

Research Article

Synthesis and Polymerization of Naphthoxazines Containing Furan Groups: An Approach to Novel Biobased and Flame-Resistant Thermosets

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Naphthoxazines are a class of compounds with potential application in obtaining high-performance polymeric materials. Such application of these compounds, however, is still scarcely explored in the literature. Combined with the search for new high-performance materials, the development of biobased polymers has gained a lot of attention. In this sense, the inclusion of furan groups in polymers has been explored as a strategy that combines the search for high-performance materials with the search for the development of biobased materials. In this work, novel naphthoxazine monomers containing furan groups were synthesized. The syntheses were carried out in a single step, without the use of solvents and catalysts, obtaining the products in satisfactory yields and high purity. The naphthoxazines had their chemical structures completely characterized by FTIR, ^1H NMR, and ^{13}C NMR techniques. The thermal analyses (DSC and TGA) showed that all naphthoxazines exhibit exothermic typical polymerization events, making these compounds suitable for obtention of poly(naphthoxazines) resins, but suffer significant mass losses at temperatures below the onset polymerization temperature. In this way, a catalyst (1 mol% MgCl_2) was used in order to allow the polymerization of the compounds before the mass loss events. The FTIR analysis showed strong evidences of the formation of poly(naphthoxazines), and TGA analyses showed that the resins have high thermal stability, with high flame resistance and self-extinguishing properties ($\text{LOI} > 28$), which makes these compounds attractive in the development of biobased and high-performance materials.

1. Introduction

The search for high-performance polymeric materials has attracted the attention of several research groups, which seek to develop new compounds with attractive characteristics, such as high thermal and mechanical resistance, especially for application in the microelectronics and aerospace industries [1].

In this context, polymers derived from compounds containing 1,3-oxazinic rings (six-membered heterocyclic containing nitrogen and oxygen heteroatoms) arise as a relatively new class of high-performance thermosetting polymers. The oxazinic polymers or polyoxazines, can be considered as substituents for the traditional phenolic polymers because of their structural similarity in the main chain [2].

In addition to the advantages of traditional phenolic polymers, such as high thermal resistance, dimensional stability, good electrical properties, flame retardancy, and low smoke generation, polyoxazines exhibit their own attractive characteristics, such as low moisture absorption, good chemical resistance, high glass transition temperature (T_g), low shrinkage, and improved mechanical and thermal properties compared to traditional phenolic polymers. In addition, they offer great flexibility of molecular design and do not generate by-products during their polymerization [2, 3].

Within this group of compounds, benzoxazines are the most well-known and studied. Benzoxazines are a class of compounds in which an oxazinic ring is fused to a benzene ring. The main field of the study and application of benzoxazines is in the development of polymeric materials [4], and in

the last years, several studies have been carried out to synthesize new compounds and to diversify their field of applications. When exposed to high temperatures, this class of molecules begins to polymerize through a process of ring-opening polymerization (ROP), generating poly(benzoxazines). These compounds have also been investigated because of their potential application in a number of biological activities [5–8].

Naphthoxazines are compounds analogous to benzoxazines, but in this class of compounds, the oxazinic ring is fusing to a naphthalene ring. Their potential application in a number of biological activities, especially their fungicide, bactericide, and principally in the treatment of Parkinson's disease [9, 10], has also attracted the attention of a number of research groups. Similarly to benzoxazines, the naphthoxazines also suffer ROP when exposed to high temperatures, generating poly(naphthoxazines). Its application in the field of materials is, however, still little explored, with only few papers reported in the literature describing the polymerization of these compounds to obtain high-performance polymeric materials. These limited activities are related in large part to the easy evaporation that some monomers of naphthoxazines exhibit during the polymerization [11], preventing their processing. However, the use of these compounds in order to obtain high-performance polymeric materials is very attractive, since polymers possessing the naphthalene group are expected to exhibit excellent mechanical property and thermal stability, resulting from high backbone rigidity and aromatic content provided by the multiaromatic ring structure [12].

Various approaches have been developed in order to obtain improvements in the properties of the polyoxazines. Especially designed molecules incorporated with naphthalene, biphenyl, or benzophenone groups were synthesized for this purpose [2, 13, 14]. These compounds showed high thermal stability but, nevertheless, presented poor processability properties, high melting, and polymerization temperatures, as also low solubility in organic solvents.

Another approach is the preparation of monomers containing other polymerizable groups, such as ethynyl, phenylethynyl, nitrile, propargyl, and allyl [12, 15–17]. The polyoxazines obtained from these compounds showed high glass transition temperature and good thermal stability. However, complicated polymerization reactions and high cure temperatures occur in these compounds. In addition, cross-linked structures formed from the first polymerization of these additional polymerizable groups may form barriers to subsequent polymerization reactions, reducing the total conversion of the polymerization reactions and increasing their temperature [1].

It is known that, in addition to the chemical structures, the hydrogen bonds present in the polyoxazines also play an important role in a wide variety of properties of these compounds. A number of studies have observed the existence of bonds of the type $\text{-OH}\cdots\text{O}$, $\text{-OH}\cdots\text{N}$, and $\text{-OH}\cdots\pi$ in poly(oxazines) and demonstrated that such bonds contribute to the improvement of their thermal properties, such as elevated glass transition temperatures [18–20]. Thus, the insertion of groups that promote the formation of these bonds in

polyoxazine compounds is also a strategy for obtaining materials with improved properties.

Associated with the search for high-performance materials, there is a growing interest in green and sustainable chemistry. In this sense, the use of renewable raw materials is one of the principles of green chemistry [21] and one of the main goals of those working on the development of new compounds. Thus, the use of renewable raw materials in the synthesis of benzoxazines has been widely explored. Several studies have reported the replacement of petrochemicals with materials from renewable sources, such as resorcinol and hydroquinone [22], cardanol [23], and furfurylamine [24]. However, to the best of our knowledge, no works are reported in the literature regarding biobased naphthoxazines.

The insertion of furan groups into polymers has been explored as a strategy that combines the search for high-performance materials with the search for the development of biobased materials, since these groups have shown to be able to confer good thermal and mechanical properties to the materials and can be obtained from renewable raw materials such as hemicellulose. Works have been developed to synthesize benzoxazines containing these groups [1, 22], but this strategy has not yet been addressed in order to obtain high-performance and biobased naphthoxazines and poly(naphthoxazines).

Based on the above, naphthoxazines have potential to form polymers with high thermal resistance and the incorporation of a furan ring to its structures tends to provide new polymerizable groups and promote the formation of hydrogen bonds. Therefore, the main objective of this work was to synthesize and polymerize three naphthoxazines containing furan groups (Figure 1), starting from two lignocellulose-based bioproducts, furfurylamine, and furfural. The monomers synthesized were characterized by spectroscopic techniques (^1H and ^{13}C NMR, FTIR), and their thermal properties were evaluated by DSC and TGA techniques. After spectral and thermal characterization, their polymers were analyzed by FTIR and TGA.

2. Materials and Methods

2.1. Materials. 2-Naphthol (99%) and furfurylamine (99%) were used as received by Sigma-Aldrich (USA). Formaldehyde (37%) was used as received by Dinâmica (Brazil). Furfural (99%, Sigma-Aldrich) was previously vacuum distilled prior to use in the syntheses. Ammonium acetate was produced from the reaction between ammonium hydroxide (28–30%, Dinâmica) and glacial acetic acid (Dinâmica). Methylene chloride, methanol, sodium hydroxide, and anhydrous sodium sulfate were used as received by Labsynth (Brazil).

2.2. Methods

2.2.1. Microwave-Assisted Synthesis. The microwave-assisted synthesis was carried out in a Milestone microwave reactor, model Start SYNTH, under atmospheric pressure. The

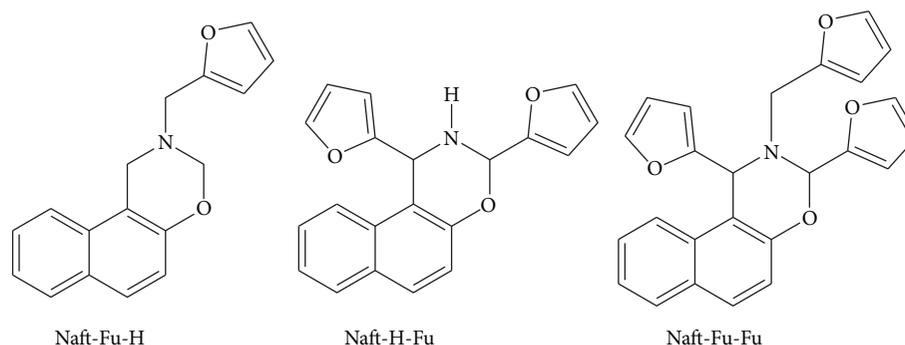


FIGURE 1: Naphthoxazines containing furan groups studied in this work.

temperature of each reaction was controlled by an infrared sensor, and the applied power was limited by 500 W.

2.2.2. ^{13}C and ^1H Nuclear Magnetic Resonance Spectroscopy (^1H NMR and ^{13}C NMR). The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer, model Avance DPX, operating at 300 MHz for ^1H and at 75 MHz for ^{13}C . Deuterated chloroform (CDCl_3) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as the solvent to solubilize the samples, and tetramethylsilane (TMS) was used as an internal standard.

2.2.3. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were obtained on a PerkinElmer spectrometer model FTIR/NIR Frontier, using an attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal surface, and resolution of 4 cm^{-1} using the arithmetic average of four scans in the wavenumber range of $4000\text{--}550\text{ cm}^{-1}$.

2.2.4. Differential Scanning Calorimetry (DSC). DSC analyses were made using Mettler Toledo DSC 823e, using 10 mg of samples in aluminum pans. Nonisothermal measurements were made with a heating rate of $10^\circ\text{C}/\text{min}$, in a temperature range of 30 to 400°C , under nitrogen (N_2) purge at a flow rate of $50\text{ mL}/\text{min}$.

2.2.5. Thermogravimetric Analyses (TGA). TGA analyses were performed on a Mettler Toledo TGA/SDTA 851e, conducted under N_2 atmosphere (flow rate of $50\text{ mL}/\text{min}$) with a heating rate of $10^\circ\text{C}/\text{min}$ in a temperature range of 30°C to 800°C . Alumina crucibles were used with approximately 10 mg of samples.

2.3. Synthesis of Naphthoxazines

2.3.1. Synthesis of 3-(Furan-2-ylmethyl)-3,4-dihydro-2H-naphtho[1,2-e][1,3]oxazine (Abbreviated as Naft-Fu-H). In a round bottom flask (25 mL) containing formaldehyde (13.86 mmol), furfurylamine (6.93 mmol) was slowly added under magnetic stirring. Then, 2-naphthol (6.93 mmol) was added, and the reaction mixture was homogenized before being brought to the microwave reactor. The flask was placed in the microwave cavity, equipped with a 50 cm Vigreux condenser, and distillation head. The microwave was set to a maximum power of 500 W and programmed to increase

from ambient temperature to 70°C in a period of 2 minutes until the temperature stabilized and held for a further 5 minutes, totaling 7 minutes of irradiation. At the end of the reaction, the mixture was cooled to room temperature and methylene chloride (20 mL) was added to the flask. The organic solution was transferred to a separatory funnel (250 mL) and treated with 2 mol L^{-1} aqueous NaOH solution ($2 \times 20\text{ mL}$) and then with a saturated aqueous sodium chloride solution ($2 \times 20\text{ mL}$). The organic phase was collected, dried over anhydrous sodium sulfate, and filtered, and the solvent was removed under reduced pressure to give an oily orange-colored product. The product was purified from that oil by recrystallization from methanol (20 mL) to give the pure product as light beige crystals in 60% yield. The product was characterized by FTIR, ^1H NMR, and ^{13}C NMR.

- (i) ^1H NMR (300 MHz, CDCl_3): δ 7.76 (d, $J=8.0\text{ Hz}$, 1H), 7.65 (d, $J=8.9\text{ Hz}$, 1H), 7.56 (d, $J=8.4\text{ Hz}$, 1H), 7.47 (dd, $J=6.8, 1.3\text{ Hz}$, 1H), 7.43 (dd, $J=1.8, 0.8\text{ Hz}$, 1H), 7.35 (ddd, $J=8.0, 6.8, 1.2\text{ Hz}$, 1H), 7.05 (d, $J=8.9\text{ Hz}$, 1H), 6.33 (dd, $J=3.1, 1.9\text{ Hz}$, 1H), 6.24 (dd, $J=3.1, 0.5\text{ Hz}$, 1H), 4.95 (s, 1H), 4.35 (s, 1H), 3.97 (s, 1H)
- (ii) ^{13}C NMR (75 MHz, CDCl_3): δ 151.87, 151.84, 142.82, 132.06, 129.25, 128.83, 128.31, 126.75, 123.74, 121.22, 118.72, 111.52, 110.42, 109.23, 81.80, 48.89, 47.32
- (iii) FTIR (cm^{-1}): 3016, 2948, 1633, 1599, 1515, 1470, 1431, 1403, 1357, 1285, 1224, 1126, 1058, 1011, 943, 899, 854, 807, 776, 733

2.3.2. Synthesis of 2,4-Di(furan-2-yl)-3,4-dihydro-1H-naphtho[1,2-e][1,3]oxazine and 2,4-Di(furan-2-yl)-3-(furan-2-ylmethyl)-3,4-dihydro-1H-naphtho[1,2-e][1,3]oxazine (Abbreviated as Naft-H-Fu and Naft-Fu-Fu, Respectively). In a round bottom flask (25 mL) containing furfural (13.86 mmol), ammonium acetate (6.93 mmol) or furfurylamine (6.93 mmol) was slowly added. Then, 2-naphthol (6.93 mmol) was added, and the reaction mixture was left under magnetic stirring for 24 h. At the end of the reaction, the products were treated and purified similarly to the procedure described for the compound Naft-Fu-H (Section 2.2.1). The Naft-H-Fu compound was obtained as a white material with

cotton-like fibrous appearance (62% yield), and the Naft-Fu-Fu compound was obtained as a light brown powder (yield 44%). Both compounds were also characterized by FTIR, ^1H NMR, and ^{13}C NMR.

(i) Naft-H-Fu

- (1) ^1H NMR (300 MHz, CDCl_3): δ 11.59 (s, 1H), 8.41 (s, 1H), 7.89–7.61 (m, 5H), 7.61–7.00 (m, 11H), 6.94 (d, $J=2.8$ Hz, 1H), 6.44 (d, $J=35.0$ Hz, 3H), 6.38–6.34 (m, 1H), 6.23 (d, $J=12.1$ Hz, 2H), 5.83 (d, $J=59.1$ Hz, 3H), 5.70 (s, 1H), 3.02 (s, 1H)
- (2) ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 10.95 (s, 4H), 8.53 (s, 1H), 8.10 (s, 2H), 8.08–7.69 (m, 97H), 7.55 (dd, $J=33.3, 17.0$ Hz, 41H), 7.43–6.91 (m, 103H), 6.62 (dd, $J=37.6, 20.8$ Hz, 57H), 6.35 (s, 30H), 6.07 (s, 2H), 6.07–5.74 (m, 40H), 5.66 (s, 13H), 4.57 (d, $J=9.4$ Hz, 13H), 2.50 (s, 11H)
- (3) ^{13}C NMR (75 MHz, CDCl_3): δ 156.09, 154.66, 152.81, 152.12, 151.02, 150.41, 146.46, 143.12, 142.72, 132.04, 131.47, 130.27, 129.84, 129.31, 128.55, 126.89, 123.72, 122.88, 122.52, 121.46, 120.70, 119.26, 117.13, 113.40, 112.43, 110.97, 110.49, 108.64, 108.31, 67.64, 48.72
- (4) ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 155.60, 151.69, 151.14, 150.38, 146.67, 142.89, 142.57, 131.97, 130.99, 129.70, 129.15, 128.64, 128.14, 126.64, 126.06, 123.25, 122.53, 122.12, 118.95, 117.53, 112.96, 112.37, 110.50, 109.27, 107.99, 106.98, 77.65, 64.10, 63.84, 47.24
- (5) FTIR (cm^{-1}): 1622, 1598, 1504, 1467, 1434, 1400, 1355, 1329, 1309, 1265, 1230, 1201, 1172, 1154, 1125, 1070, 1042, 1009, 987, 932, 909, 821, 742

(ii) Naft-Fu-Fu

- (1) ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J=8.9$ Hz, 2H), 7.55 (s, 1H), 7.52 (s, 1H), 7.47 (s, 2H), 7.42 (s, 1H), 7.40 (d, $J=4.0$ Hz, 1H), 7.30 (d, $J=8.9$ Hz, 1H), 6.75 (d, $J=2.6$ Hz, 1H), 6.50 (s, 1H), 6.38 (m, 2H), 6.30 (s, 2H), 5.98 (d, $J=2.7$ Hz, 1H), 5.63 (s, 1H), 4.19 (d, $J=15.2$ Hz, 1H), 3.69 (d, $J=15.1$ Hz, 1H)
- (2) ^{13}C NMR (75 MHz, CDCl_3): δ 154.59, 152.14, 152.00, 149.71, 142.95, 142.81, 142.48, 132.55, 129.64, 129.45, 128.63, 126.80, 123.72, 122.51, 118.62, 111.18, 110.46, 110.38, 110.29, 110.18, 109.32, 108.48, 82.17, 53.38, 43.63
- (3) FTIR (cm^{-1}): 3016, 2948, 1623, 1505, 1467, 1436, 1404, 1331, 1267, 1224, 1140, 1069, 1015, 936, 883, 821, 739

2.4. Polymerization of Naphthoxazine Monomers. Monomer powders, in an aluminum pan, were placed in a muffle oven and heated for a total of 4 h: 1 h at 150°C, 1 h at 170°C, 1 h

at 190°C, and 1 h at 210°C in air. Dark brown cross-linked materials, poly(naphthoxazines), were obtained for all cases after the polymerization processes.

3. Results and Discussion

3.1. Synthesis of Naphthoxazines Containing Furan Groups.

The naphthoxazines studied in this work were obtained by a one-pot reaction between 2-naphthol, an aldehyde (formaldehyde or furfural), and a nitrogenated compound (furfurylamine or ammonium acetate) under solvent-free conditions and without the use of catalysts, as shown in Figure 2. As far as it can be ascertained, the synthesis of the Naft-Fu-H and Naft-Fu-Fu compounds is not reported in the literature and even the Naft-H-Fu compound is reported in only one single work [25], where the thermal properties or polymerization behavior of this compound was not explored.

The synthesis of Naft-Fu-H was conducted under microwave heating, with satisfactory yield (60%), in a few minutes (7 min), especially if compared to the syntheses of oxazinic compounds conducted under traditional heating described in literature, which normally require several hours of reaction, thus demonstrating the efficiency of this method in the synthesis of this type of compound, as already reported in previous studies [3].

For the synthesis of the Naft-H-Fu and Naft-Fu-Fu compounds, it was chosen to conduct the syntheses at room temperature to avoid the polymerization of furfural, which would consequently reduce the yields of the reactions. The Naft-H-Fu compound was obtained in 62% yield, and the Naft-Fu-Fu compound was obtained in 44% yield. The lower yield of the Naft-Fu-Fu compound may be related to the greater steric hindrance caused by the three substituent groups present on the oxazinic ring, which would make it difficult to close the ring and consequently the formation of that compound.

It is worth mentioning that oxazinic compounds have been synthesized traditionally through Mannich condensation, between a phenolic compound, a primary amine, and formaldehyde, in a single step [4]. The synthesis of oxazinic compounds with aldehydes other than formaldehyde leading to the formation of compounds with substituents on the oxazinic ring carbons (2,4-substituted) is, however, uncommon and little reported in the literature; their methodologies for obtaining, reaction mechanisms and thermal properties are poorly exploited. In this sense, the synthesis and studies of the properties of Naft-H-Fu and Naft-Fu-Fu therefore represent an advance in the study of oxazinic compounds containing aldehydes other than formaldehyde.

3.2. Structural Characterization of Naphthoxazines Containing Furan Groups

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR). In Figure 3, the FTIR spectra of 2-naphthol and naphthoxazines are compared. It is possible to observe that the broad band attributed to the stretching of the O-H bond present on the 2-naphthol spectrum (3248 cm^{-1} , indicated by the black arrow) is completely absent in the spectra of the naphthoxazines, indicating the transformation of the

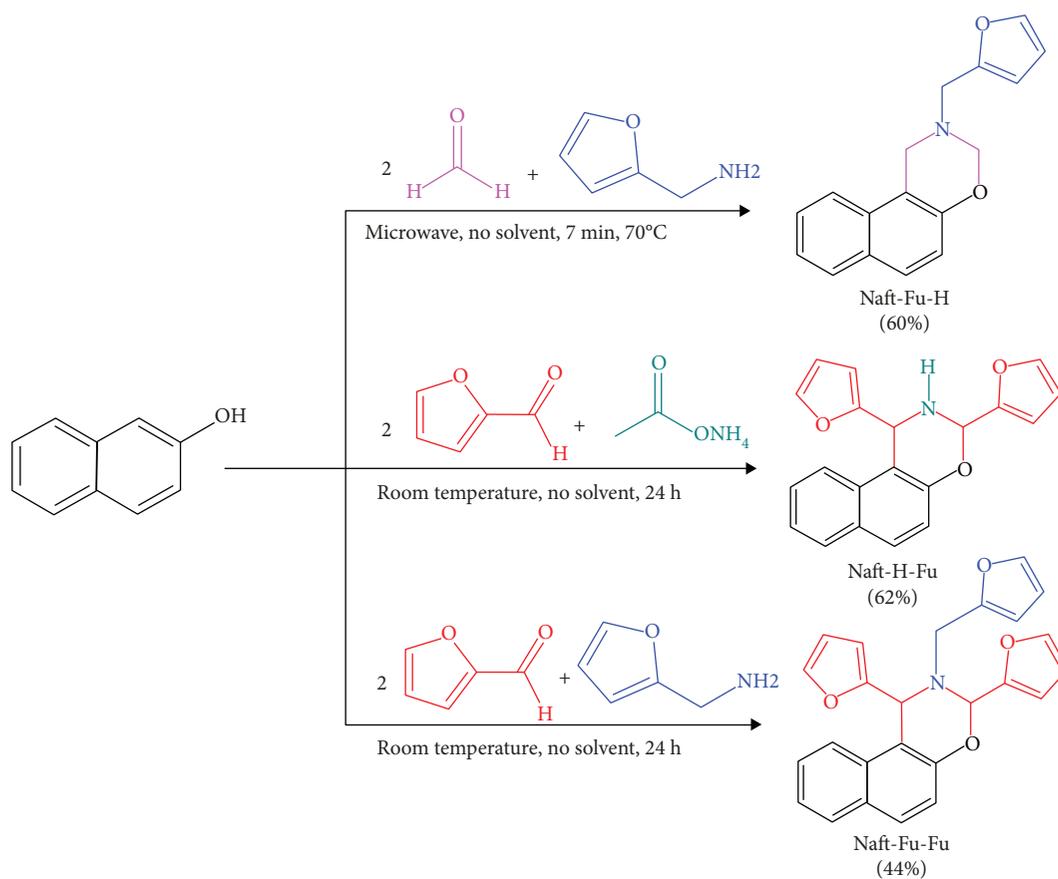


FIGURE 2: Synthetic scheme for the naphthoxazines containing furan groups.

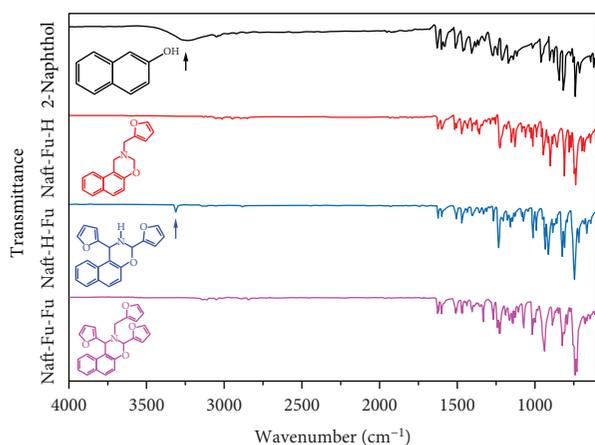


FIGURE 3: FTIR spectra of the naphthoxazines containing furan groups.

hydroxyl group, which can be attributed to the formation of the oxazinic ring. It is also possible to observe in the spectrum of the Naft-H-Fu a single sharp band attributed to the stretching of the N-H bond (3317 cm^{-1} , indicated by the blue arrow), which helps to confirm the proposed structure for that compound.

In the fingerprint region of the naphthoxazine spectra (Figure 4), the bands observed at 1624 and 1598 cm^{-1} are attributed to the stretching of the C=C bonds of the

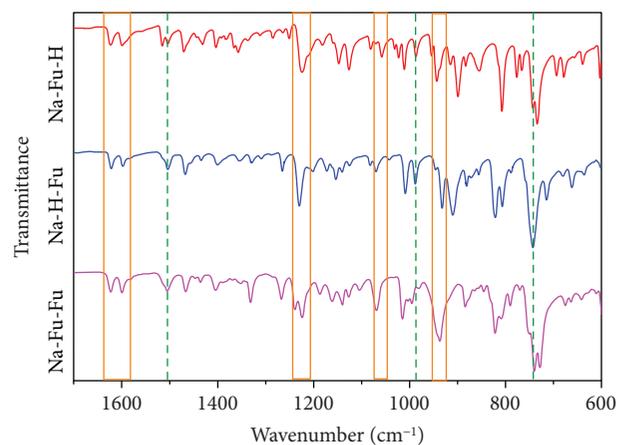


FIGURE 4: FTIR spectra of the naphthoxazines in the fingerprint region.

naphthalene ring. The presence of characteristic bands around $930\text{--}940\text{ cm}^{-1}$, attributed to the out-of-plane deformation mode of the α,β -disubstituted naphthalene ring, indicates the formation of the oxazinic ring in all compounds. The bands observed at $1223\text{--}1229\text{ cm}^{-1}$ and $1058\text{--}1070\text{ cm}^{-1}$, assigned, respectively, to the asymmetric and symmetrical stretches of =C-O-C bonds, help to confirm the proposed structures for naphthoxazines containing furan groups [26]. The presence of the furan groups in all compounds was

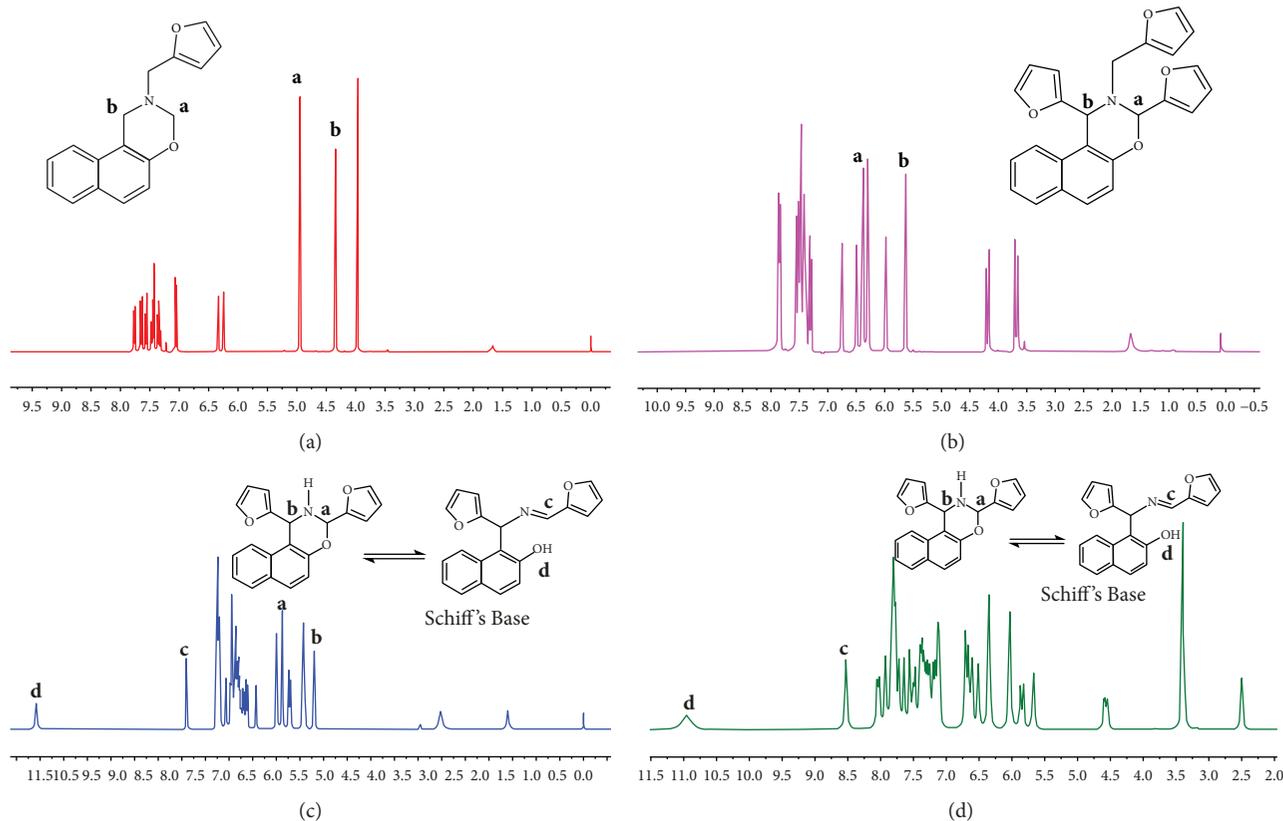


FIGURE 5: ^1H NMR of naphthoxazines containing furan groups. (a) Naft-Fu-H, (b) Naft-Fu-Fu, (c) Naft-H-Fu, and (d) Naft-H-Fu (in DMSO-d_6).

confirmed by the observation of the characteristic peaks of this group in 1504 , 987 , and 742 cm^{-1} [1], indicated by dashed lines in Figure 4.

3.2.2. ^1H and ^{13}C Nuclear Magnetic Resonance (^1H NMR and ^{13}C NMR). The ^1H NMR spectra of the naphthoxazines are displayed in Figure 5. The two singlets attributed to $\text{O-CH}_n\text{-N}$ (marked as **a**) and $\text{Ar-CH}_n\text{-N}$ (marked as **b**) of the oxazinic ring were observed at 4.94 and 4.34 ppm, 6.38 and 5.40 ppm, and 6.38 and 5.63 ppm for the compounds Naft-Fu-H, Naft-H-Fu, and Naft-Fu-Fu, respectively. These specific resonances of naphthoxazines have already been reported in previous works and are consistent with the formation of naphthoxazine rings [26–28].

Interestingly, the compound Naft-H-Fu exhibits ring-open-chain tautomerism in solution. This fact has already been observed in a similar compound by Karthikeyan et al. [29] and was attributed to a residual acidity of CDCl_3 . In the ^1H NMR spectra of this compound, it is possible to observe the signals attributed to Schiff's base at 8.40 ppm ($-\text{CH}=\text{N}$, marked as **c**) and 11.58 ppm (O-H , marked as **d**). The ^1H NMR spectrum of Naft-H-Fu was also performed in DMSO-d_6 (Figure 5(d)), a solvent less acidic than CDCl_3 , in order to avoid the ring-open-chain tautomerism, but even in this solvent, it was possible to observe the signals attributed to Schiff's base.

The ^{13}C NMR spectra of naphthoxazines are displayed in Figure 6 and, in the same way of ^1H NMR spectra, it is

useful to verify the characteristic signals of naphthoxazines. To the compounds Naft-Fu-H and Naft-Fu-Fu, the signals attributed to $\text{O-CH}_n\text{-N}$ (marked as **a**) and $\text{Ar-CH}_n\text{-N}$ (marked as **b**) were observed at 81.8 and 48.8 ppm and 82.17 and 53.38 ppm, respectively. To the compound Naft-H-Fu, in the spectra performed in CDCl_3 , it was possible to observe just the signal attributed to $\text{O-CH}_n\text{-N}$ at 67.64 ppm. The signals attributed to Schiff's base were observed at 67.64 ppm (C-N , marked as **d**) and at 156.09 ppm ($\text{C}=\text{N}$, marked as **c**). It was possible to observe the signal attributed to $\text{O-CH}_n\text{-N}$ only in the spectra performed in DMSO-d_6 , at 77.78 ppm. This fact can be attributed to the lower acidity of DMSO-d_6 in relation to CDCl_3 , which causes the equilibrium displacement towards the naphthoxazine, allowing the observation of the signal.

3.3. Thermal Characterization of Naphthoxazines Containing Furan Groups

3.3.1. Differential Scanning Calorimetry (DSC). The polymerization behavior of naphthoxazines containing furan groups was studied by differential scanning calorimetry (DSC). The nonisothermal DSC thermograms for each compound are shown in Figure 7. Thermal properties, including melting temperature (T_m), polymerization enthalpy (ΔH), and onset polymerization temperature (T_{onset}) of the naphthoxazines are summarized in Table 1.

In all DSC curves, it was observed an endothermic event corresponding to the fusion of the compounds. Such events

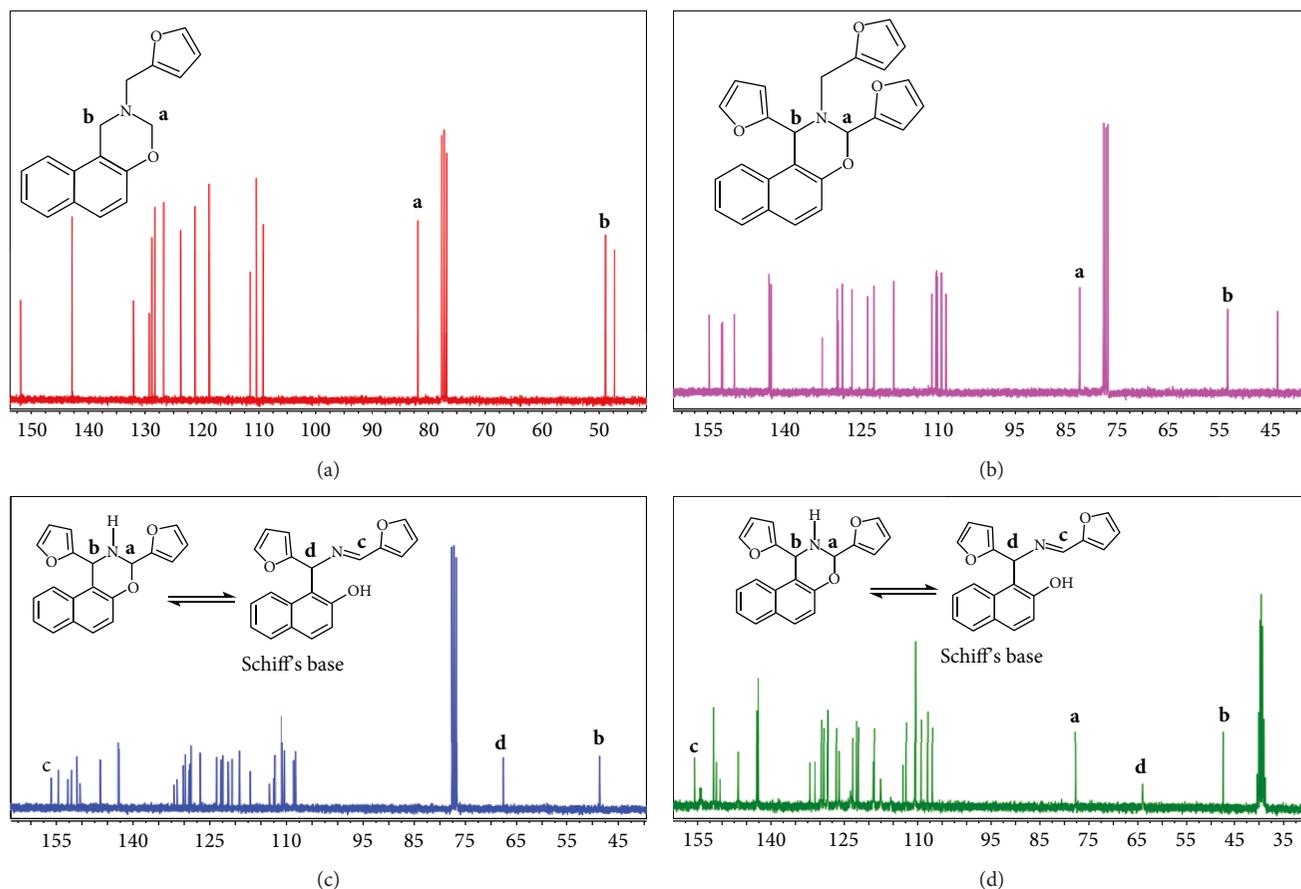


FIGURE 6: ^{13}C NMR of naphthoxazines containing furan groups. (a) Naft-Fu-H, (b) Naft-Fu-Fu, (c) Naft-H-Fu, and (d) Naft-H-Fu (in DMSO-d_6).

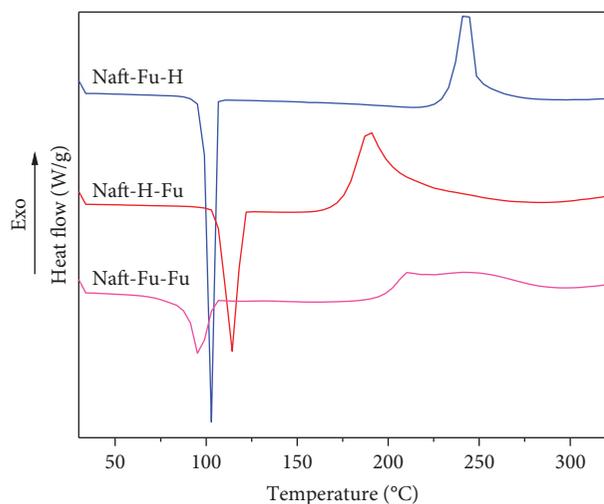


FIGURE 7: DSC thermograms of naphthoxazines containing furan groups.

are centered at 114°C , 100°C , and 95°C for Naft-H-Fu, Naft-Fu-H, and Naft-Fu-Fu, respectively.

The exothermic events observed at higher temperatures are associated with the opening of the oxazinic ring, initiating the process of the polymerization of the naphthoxazines.

TABLE 1: Summary of the values of the nonisothermal DSC thermograms of the naphthoxazines.

Monomer	T_m ($^\circ\text{C}$)	T_{onset} ($^\circ\text{C}$)	ΔH (J g^{-1})
Naft-H-Fu	114	176	-132.3
Naft-Fu-H	100	236	-95.0
Naft-Fu-Fu	95	198	-119.3

Figure 8 shows a proposed mechanism for the polymerization of Naft-Fu-Fu. The mechanism of polymerization of oxazinic compounds is divided into two main steps: the first is the opening of the oxazinic ring after the absorption of heat and the second occurs through electrophilic substitutions from the iminium ion formed in the ring opening. Depending on the conditions of this second step, two main polymeric structures can be formed in this mechanism: (i) a phenolic type, where phenolic hydroxyl groups are formed, and (ii) a phenoxy type, where is formed an ether bonding [4] (Figure 8(a)).

The onset polymerization temperature of Naft-Fu-H ($T_{\text{onset}} = 236^\circ\text{C}$) is comparable to the temperatures of other naphthoxazines found in the literature [12]. The Naft-H-Fu and Naft-Fu-Fu compounds, however, exhibit considerably lower starting polymerization temperatures ($T_{\text{onset}} = 176^\circ\text{C}$ and 198°C , respectively) than the naphthoxazines reported

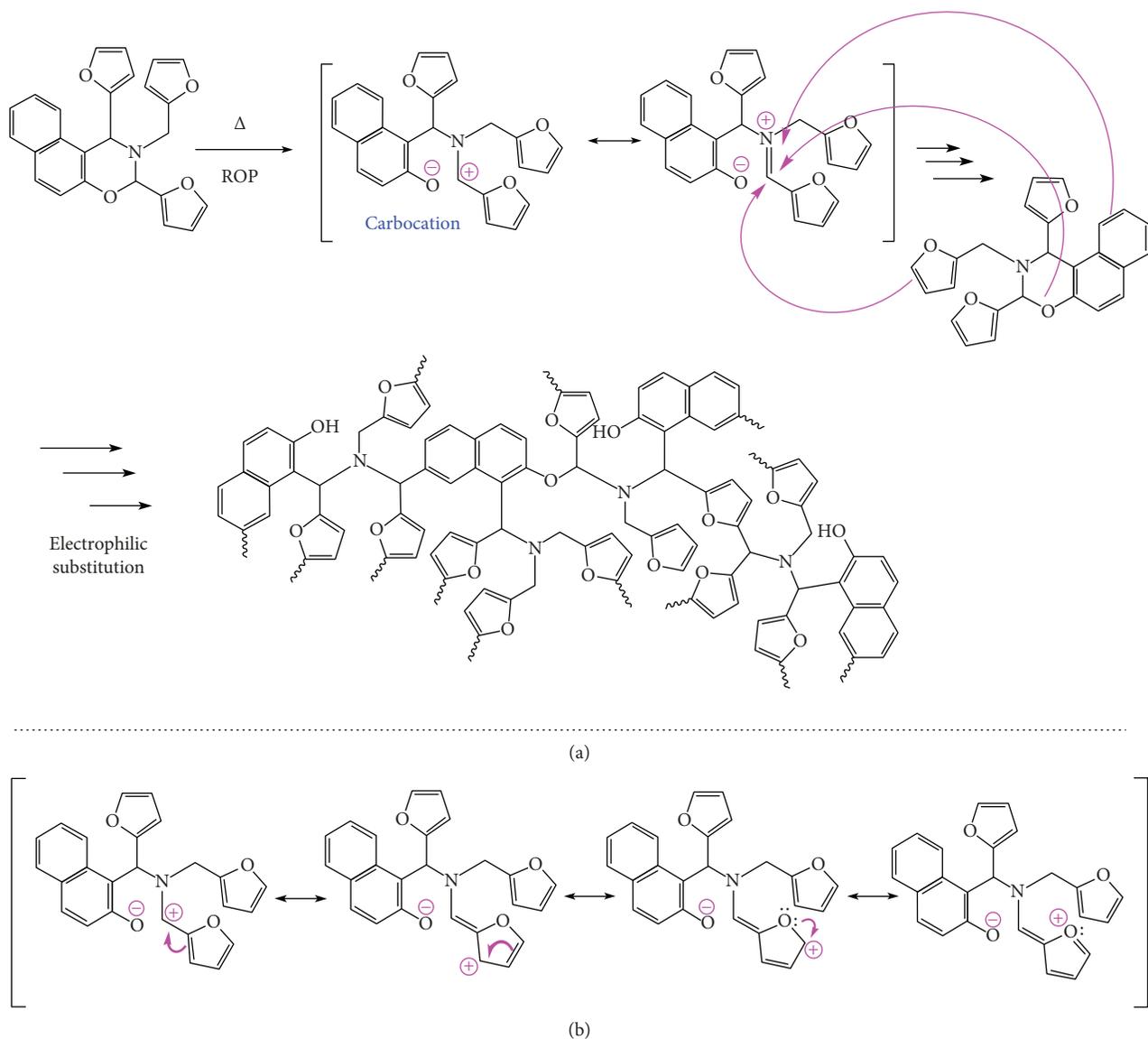


FIGURE 8: (a) Proposed mechanism for the polymerization of the compound Naft-Fu-Fu. (b) Stabilization of carbocation by resonance with the furan group.

in the literature. This effect may be associated with the fact that these compounds have substituents at the 2-position of the oxazinic ring, which facilitate the ring-opening process, since furan groups help to stabilize the carbocation formed at the opening of the oxazinic ring by resonance (Figure 8(b)) [30].

Furan groups may also participate in the polymerization mechanism through electrophilic substitution reactions, as reported in previous work involving the polymerization of benzoxazines containing furan groups [22, 24]. It is assumed, therefore, that the exothermic events observed in the thermograms are due to the simultaneous occurrence of cross-links of the furan groups and the opening of the oxazinic ring. The participation of the furan groups in the polymerization of these compounds is even more evident due to the high values of enthalpy of polymerization (ΔH) and to the fact that the exothermic events associated with the polymerization process are enlarged.

The temperature difference between T_m and T_{onset} is defined as the processing window of a monomer. Naft-H-Fu, Naft-Fu-H, and Naft-Fu-Fu presented processing windows of 62.4°C, 135.5°C, and 102.2°C, respectively. These values are considered satisfactory, reinforcing the potential application of these compounds in material chemistry.

3.3.2. Thermogravimetric Analyses (TGA). The study of the thermal stability of the monomers is an important factor for obtaining polymers since, if the monomers undergo evaporation and/or degradation at temperatures below the polymerization temperature, this process will be impaired or even impossible.

The literature reports that one of the main limiting factors for obtaining poly(naphthoxazines) is the evaporation process that some monomers undergo before the polymerization process. In this way, the thermogravimetric analysis (TGA) of the synthesized naphthoxazines was carried

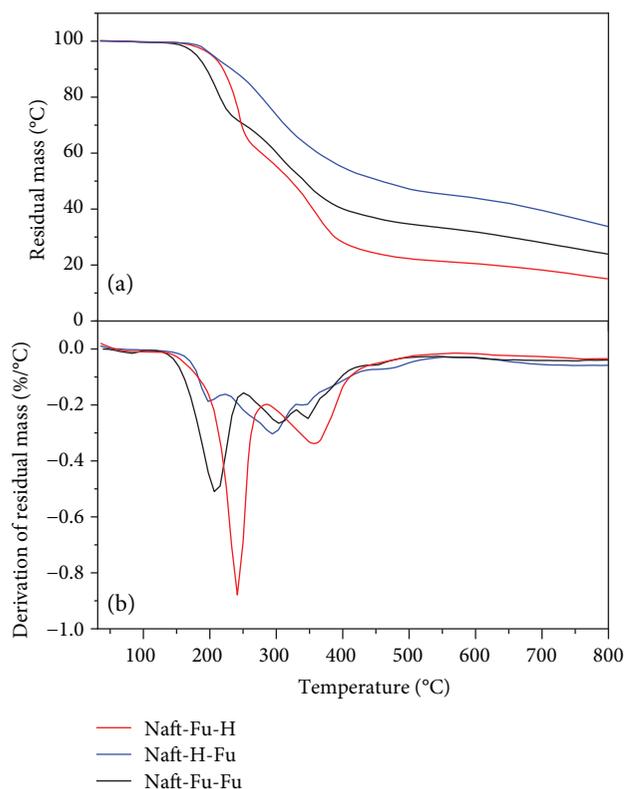


FIGURE 9: Thermograms of naphthoxazines containing furan groups. (a) TGA, (b) DTGA.

TABLE 2: Summary of the values of TGA thermograms of the naphthoxazines.

Monomer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield* (%)
Naft-Fu-H	186	204	14.8
Naft-H-Fu	187	222	33.3
Naft-Fu-Fu	168	186	23.9

*Measured as the residual mass at 800°C.

out in order to evaluate their thermal stabilities before the polymerization process. TGA analysis was performed under conditions similar to the DSC analysis so that a suitable comparison could be made.

In Figure 9, the TGA and DTGA curves of the naphthoxazines containing furan groups are shown. The temperature of 5% and 10% of weight loss ($T_{5\%}$ and $T_{10\%}$, respectively), as well as the char yield (%) are summarized in Table 2.

It is possible to observe that all the compounds undergo a significant mass loss at temperatures lower than the onset polymerization temperatures (T_{onset}) observed by the DSC analysis. In this way, the use of catalysts was evaluated as a way of lowering the polymerization temperature of the compounds, making it possible to obtain the polymers without higher losses, as will be discussed later.

Analyzing the DTGA curves, it is possible to observe two main events of weight loss for Naft-Fu-H and three events for the Naft-H-Fu and Naft-Fu-Fu. Such events may be associated with the evaporation of the compounds or degradation.

The formation of imines as by-products of the benzoxazine polymerization process has been hypothesized by several authors [31, 32]. The formation of this by-product appears to be favored by the presence of aromatic groups at the 2-position of the oxazinic ring, since the imine formed will be stabilized by resonance [30]. Formation followed by evaporation of such low molecular weight by-product may represent one of the additional mass loss events observed in the Naft-H-Fu and Naft-Fu-Fu compounds. In Figure 10, a mechanism for the formation of this imine is proposed.

3.4. Polymerization of Naphthoxazines Containing Furan Groups. As previously discussed (Section 3.2.2), all the compounds undergo mass loss at temperatures lower than the onset polymerization temperatures (T_{onset}). In this sense, the use of catalysts was evaluated as a way of lowering the polymerization temperature of the compounds, making it possible to obtain the polymers without higher losses.

Several catalysts have been evaluated in this sense, such as phosphorus pentachloride (PCl_5) [33], lithium iodide (LiI) [34], and *p*-toluene-sulfonates [35]. However, these compounds are difficult to handle, expensive, and toxic, which make this catalyst not suitable for large-scale production. In the previous work by our group, Kotzebue and coworkers [23] have demonstrated that magnesium chloride (MgCl_2) can be used as an efficient, safe, and inexpensive catalyst in the polymerization of benzoxazines. Thus, this compound was evaluated as an alternative to catalyze the polymerization of the naphthoxazines studied in this work.

As seen in Figure 11, the use of MgCl_2 (1 mol%) reduced significantly the onset polymerization temperature to all naphthoxazines. Kotzebue and coworkers [23] explained that the catalyst could coordinate with oxygen atom of oxazinic ring, making the C-O bond more susceptible to be broken by a small amount of heat absorption.

Once the problem of mass loss during the polymerization process was overcome through the use of the catalyst, the polymerization of the naphthoxazines was performed. The temperature program used in this work (described in Section 2.4) was chosen in the sense to ensure the complete melting of the monomers before the polymerization (to avoid heterogeneity in the polymer) as well as to ensure the curing, once 210°C is higher than onset temperature of all catalyzed compounds (Figure 11).

The thermal stabilities of the poly(naphthoxazines) obtained were studied by TGA under nitrogen atmosphere. The thermograms (TGA and DTGA) of poly(naphthoxazines) are shown in Figure 12, and the obtained data are summarized in Table 3.

Among the polymers, poly(Naft-Fu-FU) has the highest thermal stability, while poly(Naft-Fu-H) and poly(Naft-H-Fu) have very similar $T_{5\%}$ and $T_{10\%}$ values. It was also observed that the poly(Naft-H-Fu) and poly(Naft-Fu-Fu) presented the highest char yield than poly(Naft-Fu-H). This fact can be attributed to the greater number of furan groups present in these compounds which are able to increase the cross-linked density in the polymers since their unsubstituted 5-position is electronically activated for electrophilic substitutions.

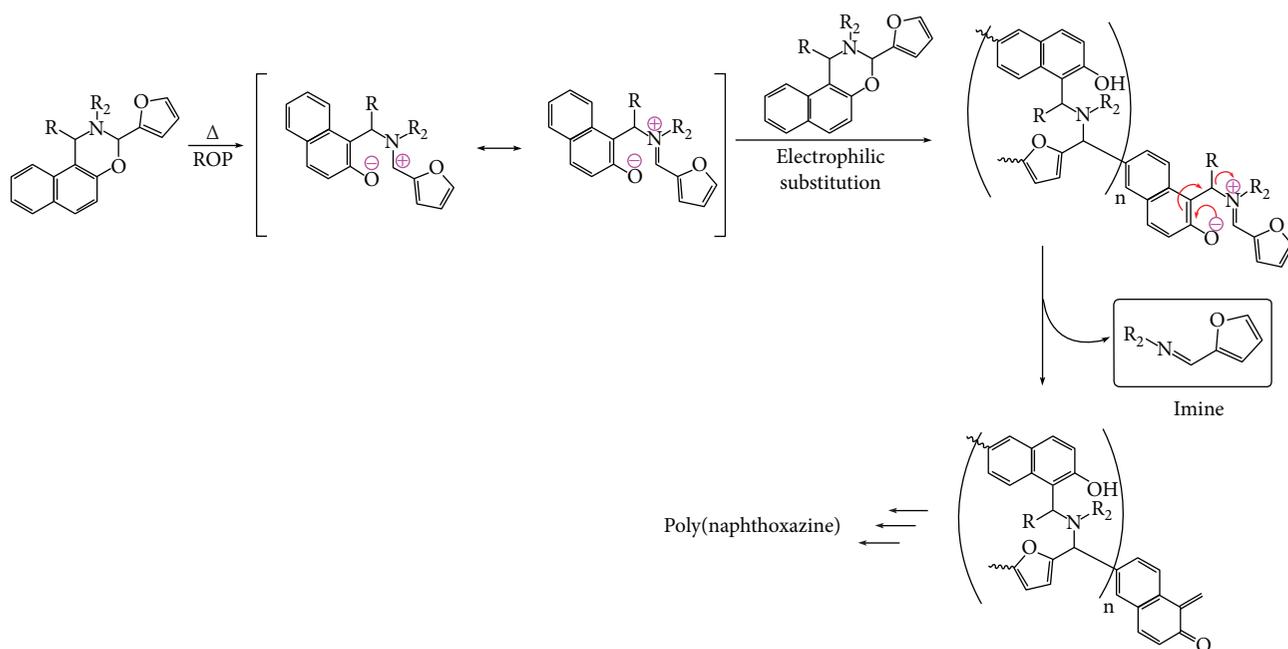


FIGURE 10: Proposed mechanism for the formation of an imine as a by-product of the polymerization process.

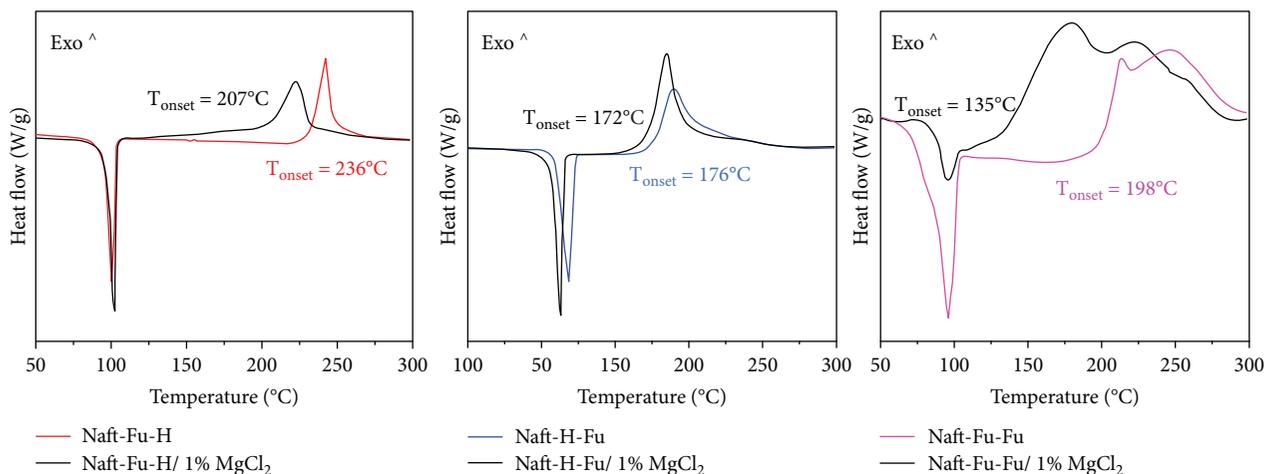


FIGURE 11: DSC curves of naphthoxazines with and without MgCl₂ (1 mol%).

The flame resistance of a polymer is a suitable property that can be evaluated by the determination of the limiting oxidation index (LOI), which is the minimum O₂ concentration to let the material ignite to cause flammability. Materials with LOI values ≤ 26 are considered flammable, and an interesting way to estimate LOI values of halogen-free polymers is by using the char yields (CY) of TGA analyses using the van Krevelen equation [36] (1). The LOI determination was recently utilized to determine the flame resistance of polybenzoxazines [37], and considering the elevated values of char yield observed in Table 3, TGA results were also employed to evaluate the flame retardancy of the poly(naphthoxazines) in this work.

$$\text{LOI} = 17.5 + 0.4(\text{CY}). \quad (1)$$

The LOI values reported in Table 3 demonstrate that the poly(naphthoxazines) containing furan groups have outstanding flame resistance, since polymers having LOI values > 28 are considered self-extinguishing. Such high flame resistance and self-extinguishing properties are especially desirable in high-performance materials and become more attractive if considered in the use of biobased, halogen-, silane-, and phosphorus-free materials.

The polymerization of naphthoxazines containing furan groups was also confirmed by FTIR analysis (Figure 13). The main sign of polymerization of monomers is the dramatic decrease of characteristic bands around 930–940 cm⁻¹, attributed to the out-of-plane deformation mode of the α,β -disubstituted naphthalene ring, which indicates the opening of the oxazinic ring. It was also noticed the appearance of the broad band at around 3320 cm⁻¹ (O-H stretching), which

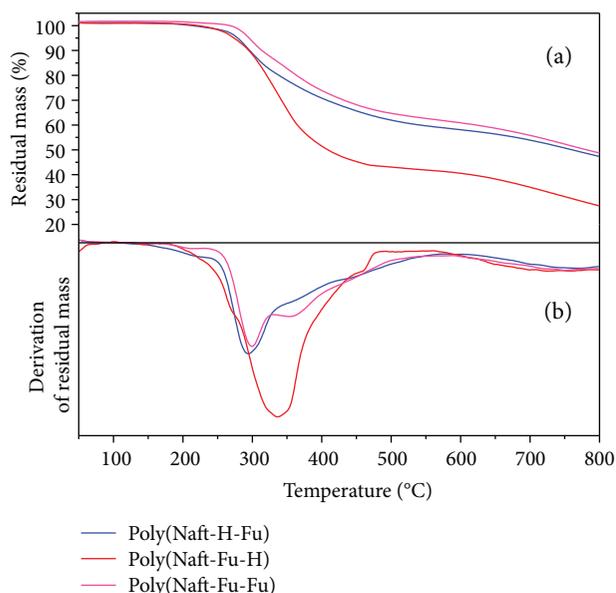


FIGURE 12: Thermograms of poly(naphthoxazines). (a) TGA, (b) DTGA.

TABLE 3: Summary of the values of TGA thermograms of the poly(naphthoxazines).

Polymer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (%)	LOI*
Poly(Naft-Fu-H)	273	294	27	28.3
Poly(Naft-H-Fu)	278	296	47	36.3
Poly(Naft-Fu-Fu)	295	313	48	36.7

*Calculated from the char yield at 800°C of TGA analysis.

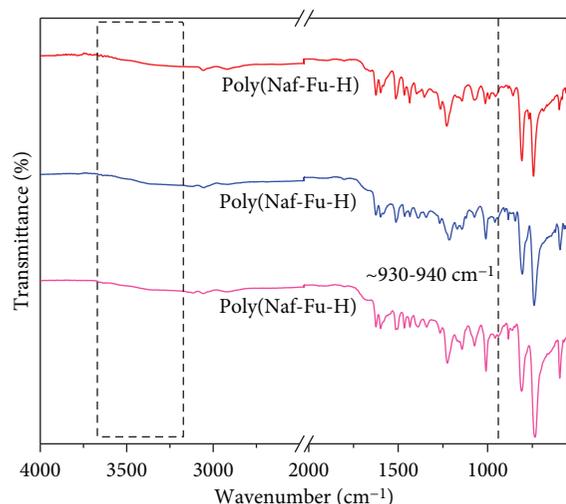


FIGURE 13: FTIR spectra of poly(naphthoxazines).

was completely absent in the monomer spectra, indicating that the polymer structure contains phenolic-type poly(naphthoxazines). The fact that was not observed an overall displacement of the bands associated with the stretching of the C=C bonds of the naphthalene ring in addition with the fact that the bands associated with furan groups becoming broad, consistent with the formation of disubstituted furan

rings, indicates that the electrophilic substitutions occur mainly in the furan groups, since the OH groups also appear.

4. Conclusions

This work reported the synthesis of novel biobased poly(naphthoxazines) containing furan groups. The syntheses were carried out in a single step, without the use of solvents and catalysts, obtaining the products in satisfactory yields and high purity. The naphthoxazines had their chemical structures completely characterized by FTIR, ^1H NMR, and ^{13}C NMR techniques. The DSC analysis showed that all naphthoxazines exhibit exothermic typical polymerization events, making these compounds suitable for obtention of poly(naphthoxazine) resins. However, TGA analysis has shown that the compounds suffer significant mass losses at temperatures below the onset polymerization temperature. In this way, a catalyst (1 mol% MgCl_2) was used in order to allow the polymerization of the compounds before the mass loss events. The poly(naphthoxazines) obtained were studied by TGA analyses and exhibited high thermal stability, with high flame resistance and self-extinguishing properties (LOI > 28), which makes these compounds attractive in the development of high-performance materials.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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