSC method has been carried out at various heating rates to evaluate the polymerization kinetics for benzoxazine reins.[17,23,24] The predicted curves based on our developed models in this study fit well with the experimental DSC thermograms. Notably, the highly purified monomers were used in the current kinetic study in order to minimize the impurity-related variation of the data within the same compound. The detailed synthetic strategy, characterization, polymerization kinetics and thermal properties of tetrahydrophthalimide functional benzoxazines are discussed in this article.

### 2. Experimental

#### 2.1 Materials

*Cis*-1,2,3,6-tetrahydrophthalic anhydride (99%), *p*-aminophenol (99%), paraformaldehyde (99%), and *o*-aminophenol (99%) were purchased from Sigma-Aldrich. Acetic acid, xylenes, aniline were received from Sahn Chemical Technologies. 2-(3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazin-8-yl)-3a,4,7,7a-tetrahydro-1*H*-isoindole -1,3(2*H*)-dione (abbreviated as *o*HTI-a), was synthesized following our recent reported method [22].

#### 2.2 Methods

Synthesis of 2-(4-hydroxyphenyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione

(abbreviated pHTI). Into 250 mL round flask placed as а were cis-1,2,3,6-tetrahydrophthalic anhydride (4.56 g, 0.03 mol), p-aminophenol (3.27 g, 0.03 mol), and 80 ml of acetic acid. The mixture was stirred and refluxed for 6 h. After cooling to room temperature, the precipitate was filtered and washed with 500 mL of deionized water. Removal of water by evaporation afforded a white powder. The resulting white product was recrystallized from isopropanol. (yield ca. 91%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>), ppm:  $\delta$  = 2.22-2.27 (m, 2H, -CH<sub>2</sub>-), 2.40-2.49 (m, 2H, -CH<sub>2</sub>-), 3.22 (t, 2H), 5.95 (t, 2H, =C-H), 6.86-6.99 (4H, Ar), 9.76 (s, 1H, -OH).

#### Synthesis

of

2-(3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazin-6-yl)-3a,4,7,7a-tetrahydro-1*H*-isoin dole-1,3(2*H*)-dione (abbreviated as *p*HTI-a). Into a 100 mL round flask were added 30 mL of xylenes, aniline (0.93 g, 0.01 mol), *p*HTI (2.43 g, 0.01 mol), and paraformaldehyde (0.61 g, 0.02 mol). The mixture was stirred at 120 °C for 6 h. The mixture was cooled to room temperature and yellow crystal was obtained. (yield ca. 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>), ppm:  $\delta$  = 2.29-2.33 (m, 2H, -CH<sub>2</sub>-), 2.70-2.75 (m, 2H, -CH<sub>2</sub>-), 3.26 (t, 2H), 4.67 (s, 2H, Ar-CH<sub>2</sub>-N, oxazine), 5.38 (s, 2H, O-CH<sub>2</sub>-N, oxazine), 6.00 (t, 2H, =C-H), 6.77-7.37 (8H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>), ppm:  $\delta$  =50.48 (1C, Ar-CH<sub>2</sub>-N-), 79.69 (1C, -O-CH<sub>2</sub>-N-). FT-IR spectra (KBr), cm<sup>-1</sup>: 1771, 1706 (imide I), 1497 (stretching of trisubstituted benzene ring), 1388 (imide II), 1239 (C-O-C asymmetric stretching), 942 (out-of-plane C-H).

Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.31%; H, 5.60%; N, 7.74%.

**Polymerization of tetrahydrophthalimide functional benzoxazine monomers.** Both tetrahydrophthalimide functional benzoxazine monomers were thermally activated polymerized at different temperature cycles without adding any initiators or catalysts. The benzoxazine reins were polymerized stepwise at 120, 140, 160, 180, 200, 220 and 240 °C for 1 h each. Afterwards, the samples were slowly cooled to room temperature, and the

dark brown polybenzoxazine films were obtained.

#### 2.3 Characterization

The <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) nuclear magnetic resonance (NMR) spectra were applied to characterize the structures of each products dissolved in CDCl<sub>3</sub> using the Bruker AVANCE II 400 NMR spectrometer with tetramethylsilane as internal standard. The average numbers of transients for <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were setting as 64 and 1024. FTIR spectra of each simple were obtained using the Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrophotometer with a range of 4000-500 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) was carried out by NETZSCH DSC of model 204f1. To study the polymerization kinetics, benzoxazine monomers were analyzed at a temperature increase rates of 2, 5, 10, 15, and 20 °C/min from room temperature (RT) to 400 °C at a constant nitrogen flow rate of 50 mL/min. The dynamic mechanical analysis (DMA) was performed on a NETZSCH DMA/242E analyzer in tension mode. An amplitude of 10 µm and a temperature ramp rate of 3°C/min at a frequency of 1Hz was applied during DMA testing. The thermal decomposition temperatures and char yields of polybenzoxazines were measured using a NETZSCH STA449-C Thermogravimetric Analyzer. Thermogravimetric analysis (TGA) was performed from RT to 800 °C at a heating rate of 10 °C/min with a flow rate of 40 mL/min under N<sub>2</sub> atmosphere.

#### 2.4 Kinetic analysis

The kinetics of non-isothermal polymerization behaviors for tetrahydrophthalimide-functional benzoxazine monomers are conducted according to the following rate equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

(1)

Where,  $\alpha$  is the conversion rate, *t* is time, k(T) is the temperature dependent reaction rate constant, and  $f(\alpha)$  is the differential conversation function depending on polymerization mechanisms. Herein, the rate constant, k(T), can be determined according to the Arrhenius equation as shown in follows:

$$k(T) = A \exp(\frac{-Ea}{RT})$$

(2)

In terms of non-isothermal reaction condition, various methods have been adopted to calculate the apparent activation energy, such as Friedman method [25], Ozawa method [26], Kissinger method [27] and Starink method [23,24]. Among those reported approaches, the Kissinger method is widely used to calculate the apparent activation energy of benzoxazine resins due to its accuracy [28,29]. The equation of Kissinger method is as follows:

$$\ln(\beta/T_P^2) = -\frac{E_a}{R} \cdot \frac{1}{T_p} + C$$
(3)

where,  $\beta$  is the heating rate,  $T_p$  is the peak polymerization temperature, Ea is the apparent activation energy of the reaction, R is the gas constant,  $C = \ln(\frac{AR}{E_a})$ , and A is the frequency factor.

However, the Kissinger method process as a single-step kinetics thus always yields a single *Ea*. The Starink method can be used to test how *Ea* varies with conversation to study the multi-step kinetic process [23,24]. The Starink method equation is as follows:

$$ln\left(\frac{\beta}{T_{\alpha}^{1.92}}\right) = C - 1.0008\left(\frac{E_{\alpha}}{RT_{\alpha}}\right) \tag{4}$$

where,  $\beta$  is the heating rate,  $T_{\alpha}$  is the temperature at conversion  $\alpha$ .



Scheme 1. Synthesis of tetrahydrophthalimide-functional benzoxazine monomers.

#### 2.5 Synthesis of tetrahydrophthalimide-functional benzoxazine monomers

The successful synthesis of tetrahydrophthalimide-functional monobenzoxazines has been achieved using primary amine (aniline), paraformaldehyde, and tetrahydrophthalimide functional phenols (pHTI and oHTI) as shown in Scheme 1. Prior to this study, various para-phthalimide functional benzoxazines have been attempted [30,31]. However, incorporation of high rigid phthalimide functionality into benzoxazine structure at *para* position required long reaction time, leading the difficulties in benzoxazine synthesis. Herein, the reaction for synthesizing *para*-tetrahydrophthalimide functional benzoxazine was completed in just six hours at 120 °C in xylenes. The tetrahydrophthalimide functionality has less rigidity compared with phthalimide, which significantly increases the solubility of tetrahydrophthalimide-related compounds in ordinary organic solvents, such as chloroform, dichloromethane, ethyl acetate and dimethylacetamide (3.0%: w/v). As a result, both pHTI-a and oHTI-a exhibit great advantages in synthesis in terms of imide-functional benzoxazines.



**Fig. 1.** <sup>1</sup>H NMR spectra of pHTI-a (a) and oHTI-a (b).

The chemical structures of *p*HTI-a and *o*HTI-a were confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR and FTIR analyses. As depicted in Fig. 1, the typical resonances attributed to the benzoxazine structure, Ar-CH<sub>2</sub>-N- and -O-CH<sub>2</sub>-N- for *p*HTI-a are observed at 4.67 and 5.38 ppm, respectively. However, two sets of doublets at around 4.65 and 5.32 ppm for the typical resonances for *o*HTI-a can be observed, which is due to the existence of atropisomerism in *o*HTI-a [22]. Besides, the protons of the vinylene group in both *p*HTI-a and *o*HTI-a appear at 6.00 ppm. In addition, the <sup>13</sup>C NMR spectra shown in Fig. 2 are

applied to identify the characteristic signal of oxazine ring and tetrahydrophthalimide group. The characteristic carbon resonances of the oxazine ring in *p*HTI-a and *o*HTI-a are assigned at 50.48 and 79.69 ppm, and 50.70 and 80.00 ppm, respectively.



Fig. 2.  ${}^{13}$ C NMR spectra of *p*HTI-a (a) and *o*HTI-a (b).

To further verify the chemical structures of *p*HTI-a and *o*HTI-a, FT-IR spectra of benzoxazine monomers have been performed, and the results are shown in Fig. 3. A number of infrared absorption bands are highlighted in Fig. 3 that are used to verify the existence of oxazine ring and tetrahydrophthalimide in each monomer. The characteristic doublets at 1771 and 1782 cm<sup>-1</sup>, and 1706 and 1709 cm<sup>-1</sup> are the typical bands for imide group, which are attributed to the imide C-C(=O)-C antisymmetric and symmetric stretching for *p*HTI-a and *o*HTI-a, respectively [32]. Additionally, the presence of imide

is also determined by the characteristic bands at 1388 and 1389 cm<sup>-1</sup> for *p*HTI-a and *o*HTI-a, respectively, which are due to the axial stretching of C-N bonding [33,34]. The characteristic bands of antisymmetric trisubstituted benzene that appear at 1497 and 1488 cm<sup>-1</sup>, confirming the incorporation of imide group into benzoxazine structure in both benzoxazines. Moreover, the presence of the benzoxazine ring aromatic ether in the monomers is indicated by band centered at 1239 and 1236 cm<sup>-1</sup> due to the C-O-C antisymmetric stretching modes [35]. Furthermore, the characteristic benzoxazine related band can be observed at 942 and 939 cm<sup>-1</sup> for *p*HTI-a and *o*HTI-a, respectively [36].



Fig. 3. FT-IR spectra of benzoxazine monomers.

### 3. Results and discussion

#### 3.1 Polymerization behaviors of benzoxazine monomers

The thermal behaviors of benzoxazine monomers were studied by DSC at the heating rate of 10 °C/min under a nitrogen atmosphere. The thermograms of *p*HTI-a and *o*HTI-a are shown in Fig. 4a. Very sharp melting peaks at 180 and 154 °C can be observed for *p*HTI-a and *o*HTI-a, respectively, further indicating the excellent purity of both monomers. Besides, two endothermic peaks can be found for *o*HTI-a during the melting behavior, which is caused by the phase change of crystal-to-crystal transition [22]. As can

be seen in the figure, there is one exothermic peak with its maximum at 267 °C and an onset temperature of about 249 °C for *p*HTI-a. *o*HTI-a exhibits a lower temperature (252 °C) for the maximum of exothermic peak compared with *p*HTI-a. The DSC results in the current study give another sample to indicate the *ortho*-functional benzoxazines possess significant advantages over the *para*-counterparts in polymerization process [21,29]. Additionally, the temperatures of processing window from the DSC thermograms for *p*HTI-a and *o*HTI-a are 87 and 98 °C, which are much higher than that of reported phthalimide functional benzoxazines [21]. Moreover, the completion for the curing of both monomers can be determined by the compete disappearance of exothermic peaks as shown in Figure 4b. Both polybenzoxazines show the characteristic of brittleness, which is similar as other polybenzoxazines dervied from monofunctional benzoxazine resins.



**Fig. 4.** (a) DSC polymerization behavior of mono-functional benzoxazine monomers. (b) DSC thermograms of polybenzoxazines.

#### **3.2 Polymerization kinetics**

Fig. 5 shows the DSC thermograms of *p*HTI-a and *o*HTI-a at heating rates of 2, 5, 10, 15 and 20 °C/min, respectively. It can be observed that the initial polymerization temperature ( $T_i$ ) and exothermic peak temperature ( $T_p$ ) shift to higher temperatures as increasing the heating rate. The polymerization parameters, including  $T_i$ ,  $T_p$  and terminal

polymerization temperature  $(T_f)$  of *p*HTI-a and *o*HTI-a are summarized as shown in Tables 1 and 2.



Fig. 5. DSC curves of *p*HTI-a (a) and *o*HTI-a (b) at different heating rates.

Heating rate $\beta$ (°C/min)	$T_i/{}^{\mathrm{o}}\mathrm{C}$	$T_p/{}^{\mathrm{o}}\mathrm{C}$	$T_f \circ \mathbf{C}$
2	212.8	234.5	256.8
5	225.3	253.9	284.0
10	232.4	267.5	289.9
15	241.4	275.2	295.4
20	245.2	281.3	307.2

**Table 1** The characteristic temperatures of *p*HTI-a at different heating rates.

Table 2 The characteristic temperatures of *o*HTI-a at different heating rates.

Heating rate $\beta$ (°C/min)	$T_i / {}^{\mathrm{o}}\mathrm{C}$	$T_p/{}^{\mathrm{o}}\mathrm{C}$	$T_{f'}$ °C
2	190.5	216.4	238.0
5	199.3	235.8	256.8
10	212.7	252.2	271.6
15	221.6	260.8	277.7
20	229.0	267.0	284.0

The apparent activation energy (Ea) values of benzoxazine monomers were then calculated by Kissinger method [25]. Basing on the data in Tables 1 and 2, the plots of  $\ln(\beta/T_p^2)$  against 1000/ $T_p$  are produced as shown in Fig. 6 for both pHTI-a and oHTI-a. As a result, the apparent Ea values of pHTI-a and oHTI-a are estimated to be 106.83 and 90.78 kJ/mol, respectively, according to Kissinger method. The estimated apparent activation energy values are lower than that of some reported benzoxazines based on Kissinger method, such as 247 KJ/mol for imide functional benzoxazine and 169 KJ/mol for amide functional benzoxazine [37]. These relatively lower values of activation energy indicate that both tetrahydrophthalimide functional benzoxazine monomers are easy to be activated to polymerize. In addition, oHTI-a also shows a relatively lower Ea value compared with *p*HTI-a. The ortho-attached electro-withdrawing group of tetrahydrophthalimide may lead a more acidic phenol species, and therefore result in a lower apparent activation energy during the polymerization of oHTI-a.



**Fig. 6.** Plots generated following the Kissinger method for determination the apparent activation energy values of *p*HTI-a and *o*HTI-a.

In addition, the Starink method was also carried out to see how *Ea* varies with conversation during the polymerization process. From the equation (4), a straight line with a slope of  $-1.0008E_{\alpha}/R$  can be obtained by taking a plot of  $ln(\beta/T_{\alpha}^{1.92})$  vs.  $1000/T_{\alpha}$  in the same conversion range for a series of dynamic DSC experiments at different heating rates for both *p*HTI-a and *o*HTI-a. The plots of  $ln(\beta/T_{\alpha}^{1.92})$  vs.  $1000/T_{\alpha}$  with a conversion rate between 0.1 and 0.9 are shown in the Fig. 7. The plots of both *p*HTI-a and *o*HTI-a and *o*HTI-a relationship.



**Fig. 7.**  $ln \beta / T_{\alpha}^{1.92}$  vs. 1000/ $T_{\alpha}$  at different conversion rates of *p*HTI-a (a) and *o*HTI-a (b).

Therefore, the  $E_{\alpha}$  values at different conversion rates can be obtained through slopes at different conversion rates as shown in Fig. 8. The average apparent activation energy values for *p*HTI-a and *o*HTI-a were calculated as 107.12 and 91.00 kJ/mol, respectively. This results for  $E_{\alpha}$  values of both benzoxazine monomers are very close to the values obtained from the Kissinger method.



**Fig. 8.** Variation of  $E_{\alpha}$  vs.  $\alpha$  by Starink method for *p*HTI-a and *o*HTI-a.

Generally, the thermally activated polymerization mechanism of thermosetting resin can be divided into two types: one is the nth-order reaction, and the other one is the autocatalytic reaction [38,39]. In case of nth-order reaction:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

And in the case of autocatalytic reaction:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{6}$$

where, n is the number of reaction stages, m is the number of autocatalytic series.

According to the basic kinetic theory, the reaction model determines the shape of the kinetic curve, that is, the shape of the kinetic curve can be used to distinguish the polymerization reaction model of benzoxazine reins. Fig. 9 shows the variation of the conversion degree  $\alpha$  as a function of temperature for *p*HTI-a and *o*HTI-a at different heating rates.



**Fig. 9.** Conversion  $\alpha$  as a function of temperature at different heating rates of *p*HTI-a (a) and *o*HTI-a (b).

To further determine the polymerization kinetic models of *o*HTI-a and *p*HTI-a, the relationship between the reaction rate  $d\alpha/dt$  and the conversion rate  $\alpha$  was obtained at a heating rate of 15 °C/min as shown in Fig. 10. It can be observed in Fig. 10 that the maximum reaction rates for both *o*HTI-a and *p*HTI-a occur at an intermediate conversion degree, which suggests that the polymerization processes of *p*HTI-a and *o*HTI-a follow the autocatalytic reaction mechanism. Ordinarily, the nth-order kinetic model shows the maximum reaction rate at the beginning of polymerization. Therefore, *p*HTI-a and *o*HTI-a and *o*HTI-a reach maximum reaction rate at the conversion values of 0.53 and 0.57, respectively.



Fig. 10.  $d\alpha/dt$  vs.  $\alpha$  at the heating rate of 15 °C/min for *p*HTI-a and *o*HTI-a.

Although the reaction mechanism of pHTI-a and oHTI-a was preliminarily judged according to the relationships of conversion vs. temperature and reaction rate vs. conversion, a further more detailed investigation was carried out by Friedman method [40,41]. The Friedman equation is as follows:

$$\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dT} = \ln [Af(\alpha)] - \frac{E_a}{RT}$$
(7)

The Friedman equation turns into Equation (8) by the combination of the nth-order reaction equation as aforementioned:

$$\ln[Af(\alpha)] = \ln\beta \frac{d\alpha}{dT} + \frac{E_{\alpha}}{RT} = lnA + nln(1-\alpha)$$
(8)

where, each character represents the same meaning as above. Notably, the *Ea* in Equation (8) was the values obtained from above apparent activation energy calculated by Kissinger method.

According to the Equation (8), it should form a linear relationship between  $\ln[Af(\alpha)]$  and  $\ln(1-\alpha)$  if the polymerization mechanisms of both *p*HTI-a and *o*HTI-a follow the nth-order reaction. Fig. 11 shows the plots of  $\ln[Af(\alpha)]$  against  $\ln(1-\alpha)$  for *p*HTI-a (Fig. 11a) and *o*HTI-a (Fig. 11b). Clearly as seen in Fig. 11, the  $\ln[Af(\alpha)]$  of the two monomers do not possess the simple linear relationship with  $\ln(1-\alpha)$ . The value of  $\ln[Af(\alpha)]$  reaches the maximum and then decreases as the value of  $\ln(1-\alpha)$  increases for both monomers. The results clearly indicate that the polymerization processes of *p*HTI-a and *o*HTI-a follow an autocatalytic reaction model rather than the nth-order reaction [38].



**Fig. 11.**  $\ln[Af(\alpha)]$  vs.  $\ln(1-\alpha)$  at different heating rates of *p*HTI-a (a) and *o*HTI-a (b).

Afterwards, by substituting Equation (6) in Equation (8), a new Equation (9) can be obtained as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-\frac{E_a}{RT}) \alpha^m (1-\alpha)^n$$
(9)

Equation (9) can be turned into Equation (10) by taking logarithm transformation:

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = -\frac{E_a}{RT} + nln(1-\alpha) + mln(\alpha) + lnA$$
(10)

Equation (10) can be solved by multiple linear regression, in which the dependence variable is  $\ln\left(\frac{d\alpha}{dT}\right)$ , and the independent variables are 1/T,  $ln(1-\alpha)$  and  $ln(\alpha)$ . Then the values of n, m, and A can be obtained using the average apparent activation energy

from Kissinger method. Herein, the interval for calculation was selected from the initial stage to the conversion  $\alpha$  reaching the maximum reaction rate ( $\alpha$ =0.1-0.5). The data of kinetic parameters for *p*HTI-a and *o*HTI-a are listed in Table 3 and Table 4, respectively.

β (°C/min)	E <sub>α</sub> (kJ/mol)	Correlation Coefficient(R <sup>2</sup> )	lnA (s <sup>-1</sup> )	Standard Error	п	Standard Error	m	Standard Error
2		0.9643	24.4100	0.1179	0.9524	0.0286	0.7022	0.0259
5		0.9716	24.4610	0.1202	1.0533	0.0229	0.7385	0.0230
10	107.12	0.9623	24.4944	0.2113	0.8746	0.0407	0.7099	0.0492
15		0.9749	24.6530	0.1248	1.0037	0.0214	0.7950	0.0306
20		0.9833	24.6360	0.0870	0.9734	0.0165	0.7618	0.0167
Average	107.12	0.9713	24.53	0.1322	0.98	0.0260	0.74	0.0291

Table 3 Polymerization kinetic parameters of *p*HTI-a.

Table 4 Polymerization kinetic parameters of oHTI-a.

β (°C/min)	E <sub>α</sub> (kJ/mol)	Correlation Coefficient(R <sup>2</sup> )	lnA (s <sup>-1</sup> )	Standard Error	n	Standard Error	т	Standard Error
2		0.9707	21.6170	0.1640	1.0331	0.0450	0.7329	0.0363
5		0.9738	21.5785	0.1548	0.9613	0.0414	0.7677	0.0275
10	91.00	0.9368	21.3972	0.2227	0.8467	0.0534	0.7061	0.0482
15		0.9558	21.4909	0.1806	0.8797	0.0544	0.7639	0.0328
20		0.9547	21.5499	0.1821	0.8293	0.0487	0.7516	0.0366
Average	91.00	0.9584	21.53	0.1808	0.91	0.0486	0.74	0.0363

From the parameters in above tables, the kinetic equations for pHTI-a and oHTI-a can be obtained as follows, respectively.

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = e^{24.53} \exp(-107120/RT) \alpha^{0.74} (1-\alpha)^{0.98}$$
(11)

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = e^{21.53} \exp(-91000/RT) \alpha^{0.74} (1-\alpha)^{0.91}$$
(12)

In order to further verify the mathematical models shown in Equations (11) and (12), a comparison between the predicted and experimental results for *p*HTI-a and *o*HTI-a was carried out. As shown in Fig. 10, the calculated data from the model equations are in good agreement with the experimental results.



**Fig. 12.** Calculated (symbol) and experimental (solid line) DSC curves corresponding to the polymerization processes of pHTI-a (a) and oHTI-a (b).

#### 3.3 Thermal properties of polybenzoxazines

Dynamic mechanical analysis (DMA) has been performed to study the thermomechanical properties of both polybenzoxazines obtained in this study. The DMA results of for the storage modulus (E'), loss modulus (E''), and tan  $\delta$  are shown in Fig. 13. As seen from Fig. 13a, The glass temperature ( $T_g$ ) determined as the peak temperature of tan  $\delta$  for poly(*p*HTI-a) is around 215 °C. In addition, the polybenzoxazine derived from the *ortho*-benzoxazine isomer has a higher  $T_g$  temperature of 241 °C as seem from Fig. 13b.



Fig. 13. Dynamic mechanical spectra of poly(*p*HTI-a) (a) and poly(*o*HTI-a) (b).

TGA was carried out to evaluate the thermal stability of polybenzoxazines from room temperature to 800 °C under nitrogen atmosphere. Thermal stability was determined by initial decomposition temperatures, the temperature at 5% (T<sub>d5</sub>) and 10% (T<sub>d10</sub>) weight loss and char yield (Yc) at 800 °C. As shown in Fig. 14, the T<sub>d5</sub> values of poly(*p*HTI-a) and poly(*o*HTI-a) are 334 and 305 °C, respectively. Besides, the T<sub>d10</sub> values of poly(*p*HTI-a) and poly(*o*HTI-a) are 377 and 346 °C, respectively. The polybenzoxazine derived from *para*-functional isomer shows higher T<sub>d5</sub> and T<sub>d10</sub> values than *ortho*-isomer. The weight loss difference in the range from 300 to 400 °C is possible caused by the benzoxazole formation from *ortho*-hydroxyimide in poly(oHTI-a) as other reported

*ortho*-imide functional benzoxazines [21]. Moreover, poly(pHTI-a) also exhibits improved thermal stability as compared to typical bisphenol A based benzoxazine (T<sub>d5</sub> 326 and T<sub>d10</sub> 344 °C) [42]. However, the derivative weight loss curves in Fig. 14 show a high weight-loss stage in the range of 400 to 550 °C for poly(*p*HTI-a). On the contrary, a much lower weight-loss stage can be observed for poly(*o*HTI-a) at the same temperature range. As a result, the Yc value of polybenzoxazine based on *ortho*-isomer (47%) is much higher than the polybenzoxazine derived from *para*-isomer (28%). Furthermore, the TGA results suggest the possibility to form thermally stable thermosets from low molecular weight monobenzoxazines.



Fig. 14. Thermogravimetric analysis of polybenzoxazines.

#### 4. Conclusions

Two benzoxazine monomers with attached tetrahydrophthalimide at *para-* and *ortho-*position have been synthesized in this study. The structure of new achieved *para-*tetrahydrophthalimide functional benzoxazine monomer was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR and FT-IR spectra. The DSC results showed the high purity and excellent processability of these benzoxazine monomers. Tetrahydrophthalimide can significantly reduce the rigidity of phthalimide group, which results an easier approach for

synthesizing benzoxazines while still maintaining excellent thermal stability of polybenzoxazines. In addition, the kinetic models of benzoxazine monomers were evaluated by multi-heating-rate DSC methods, and two autocatalytic models for the polymerization processes of both *para* and *ortho* benzoxazine isomers were confirmed. Moreover, the calculated mathematical models were in excellent agreement with the experimental data from non-isothermal DSC results.

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