Intrinsic Self-Initiating Thermal Ring-Opening Polymerization of 1,3-Benzoxazines Without the Influence of Impurities Using Very High Purity Crystals

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ABSTRACT: A phenol/aniline type monofunctional benzoxazine monomer, **PH-a**, is synthesized and highly purified to study the *intrinsic thermal ring-opening polymerization of benzoxazines* without the influence of any impurity. The successful synthesis of the monomer and its corresponding chemical structure are confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy. Purity of the compound is evaluated through differential scanning calorimetry (DSC) as well as elemental analysis (EA). Moreover, the thermal behavior of benzoxazine monomer toward polymerization is also studied by DSC, indicating that the highly purified benzoxazine monomer actually polymerize upon heating. The results present evidence of an intrinsic tendency for 1,3-benzoxazines to undergo *thermally induced ring-opening polymerization* upon heating only without any impurity participating during the reaction. This reveals that polybenzoxazines can be obtained by both the traditional *thermally accelerated (or activated) polymerization*, where impurities or purposefully added initiators are involved in the reaction; or, by the classic *thermal polymerization*, where only heat is enough to initiate the reaction. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

KEYWORDS: benzoxazines; mechanisms; polybenzoxazines; structure–activity relationships; thermal polymerizations

INTRODUCTION Benzoxazine is a newly developed thermosetting resin that can be synthesized by the Mannich condensation from phenol, amine, and formaldehyde. Upon polymerization, these resins form polybenzoxazines, which have been extensively reviewed due to their outstanding features.[1] Among the major advantages of polybenzoxazines are the low flammability,[2] high thermal resistance[3] even for fully bio-based polybenzoxazines,[4] near-zero shrinkage upon polymerization,[5] low surface free energy,[6] and excellent chemical stability.[7] One of the most interesting characteristics of this class of polymer is the extraordinarily rich molecular design flexibility that allows designing a vast variety of molecular structures to tailor the desired properties.[8]

Polybenzoxazines are in general produced *via* cationic ring-opening polymerization by heating benzoxazine monomers without added initiators and/or catalysts in the typical temperature range of 150–230 °C; however, some applications desire lower polymerization temperatures than this typical range. Many compounds have been reported to influence the polymerization temperature of benzoxazines, including (1) strong and weak carboxylic acids and even phenols;[9] (2) basic compounds such as amines and imidazoles;[10] and (3) metal-containing compounds such as metal halides.[11]

Although various promoting effects caused by catalysts on the ring-opening polymerization have been studied, the intramolecular catalyzing effect based on the units or within the structures of benzoxazine molecule itself has rarely been reported. In this regard, Andreu et al. evaluated the influence of the electronic effects caused by different substituent groups in the benzoxazine nuclei on the polymerization temperature.[12] The study particularly focused on several 3-phenyl-3,4-dihydro-2-H-1,3-benzoxazine monomers with electron-withdrawing or electron-donating groups in the 6 and 4′ positions only. Complementing the prior study, Wang

et al. reported the influence of electronic effects but in this case from the bridging groups of bisphenols on the ring-opening polymerization of benzoxazines.[13] They found that electron-withdrawing groups promoted the thermally activated polymerization, as detected from a polymerization temperature decrease by increasing the bond length and lowering the bond energy of C—O in the oxazine rings.

Recently, polybenzoxazines derived from benzoxazines containing *ortho*-functional phenolic components have been shown to possess significant advantages over their *para*-phenolic counterparts.[14] Among these *ortho*-functional benzoxazines, *ortho*-amide benzoxazine, which can act as a precursor for polybenzoxazoles,[15] has been shown to polymerize at much lower temperatures than any other known pure benzoxazine without added initiators and/or catalysts. In fact, it has long been hypothesized[16] and recently demonstrated,[4] the existence of an intramolecular 5-membered ring hydrogen bonding between the NH of the amide and the oxygen in the oxazine ring acting as an internal incentive to stimulate the ring-opening polymerization in a smart way, like a self-complementary initiator.

It is also known that existing impurities generated during the synthesis of the benzoxazine monomers can act as very efficient initiators and/or catalysts in the polymerization. For instance, free phenolic —OH groups in the resin, coming from unreacted phenols or small oligomers formed during the synthesis of the monomers, have been reported to effectively lower the polymerization temperature.[9] These impurities have played contrasting roles during the development of the benzoxazine field. While they were helpful for lowering the polymerization temperatures and broadening the range of applications, they interfered with undertaking reliable mechanistic studies strictly on pure benzoxazines. As a consequence, the most accepted mechanisms assume the participation of a very small amount of a cationic initiator or initiators. This is the main reason for which the use of the term, *thermal polymerization*, has been discouraged for benzoxazine polymerizations since the term implies a thermal event like a bond cleavage, molecular rearrangement, or spontaneous reaction induced only by heat in the absence of any other participating substance. Hence, as the mechanisms always assumed not only the existence but also the involvement of those cationic species intermolecularly, the more appropriate denomination is *thermally accelerated (or activated) polymerizations*.[16(b)] However, the close terminology which fundamentally differs very much in meaning has unfortunately continued to be misused without evidence of its existence in the literature introducing a conceptual error. To date, no paper that specifically aims at studying the possibility of ring opening *via thermally induced* mechanism has been reported.

In the last few years, as a consequence of the increasing demands for this exciting and growing new polymer field, much more emphasis has been put on the purity of the monomeric benzoxazines used to produce the resulting polybenzoxazines. Since then, although still with comprehensible minute differences, high reproducibility and consistency were experimentally observed not only in the polymerization itself but also in the polymerizations' parameters for similar systems carried out by different researchers at different places. However, if impurities were indeed the promoters for these polymerizations to happen, it would be extremely difficult to expect such a high and consistent reproducibility. The vast variety of procedures reported in the literature to obtain those resins used as raw materials, the actual different background and skills of every researcher performing the syntheses, and the unlikely possibility of having equal quality for every single chemical compound and solvents utilized, make impossible to originate the exact same impurity at the exact same ratio in every synthesis carried out in all laboratories. Thus, the existence of an uncatalyzed, common, and intrinsic mechanism for the polymerization of benzoxazine resins induced only by heat seems to be possible. It must be emphasized at this stage, that we do not disagree in any manner with the well-studied, supported, and established self-catalyzed mechanisms accepted hitherto. For example, it is well known that the polymerization of a given monomer could be achieved by different mechanisms. It is also possible for a polymerization to follow the same general mechanism, after having undergone different initiation processes. A good example here is styrene, which can undergo anionic and radical polymerization, two different mechanisms. Furthermore, the radical polymerization of styrene has also been reported by different mechanisms, such as ATRP,[17] and RAFT polymerization[18] in addition to the uncontrolled free radical polymerization.[19] Even this last uncontrolled free radical polymerization, which follows one mechanism, can still be initiated in different ways, thus establishing *thermally accelerated (or activated) polymerizations* when radical initiators are used, or *thermal polymerizations* when no radicals are added to the system. The latter has also been called spontaneous, self-initiated, or simply *thermal polymerization*, and has been extensively studied.[20]

Thus, based on these facts, we have developed a particular interest in studying the possible intrinsic self-initiating ring-opening polymerization of 1,3-benzoxazines induced only by heat and without the influence of impurities. The results will then reveal that polybenzoxazines might be obtained by *thermally accelerated (or activated) polymerizations* when impurities, or any added catalyst or initiator, are indeed participating in the process; or, by *thermal polymerizations* when only heat promotes the reaction in the absence of the initiating impurities or added initiators.

It is, therefore, one of the purposes of this paper to obtain strong experimental evidence of benzoxazine polymerization by an intrinsic-ring opening mechanism, rather than the initiation by the external initiators or impurities. To achieve this goal, meticulous effort for monomer purification was carried out. Thus, only single crystals of the monomers that were prepared under carefully controlled environment were used in this work. The detailed synthetic strategy, purifications, and polymerization mechanisms are discussed in this article.

EXPERIMENTAL

Materials

Phenol (98%) and paraformaldehyde (96%) were used as received from Sigma-Aldrich. Aniline (99%) was purchased from Sigma-Aldrich and purified by distillation. Ethyl acetate (≥99.9%), toluene (≥99.5%), hexane (≥98.5%), chloroform (≥99.8%), 1,4-dioxane (≥99%), sodium hydroxide (≥97.0%), and sodium sulfate (≥99%) were obtained from Fisher Scientific and used as received. 4-Methoxyphenol (99%) from Sigma-Aldrich was recrystallized several times in ethyl acetate before use. Anhydrous *n*-hexane (≥99.9%) was purchased from Fisher Scientific, and kept over molecular sieves and packaged under argon in resealable Chem-Seal™ bottles.

Preparation of 3-Phenyl-3,4-Hidhydro-2*H*-Benzo[e][1,3]-Oxazine (Abbreviated as PH-a)

Phenol (50 g, 0.53 mol), aniline (47.12 g, 0.51 mol), and paraformaldehyde (37.99 g, 1.265 mol) were added to a 250 mL round bottom flask. The solvent-less synthesis method was adopted by magnetically stirring the mixture at 90 °C for 2 h to minimize the presence of the solvent from the final product. The product was then dissolved in toluene and washed by NaOH (1M) three times, followed by distilled water three times. The organic layer was collected after washing. Toluene was eliminated by a rotary evaporator. The product was dissolved in methylene chloride for column chromatographic purification using hexane as the eluent. The differential scanning calorimetric (DSC) thermogram carried out for this product is designated as sample 0. Further purification was carried out and the results of these processes are presented in the section. ^{1}H NMR (DMSO-d_6), δ (ppm): 4.63 (s, 2H, Ar—CH_2—N, oxazine), 5.42 (s, 2H, O—CH_2—N, oxazine), 6.69–7.22 (mult., 9H, Ar). FTIR (KBr), cm^{-1}: 1225 (C—O—C asymmetric stretching), 937 (benzoxazine-related band). Elemental analysis: detailed data and discussion about the elemental analysis results will be shown in the Results and Discussion sections.

Recrystallization of PH-a

First Recrystallization of PH-a

Column chromatographically purified **PH-a** (20 g) was mixed with normal hexane (80 mL) and the system was slowly heated to 40 °C until all **PH-a** was dissolved. After 10 min at room temperature, needle-like white crystals formed. The crystals were dried in a vacuum oven overnight at 30 °C. The DSC thermogram obtained for this sample is designated as sample 1.

Second Recrystallization of PH-a

PH-a (16 g) obtained from the first recrystallization was dissolved in normal hexane (100 mL) with stirring. After 30 min at room temperature, needle-like white crystals formed. The crystals were dried in a vacuum oven overnight at 30 °C. DSC thermogram obtained for this sample is designated as sample 2.

Third Recrystallization of PH-a

PH-a (5 g) obtained from the second recrystallization was dissolved in anhydrous *n*-hexane (100 mL). The solution was placed in a 250 mL flask and covered with aluminum foil with small holes. This flask was covered by an upside-down 1 L flask to reduce the rate of solvent evaporation. After 10 days, transparent square-rectangular cross-section columnar crystals formed. The crystal was dried in a vacuum oven overnight at 30 °C. Thermogram obtained for these crystals is designated as sample 3.

Fourth Recrystallization of PH-a

This fourth recrystallization was carried out in a glove box. **PH-a** (2 g) that were recrystallized three times as before described were dissolved in anhydrous *n*-hexanes (8 mL) in a 20 mL glass vial. Additional small amounts of anhydrous *n*-hexanes (2 mL) were added every hour. After the fourth time, all **PH-a** totally dissolved. The vials were covered with aluminum foil with small holes. The vials were then covered by an upside-down flask to ensure slow evaporation of the solvent. The dryness of the glove box was monitored by placing a piece of Na metal and checking the metallic shiny surface of the metal. After 8 days, transparent square-rectangular cross-section columnar crystals formed. The crystals were dried in a vacuum oven overnight at 30 °C. DSC thermogram carried out for of these samples are designated as sample 4.

Fifth Recrystallization of PH-a

Sample 4 was used to carry out the fifth recrystallization. The procedure followed at this instance was a repetition of the fourth recrystallization of **PH-a**. The obtained sample was named sample 5.

Sample Preparation by the Addition of a Known Concentration of 4-Methoxyphenol

Phenol is widely used as an initiator and catalyst for benzoxazine polymerization, yet not easy to work with especially at low and quantitative conditions. Given the close chemical structure, 4-methoxyphenol was chosen as a model compound for this purpose, in additions to the advantage of being crystalline and having the melting temperature of 57 °C, which is very close to the melting temperature of **PH-a** (59 °C). As a result, it makes the mixing easier and even more as the two-phase will melt together at the same time. Homogeneity of the two compounds is essential to evaluate the effect of the added initiator and/or catalyst (4-methoxyphenol) to the monomer (**PH-a**). The **PH-a** and 4-methoxyphenol were weighed using a quartz balance with a sensitivity of ± 1 μg. The two compounds were mixed in a glass vial and heated to 65 °C, followed by keeping it at the melt state for 2 min. The mixture was fully mixed by shaking in the glass vial. After cooling to room temperature, the mixture was kept at room temperature overnight to recrystallize. The sample was grounded by a mortar and pestle to fully and evenly mix before recording the DSC thermograms. The programed ramp rate was set as 10 °C/min until 65 °C, keeping at 65 °C for 2 min to fully melt the crystals and

homogenize and stabilize the system, and further heated to 300 °C at a ramp rate of 10 °C/min.

Preparation of Poly (PH-a)

Polymerization of **PH-a** was done by heating at a rate of 10 °C/min until onset temperature (260 °C), isothermal heating for 1 h at 260 °C. Next, **PH-a** was heated at a rate of 10 °C/min until exothermic peak temperature, isothermal heating for another 1 h. **Poly (PH-a)** was obtained.

Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on a Varian Oxford AS600 at a proton frequency of 600 MHz. The average number of transients for ^{1}H and ^{13}C NMR measurement was 64 and 1024, respectively. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddition of 64 scans were recorded at a resolution of 4 cm^{-1}. A TA Instruments Differential Scanning Calorimeter (DSC) Model 2920 was used with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min. In the analysis to determine the activation energy of benzoxazine polymerization, the samples (2.0 ± 0.2 mg) were scanned at the different heating rates of 2, 5, 10, 15, 20 °C/min. All samples were sealed in hermetic aluminum pans. Elemental analysis (carbon, hydrogen, and nitrogen) was performed at Galbraith Laboratories, Inc. The samples were shipped under argon. PerkinElmer 2400 Series II CHNS/O Analyzer was used for the elemental analysis. Samples were dried before the measurement. Elemental analysis was performed under argon atmosphere. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 TGA with a heating rate of 10 °C/min under nitrogen at a flow rate of 60 mL/min.

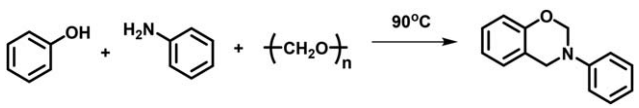
RESULTS AND DISCUSSION

Synthesis and Exhaustive Purification of PH-a

Synthesis of **PH-a** was carried out in a solvent-less method following a modified reported procedure,[21] as shown in Scheme 1.

The workout of the reaction crude was performed as usual. The crude was dissolved in toluene, washed three times with NaOH (1 M), and then three more times with distilled water. Toluene was evaporated from the organic layer, thus generating the crude product.

Purification of a synthesized compound is typically a routine operation, which often does not require fully detailed descriptions if known procedures, such as column



SCHEME 1 Solvent-less **PH-a** synthesis.

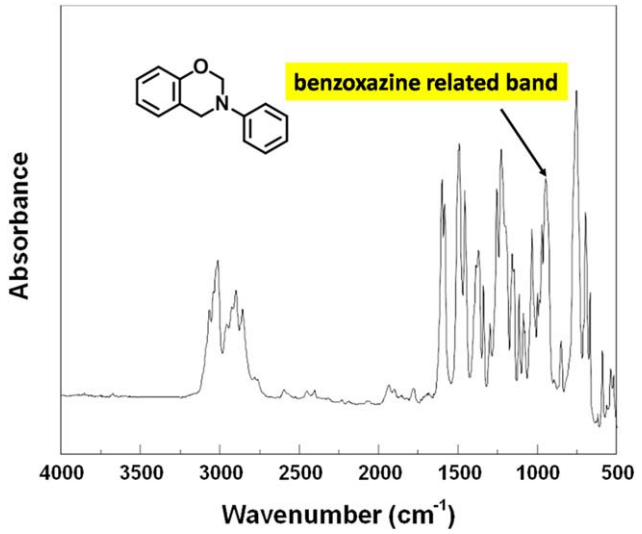


FIGURE 1 FTIR spectrum of benzoxazine monomer, **PH-a**. [Color figure can be viewed at wileyonlinelibrary.com]

chromatography and recrystallization, are followed. However, the nature of impurities and purity of the benzoxazine used in this work are essential parameters for this study. Therefore, the full detailed description of the purification procedure, followed by the characterization of the materials obtained after each step to evaluate its successfulness throughout the entire purification process is reported in the Experimental section. Briefly, the product was first redissolved in methylene chloride and then purified by column chromatography using hexane as eluent. An aliquot of this sample was kept apart as well as studied by DSC. Next, the column chromatographed product was further purified by successive recrystallization steps following different conditions, every time more exhaustive than before, as fully described in the Experimental section. After each recrystallization performed, aliquots were separated and evaluated by DSC. All results will be discussed in the following section.

However, before going forward, a deeper spectroscopic characterization of the obtained **PH-a** was necessary. In this regard, FTIR allowed us to monitor the success of the syntheses. The FTIR spectra of the benzoxazine monomer, **PH-a**, using the KBr pellet method is shown in Figure 1. The presence of the aromatic oxazine ring in the **PH-a** monomer is indicated by bands centered at 1225 cm^{-1}, which is due to the C—O—C antisymmetric stretching modes, and the characteristic oxazine mode is observed at 937 cm^{-1} for **PH-a**.[22]

Figure 2 shows the ^{1}H NMR spectra of ultrapure **PH-a**. The ^{1}H NMR spectrum is consistent with the ultra-high purity of the compound.

It shown in Figure 2 the characteristic spectrum of **PH-a** where no signals other than those belonging to **PH-a** are observed. It is worth noticing the two groups of signals symmetrically located at each side of the peaks associated to H_2 and H_4 from the oxazine ring of **PH-a**. These signals are

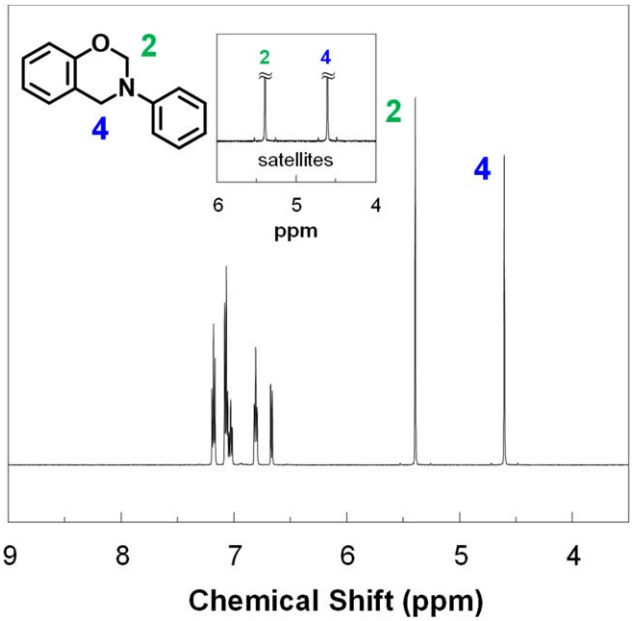


FIGURE 2 ^{1}H NMR spectrum of **PH-a**. Satellites of each —CH_2— peak corresponding to H_2 and H_4 can be better observed in the inset of the figure, which shows a close look near the baseline within the region between 4 and 6 ppm. Spectrum recorded at 25 °C, using DMSO-d_6 as solvent. [Color figure can be viewed at wileyonlinelibrary.com]

called satellites and are important because often they are an observable characteristic on the spectra of highly pure samples even though they are in no way proof of purity.

Evaluation of Purity

From the ^{1}H NMR spectra, one can clearly see that no other signals other than those strictly belonging to the compounds are observed in the spectra, except for the solvent peak (DMSO-d_6) and H_2O contained in that solvent. However, NMR spectroscopy is not sensitive enough to be considered as a purity criterion. Therefore, it was important to use complementary techniques to evaluate the purity of the resin synthesized in this work. Thus, elemental analysis and DSC studies were carried out for each crystalline benzoxazine resin system, and the results are presented in Table 1 and Figure 4, respectively.

After the first two recrystallizations, needle-like crystals of **PH-a** were obtained due possibly to the small amount of impurities influencing the molecular packing. The third and fourth time, the recrystallizations were carried out with anhydrous *n*-hexane. As the purity of the crystals improved, the form of the crystals changed from needle-like to a square-rectangular cross-section column nature [Fig. 3(b)]. The fourth recrystallization was carried out in a glove box under dried argon atmosphere, with copper catalyst to capture oxygen, which was a more stable environment. In those conditions, the crystals of **PH-a** grew without the influence of oxygen and moisture. As shown in Figure 3(a), the polymerization temperature of **PH-a** increased with the increasing number of recrystallizations performed, indicating that

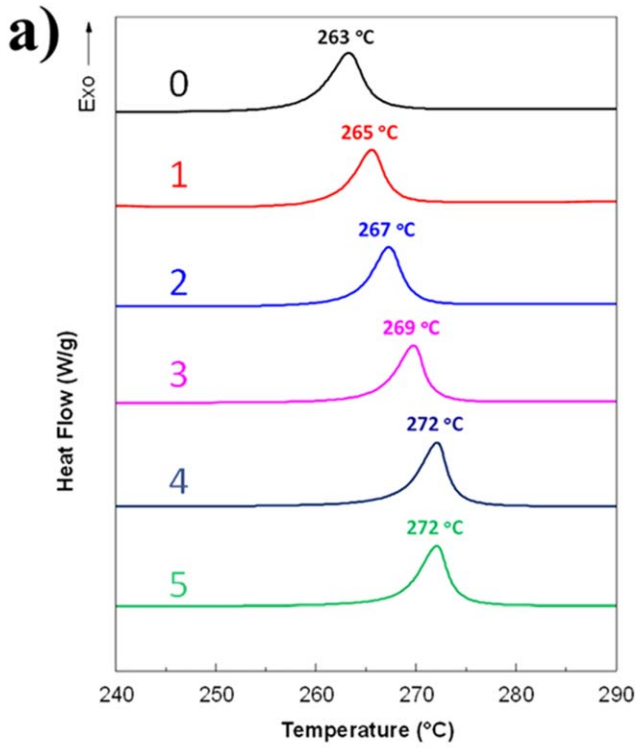


FIGURE 3 (a) DSC thermograms showing the change in the polymerization temperature of **PH-a** after successive recrystallization processes. (b) Crystals of **PH-a** after all recrystallization processes. [Color figure can be viewed at wileyonlinelibrary.com]

the purity of **PH-a** increased with each recrystallization step. The polymerization temperature 272 °C of the final sample was the highest since further purifications did not increase the polymerization temperature (sample 5).

TABLE 1 Elemental Analysis Results of **PH-a**

Element	Calculated	Found
C	79.59	79.46
N	6.63	6.64
H	6.20	6.34
O	7.58[a]	7,56[a]

[a] These values are obtained by difference.

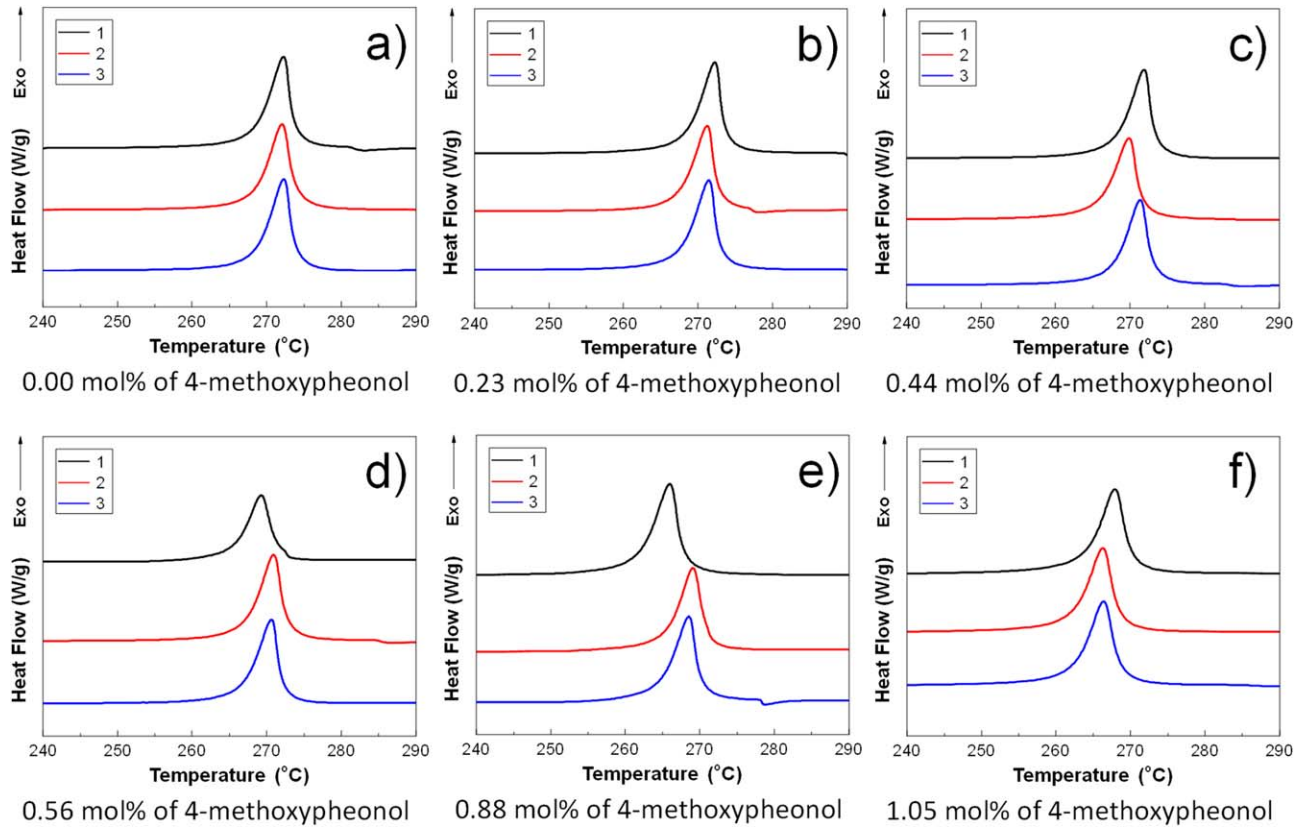


FIGURE 4 DSC thermograms, region between 240 and 190 °C showing the exothermic polymerization peaks of different mixture samples with increasing percentages of 4-methoxyphenol: (a) 0.00% of 4-methoxyphenol (pure **PH-a**), (b) 0.23 mol% of 4-methoxyphenol, (c) 0.44 mol% of 4-methoxyphenol, (d) 0.56 mol% of 4-methoxyphenol, (e) 0.88 mol% of 4-methoxyphenol, and (f) 1.05 mol% of 4-methoxyphenol. [Color figure can be viewed at wileyonlinelibrary.com]

Table 1 shows the elemental analysis results. Samples were dried before analysis for 24 h at 30 °C under vacuum; however, tiny amounts of water, moisture, or even humidity will influence the results. Furthermore, the precaution of working under argon as inert atmosphere instead of molecular nitrogen (N_2) was taken into consideration thus minimizing the influence of atmospheric N_2 on the nitrogen content of our samples. The results are summarized as follows.

The elemental analysis results summarized in Table 1 show the excellent agreement between the calculated and found percentage values for each element, thus evidencing that the targeted compound, **PH-a**, was obtained in high purity.

Polymerization Study of PH-a with Known Amounts of an Added Initiator/Catalyst

Working with a benzoxazine monomer which have demonstrated to have a very high purity, allows us now to examine the effect of a phenol-containing compound at precisely known amounts on the polymerization temperature. By systematically varying the amount of a phenol-containing compound, one might examine the mechanism of oxazine ring opening, whether or not the ring opening is intermolecularly induced by the presence of such a phenolic compound or intramolecularly even in the absence of an external substance. If in fact the external phenolic compound (in many cases impurities from the synthesis) is required, the polymerization exotherm peak temperature should increase as the amount of the added phenolic compound approaches zero mole %. However, if the intramolecular mechanism based on an intrinsic ring-opening dominates without the effect of the external initiator, the exotherm peak temperature should reach an asymptotic value.

To maintain the homogeneity of the samples and reproducibility of the DSC analyses results, two strategies were adopted:

1. 4-methoxyphenol was chosen for this experiment because it has a melting point of 57 °C, which is very close to **PH-a** (59 °C), shows similar solubility as well as good miscibility with **PH-a**, and does not bear any polymerizable group.
2. The different phenolic content mixture sample was prepared as shown in Table 2. The mixture samples were all weighed at similar weights, approximately 1.5 ± 0.2 mg. The specific weight of each sample is shown in Table 3. Controlling the weight will maintain similar mass/heat transfer balance, thus minimizing the influence on the polymerization temperature triggered by any small difference in the amount of material in each specific sample.
3. The temperature program was set as follow: ramp rate at 10 °C/min to 65 °C, kept at 65 °C for 2 min, and new ramp rate

TABLE 2 Weight of 4-Methoxyphenol and **PH-a** of Different Phenolic Content Mixture Sample

Phenol content (mol%)	4-Methoxyphenol (mg)	**PH-a** (mg)
0.23	0.045	32.745
0.44	0.057	21.770
0.56	0.079	23.843
0.88	0.088	16.865
1.05	0.071	11.400

at 10 °C/min to 300 °C. The stabilization temperature (65 °C) was chosen safely right above the melting temperature of both compounds and way below the onset of the exothermic peak, thus avoiding premature polymerization.

Figure 3 presents the results obtained by DSC showing the exotherm peaks corresponding to the polymerization process of all studied mixture samples. To evaluate the reproducibility of the results, each system was measured three times. The average polymerization temperature and standard deviation were calculated and are shown in Table 4 and Figure 4.

Figure 5 shows the change in the polymerization temperature of **PH-a** as a function of the increasing molar concentrations of 4-methoxypheonol. The fitted data is represented by the polynomial equation described by eq 1.

$$T_p = 271.96 - 0.78[C] - 4.21[C]^2 \quad (1)$$

where $[C]$ is the molar concentration of 4-methoxyphenol.

This correlation indicates an extrapolated polymerization temperature of 271.96 °C at zero concentration of the phenolic compound. This temperature is therefore considered as the *intrinsic ring-opening polymerization temperature* of the oxazine ring of **PH-a** without the influence of any residual impurity behaving as initiator or catalyst.

Thermal Behavior of PH-a

As briefly mentioned in the Introduction section, Andreu et al. as well as Wang et al. presented extensive studies on how the nature and strength of different substituents in the benzoxazine monomers affect the polymerization temperature.[12,13] To enhance the reliability of the influence of those substituents on the polymerization mechanism, which should not be affected by impurities, they have particularly paid great attention to the purity of each one of the monomers

TABLE 3 Phenolic Content in Each **PH-a**/4-Metoxyphenol Mixture and the Specific Weight of Every Sample Studied by DSC

Phenol content (mol%)	1 (mg)	2 (mg)	3 (mg)
0	1.529	1.398	1.420
0.23	1.621	1.559	1.505
0.44	1.574	1.580	1.360
0.56	1.365	1.300	1.577
0.88	1.508	1.371	1.717
1.05	1.364	1.376	1.359

TABLE 4 DSC Exotherm Peaks for the Polymerization Process of Mixture Samples

Phenol content (mole %)	1 (°C)	2 (°C)	3 (°C)	Average (°C)	Standard deviation
0	272	272	272	272.00	0.00
0.23	272	271	271	271.33	0.58
0.44	272	270	271	271.00	1.00
0.56	269	271	271	270.33	1.15
0.88	266	269	268	267.67	1.53
1.05	268	266	266	266.67	1.15

used in such elegant publications. They have demonstrated in their articles such good purity through melting point and elemental analysis. What needs to be mentioned is that they have achieved such a high purity of the monomers, and yet these benzoxazine monomers polymerized upon heating. The controversy arises in the fact that if we take for granted the accepted mechanism of benzoxazine polymerization where only the impurities are the promoters for initiating the polymerization, these polymerizations should not have occurred using monomers with such a purity. These results are in accordance with our interest in elucidating a possible intrinsic ring-opening polymerization of benzoxazines. In other words, the capacity of benzoxazine to polymerize only upon heating without any other substance participating in the reaction. This would scientifically establish for the first time the concept of *thermal polymerization of benzoxazines*, in addition-but not instead-to the general accepted *thermally accelerated (or activated) polymerization of benzoxazines* mechanism. Thus, the polymerization studies of the high purity **PH-a** is presented next.

The thermal behavior of **PH-a** toward polymerization was then studied by DSC as depicted in Figure 6.

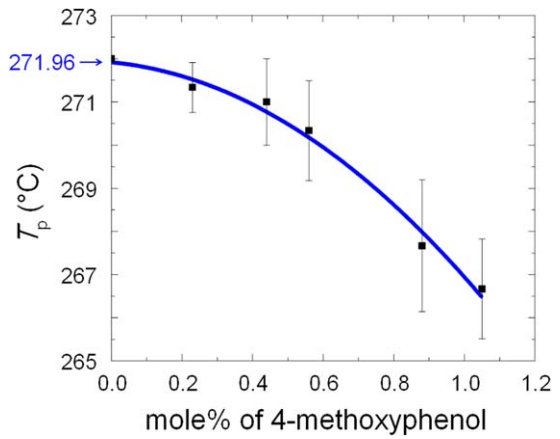


FIGURE 5 DSC exotherm maximum corresponding to the polymerization process as a function of the concentration of a phenol-containing compound (4-methoxypheonol). [Color figure can be viewed at wileyonlinelibrary.com]

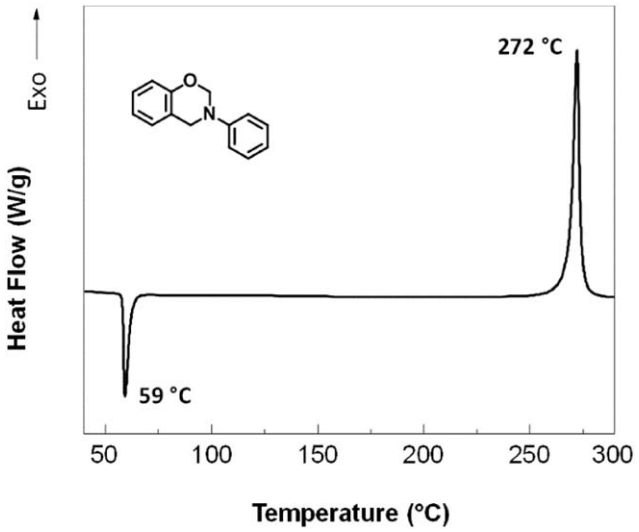


FIGURE 6 DSC thermogram of **PH-a** from 30 to 300 °C. The endothermic peak at 59 °C is assigned to the melting while the exothermic one at 272 °C to the polymerization of **PH-a**.

The thermogram of **PH-a** shows that this compound does polymerize despite its high purity. The exothermic peak assigned to polymerization has its maximum centered at 272 °C. It must be highlighted, however, that **PH-a** in this condition has polymerized at a noticeably much higher temperature than the usual temperatures reported for this compound, usually around 260 °C.[12,23] What is shown in this study, however, is that even though the polymerization temperatures is indeed affected, increased by the absence of impurities, there is real polymerization of **PH-a**.

Polymerizations

In recent years, extensive works on polybenzoxazine chemistry have been reported by benzoxazine researchers.[1(a)] After intensive studies of various cationic, anionic and radical initiators, and mechanistic understanding, it is accepted that the ring-opening polymerization of benzoxazines proceeds through a cationic mechanism. As any other polymerization mechanism, the polymerization of benzoxazine proceeds through the initiation, propagation, and finally termination steps.

For many years, polymerization of benzoxazine resins have been thought to be initiated without added initiators because of the presence of cationic impurities remaining from the monomer synthesis. Nevertheless, there was no detailed study reported on this subject. From a different perspective and despite achieving high purity and using only benzoxazine single crystals in this study, benzoxazine reins still polymerized with similar rates, albeit somewhat at higher temperatures, as shown in Figure 6.

It is known that for a reaction between two species to happen both species should be sufficiently activated. The cases presented in this study evaluate a single compound reacting with itself. Under these conditions, the compound should then present at least two different positions appropriately and sufficiently activated to be able to react between them. In this regard, compound **PH-a** can be analyzed in detail as follows.

Figure 7 shows the positions in the benzoxazines that are actually rich in a negative density, induced by electronic delocalization along the structure. It can be clearly seen that all these positions are not only activated but also reactive, although perhaps at different and specific temperatures in each case, to some chemical reactions. Thus, while a given position may be responsible for the initiation process, another one less favored might be the cause for crosslinking and even side reactions.

As has been mentioned earlier, the main interest in this study is in evaluating the possibility of an intrinsic ring-opening polymerization of benzoxazines. This will then set the bases for establishing a complementary form of initiation for polymerizing benzoxazines. It is important at this point to remember that the accepted mechanism is a *thermally accelerated (or activated) polymerization* since there must exist an impurity able to react with the benzoxazine to only

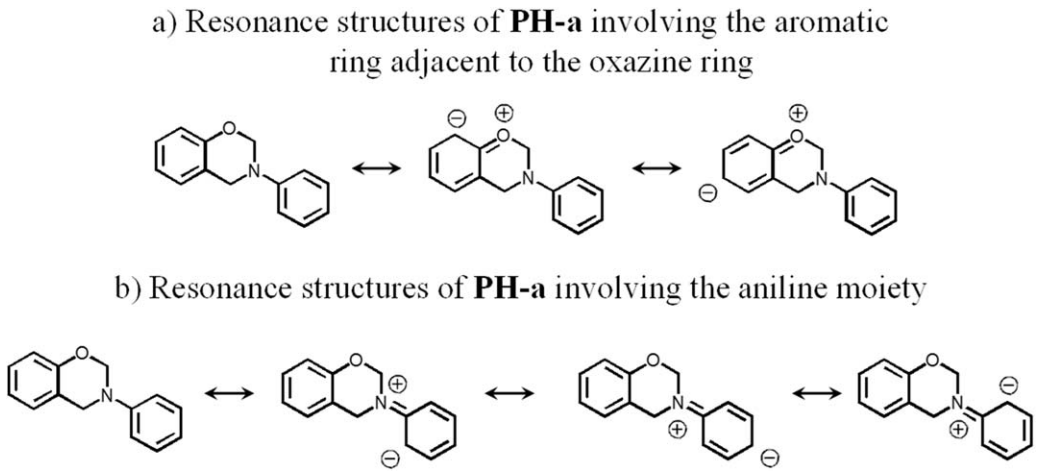


FIGURE 7 Resonance structures of the unsubstituted benzoxazine **PH-a**. Structures in involving the aromatic ring that was adjacent to the oxazine ring (a) and the aniline moiety (b).

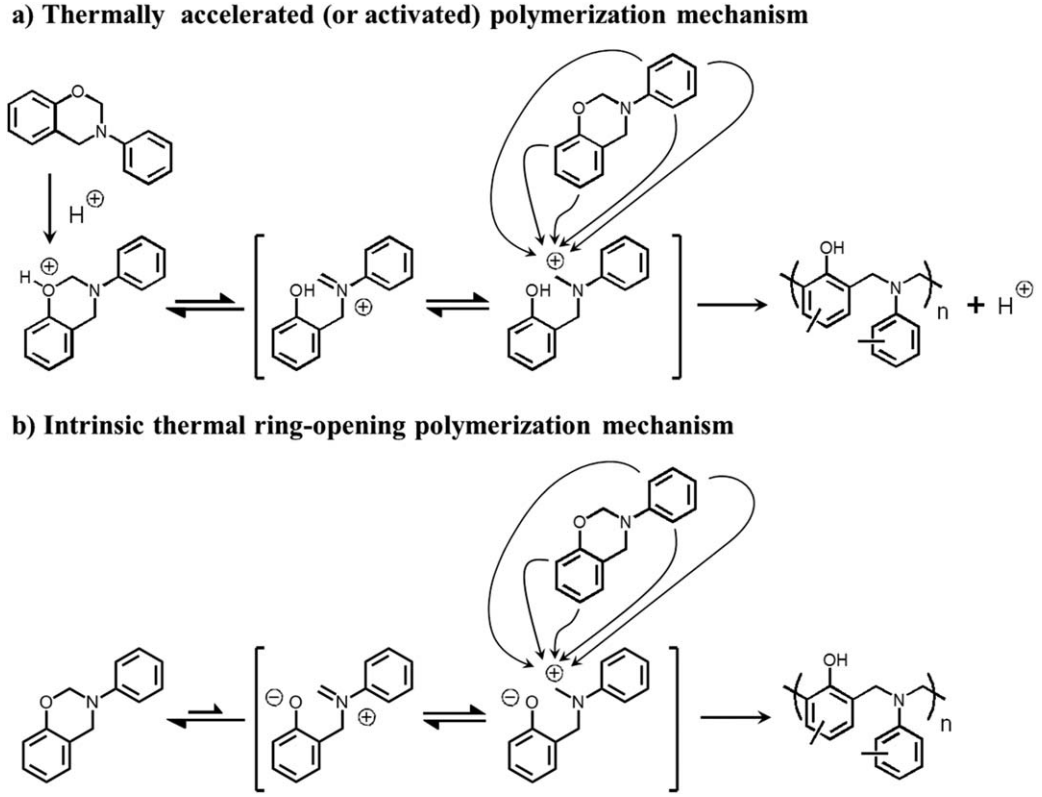


FIGURE 8 Simplified mechanisms for the polymerization of benzoxazines. (a) The classically accepted *thermally accelerated (or activated) polymerization mechanism*, where in addition to heat impurities must participate in the initiation step; and (b), *thermal polymerization mechanism*, induced only by heat.

then be capable of undergoing propagation. A simplified representation of this mechanism is depicted in Figure 8(a), where the H^+ provided by the impurity promotes the polymerization at a certain temperature. It is worth remembering that benzoxazines polymerize *via* a cationic polymerization, where the cation in the chain-like tautomer is attacked by a nucleophile present in the reaction medium. Nevertheless, and in agreement with reported data,[12,13] the benzoxazine single crystals synthesized in this work does undergo polymerization induced only by heat without any impurity participating in or during the reaction. Therefore, under this condition, benzoxazines are polymerized through a strictly *thermal polymerization*. This conceptually new, but somehow expected, mechanism is illustrated in Figure 8(b), where no impurities are present and the polymerization occurs at a certain temperature, which is understandably higher than the temperature needed for the previous mechanism including an impurity. It must be highlighted that both initiation processes are, in a way, similar since both proceed establishing the ring-chain tautomeric equilibrium induced by thermal treatment. One important difference between these two mechanisms is that in Mechanism A the presence of impurities will cause a significant shifting in the equilibrium toward the chain-like tautomers as well as induce this equilibrium to happen at lower temperature, thus promoting eventually a lower polymerization temperature. A similar equilibrium is present in Mechanism B, although this time the equilibrium is much less favored than in the previous case, thus needing higher temperatures to happen. Thus, the absence of such impurities might be the simple reason for the resins to need a higher temperature to yield the same ring-chain tautomerism. Once the tautomeric pair is formed, the carbocation will react through an electrophilic substitution on any activated position (preferably on the *ortho*-position since is the most activated one) of other benzoxazine monomer, thus starting and establishing the propagation step. From this stage forward both mechanisms are very likely to proceed in the same manner. The proposed mechanisms are consistent with the previous concentration dependent experiments where not only the presence of the impurity influences the polymerization temperature but also permits to see that increasing the concentration of the impurity shifts the ring-chain tautomeric equilibrium to the chain-like form thus inducing the polymerization to happen at lower temperatures.

The ring-chain tautomeric equilibrium of benzoxazine resins is where the cation responsible for the cationic polymerization of benzoxazines is formed. This equilibrium is often simplified as depicted in Figure 9.

However, a closer look to the chain-like tautomer shows that not only the two zwitterionic structures often described are

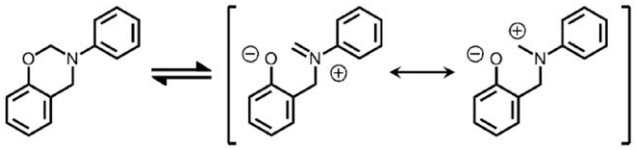


FIGURE 9 Ring-chain tautomeric equilibrium of the unsubstituted benzoxazine **PH-a**.

possible, but instead there are at least six (6) different structures resonating, as shown in Figure 10.

Resonance structures of the chain-like tautomer of **PH-a** involving the charge delocalization in the aniline moiety are much less favored and therefore unlikely to form. One reason for this less favored charge delocalization on the aniline moiety is that two positive charges will have to be far too close, in fact right next to each other and competing for the same nitrogen atom, thus making the system very unstable. It must be emphasized, however, that the aniline moiety does have the ability to delocalize those charges, although not in the chain-like tautomer form.

All these frequently overlooked chemical structures, most likely present in very little amounts, bear their own reactivity and are reactants for side reactions to happen during the entire polymerization process, including the initiation, propagation, and termination steps. Thus, the combination of all these systems reacting simultaneously makes difficult a fair comparison on how an "*initiator*" acts in a conventional controlled/living (radical or ionic) polymerization or in benzoxazine polymerization. This is, for instance, why there is not clear relationship between the impurity concentration and the molecular weight reached after polymerization of benzoxazines.

As the herein uncovered self-initiation process occurs without disrupting the rest of the mechanism for this resin, the entire polymerization should proceed through a single mechanism. Therefore, the graphical manner to calculate the activation energy (E_a) of this system can easily be applied to corroborate this behavior. Specifically, a single mechanism

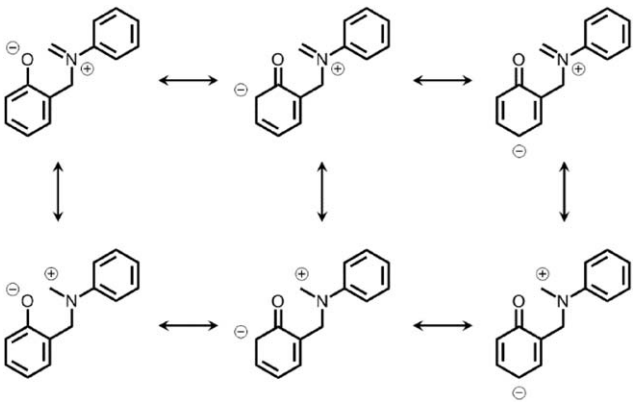


FIGURE 10 Resonance structures of the chain-like tautomer of the unsubstituted benzoxazine **PH-a** involving the aromatic ring that was adjacent to the oxazine ring.

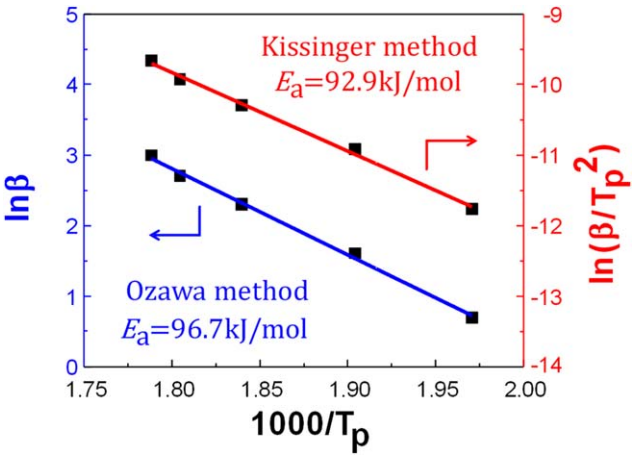


FIGURE 11 Plots to graphically calculate the activation energy (E_a) of the polymerization reaction of **PH-a** applying the Kissinger and Ozawa methods. In the plots, β is the constant heating rate and T_p is the maximum value of the exothermic polymerization peak. Linear regression obtained for each method is: $R^2 = 0.996$ for the Kissinger method and $R^2 = 0.997$ for the Ozawa method. [Color figure can be viewed at wileyonlinelibrary.com]

can be assumed to happen if the plots of ln (β/T_p^2) and ln β as a function of $1/T_p$ are linear (being β the constant heating rate and T_p the maximum value of the exothermic polymerization peak).[24] Therefore, based on this concept, we graphically calculated the E_a of the polymerization reaction of **PH-a** applying the Kissinger and Ozawa methods, and the results are presented in Figure 11.

As shown in Figure 11, the E_a is easily calculated from the slope of the resulting straight lines for the polymerization reaction of **PH-a**, being 92.9 and 96.7 kJ/mol for the Kissinger and Ozawa methods, respectively.

The most meaningful result at this point, however, is the fact that in both cases the plots resulted in perfect straight lines. This result indicates that the polymerization of the highly purified **PH-a** follows a single mechanism, same as the accepted mechanisms where initiation is promoted by impurities.

Having observed an efficient self-initiated polymerization occurring through a single mechanism for this benzoxazine monomer, we developed an interest in comparing the thermal properties of the resulting polymer against the ones commonly reported in the literature which polymerizations are based on impurities acting as initiators. This comparison serves as an indication on the similarity between the possible chemical structures of the polybenzoxazines obtained in each process. In this regard, thermogravimetric analysis (TGA) is a very useful tool to evaluate, although indirectly, the possible similarities between those polymeric structures. This might be achieved by studying the degradation profile and measuring the typical thermal properties of the corresponding polymers.

Thermal analysis and degradation studies of **PH-a** have been reported and are often used for comparison, although the

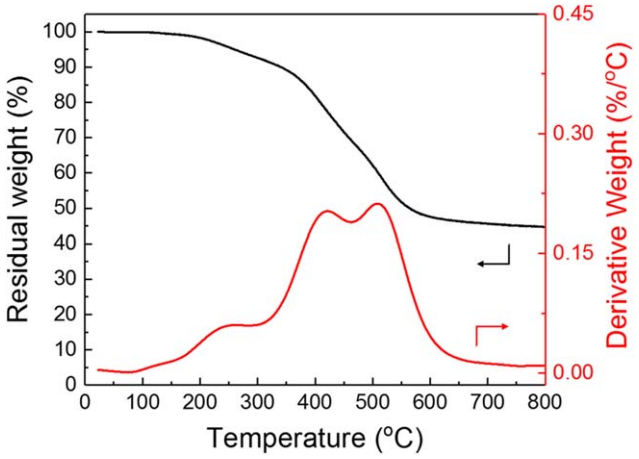


FIGURE 12 TGA thermogram of the highly purified **poly(PH-a)**. [Color figure can be viewed at wileyonlinelibrary.com]

resin never presented the level of purity reported herein. As most polybenzoxazines, **poly(PH-a)** presents a degradation profile consisting of three main steps, being the evaporation of amine moieties at the chain ends and branches the first one, followed by loss of amines from the main chain, to finally undergo simultaneous breaking of phenolic bonds and decomposition of remaining Mannich bases.[25] Similar results have been obtained by TGA and pyrolysis when comparing the respective first derivative mass loss with the total ion current, TIC, curves.[26]

The first step of this study was the actual polymerization of the highly purified **PH-a** sample, which was carried out reproducing a reported method to enhance the validity of the comparison.[27] Then, TGA was performed as usual and the results obtained for the highly purified **poly(PH-a)** are shown in Figure 12.

As shown from Figure 12, the TGA thermogram of the **poly(PH-a)** synthesized in this work presents the typical three-step degradation profile. Specific data and thermal properties are summarized in Table 5.

The data shown in Table 5 shows good agreement for each property between the different **poly(PH-a)** polymers synthesized using different **PH-a** resins, thus suggesting that polymeric structure should in consequence be reasonably similar.

This last result complements our hypothesis where the initiation step of the *intrinsically self-initiated thermal polymerization* does not affect in any way the propagation and termination steps since the polymer structure should, in principle, be the same.

Combining the previous results, it can be demonstrated that benzoxazines are capable of undergoing self-initiation upon heating and without the influence of any impurity, thus initiating a strictly and intrinsic *thermal polymerization*. Then, this self-initiation step is followed by the same propagation and termination steps as the already proposed and accepted *thermally accelerated (or activated) polymerization* promoted by impurities. In other words, this self-initiating *thermal polymerization* of benzoxazines is in full agreement with the well-studied and established *accelerated (or activated) polymerization* mechanisms initiated/catalyzed by impurities accepted hitherto.

CONCLUSIONS

A phenol-aniline based benzoxazine single crystal was successfully prepared and highly purified. A novel initiation step for an intrinsic ring-opening polymerization of benzoxazines is herein proposed. We have demonstrated in this study that temperature alone is sufficient to initiate the polymerization of benzoxazines.

The results presented in this work demonstrating the intrinsic *thermal polymerization* of benzoxazines are in no way in disagreement with any of the *thermally accelerated (or activated) polymerization* studies well-known and accepted in the past. Instead, they are complementary. The relevance of the herein presented results is that it has now been shown that impurities are not necessarily needed to initiate the polymerization. However, they do help to lower the polymerization temperature. The implications of this result are not only in proving the possibility of this inherent new property of benzoxazines, namely "*intrinsic ring-opening polymerization*," but also in the purity in which new benzoxazines and polybenzoxazines might be generated.

TABLE 5 Summary of Thermal Properties for the Highly Purified **Poly(PH-a)** Compared with Others from the Literature

					Degradation step (°C)			
	T_g (°C)	T_{d5} (°C)	T_{d10} (°C)	Char yield (%)	From – to	From – to	From – to	References
Poly(PH-a)	120	259	341	44	180–300	300-450	450–650	This work
Poly(PH-a)	163	288	343	40	190–315	315-460	460–650	27(b)
Poly(PH-a)[a]	n.r.[c]	326	353	35	190–330	330-440	440–550	25(a), 26
Poly(PH-a)[b]	n.r.[c]	260[d]	340[d]	n.s.[e]	190–350	350-460	460–650	26

[a] Data obtained by TGA.
[b] Data obtained by pyrolysis.
[c] n.r.: not reported.
[d] Data estimated from the figure shown in original paper.
[e] n.s.: not shown.

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