STUDIES ON THE RING-OPENING POLYMERIZATION OF BENZOXAZINES: UNDERSTANDING THE EFFECT OF THE SUBSTITUENTS

Alba Martos, Rosa M. Sebastián*, and Jordi Marquet*

Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola del Vallés, 08193 Barcelona, Spain.

jordi.marquet@uab.cat

Keywords: Polybenzoxazines; Polymerization Temperature; Substituent Effects; Phenolic Resins; Mechanism of Polymerization

Abstract

A wide set of differently substituted 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine derivatives (models of thermosetting benzoxazine resins) were synthesized and their polymerization temperature was studied using Differential Scanning Calorimetry (DSC). The effect of the electronic properties of different substituents in different positions of the alkoxyphenyl ring on the polymerization temperature was analyzed by the Hammett equation. A non-linear Hammett plot was obtained indicating a change in the polymerization mechanism. Based on these results, different ring-opening polymerization (ROP) mechanisms are proposed to operate depending on the electronic character of the substituents. Thus, the previously unpredictable dependence of the polymerization temperature with the electronic character of the substituents in the alkoxyphenyl ring can be now understood and even advanced for future developments.

1. Introduction

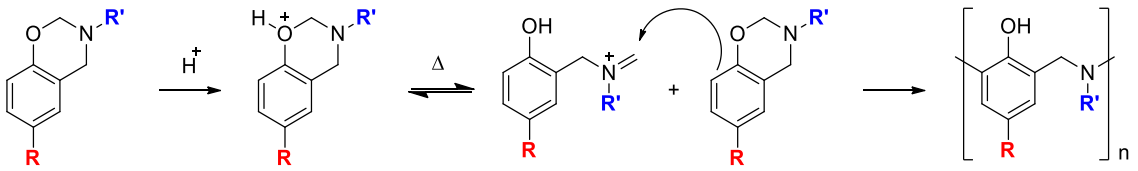
Benzoxazines are a recently developed type of thermosetting resins that are getting much attention as alternative to the traditional phenolic resins due to their improved properties [1,2]. Polybenzoxazines not only have the properties of traditional phenolic resins such as good chemical resistance and excellent thermal behavior like flame resistance and high char yield, but they also show other interesting features like high molecular design flexibility, near-zero shrinkage upon curing, very low moisture absorption, low melt viscosities and high glass transition temperature [3,4,5].

Generally, polybenzoxazines are made via thermally induced ring opening polymerization of bisbenzoxazine monomers (the thermosetting resins) without the need of using catalysts, and without releasing byproducts such as water, ammonia or any other compound during the curing

process. These volatile compounds sometimes give rise to the formation of microvoids, weakening the mechanical properties of phenolic-based materials [6]. The existence of inter- and intramolecular interactions via hydrogen-bonding due to the presence of acidic phenols and basic amino groups provides extra structural rigidity and justifies the excellent mechanical properties to these materials [7,8,9]

Polybenzoxazines represent an advanced type of phenolic resins that have found already special applications in the electronics, automotive, aerospace, and other industries. However, their wider implantation as reference materials has been hampered by the slow reactivity of benzoxazine monomers that require high temperatures in order to achieve the polymerization (about 250 ^{o}C) [10,11]. In order to reduce those very high temperatures, it is very important to acquire a good knowledge of the polymerization reaction mechanism.

The oxazine ring in benzoxazines is a distorted semi-chair structure which is responsible for an appreciable ring strain. Because of the six-membered ring strain, the benzoxazine undergoes ring-opening reaction upon certain conditions [12]. A general mechanism has been proposed in the literature for the cationic ring-opening polymerization (ROP) of benzoxazines (Scheme 1) [13]. In this proposal, oxygen protonation of the oxazine ring would happen causing the ring-opening, giving rise to the formation of an iminium ion structure. Finally, the charged methylene group would be attacked by the *ortho* position of the phenolic ring of other benzoxazine and an electrophilic aromatic substitution would occur [5].



Scheme 1. Previously reported mechanism for the cationic ROP of benzoxazines [13]

Some studies have been reported focusing on the reduction of the polymerization temperature of this process, but most of them rely in the use of catalysts [14,15,16,17,18]. Monoley *et al.* analyzed the importance of the electronic nature of the substituents on the stability of the oxazine ring in aqueous solutions in a series 3,4-dihydro-2*H*-1,3-benzoxazine and 3,4-dihydro-2*H*-1,3-pyridooxazine derivatives [19]. Ronda *et al.* studied the influence of substituents with different electronic character in substituted 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine monomers on the polymerization temperature. Their results showed that electron-withdrawing groups substituted in the *para* positions of the phenolic ring produce a perceptible decrease of the polymerization temperature [20]. However, no mechanistic conclusive evidences could be derived from those studies since they were limited to a few cases of para-substituted benzoxazine monomers.

In this work, we aim to deepen in the knowledge of different aspects of the mechanism of polymerization of benzoxazines through a systematic study of the electronic effects of several

substituents in different positions of the alkoxyphenyl ring of benzoxazines on the polymerization temperature. Hammett equation has been used to rationalize the obtained results. A total of 18 benzoxazines have been synthesized and their polymerization has been studied by differential scanning calorimetry (DSC) (Table 1 and Table 2).

2. Experimental Section

2.1. Materials

Commercially available reagents obtained from Sigma Aldrich, Alfa Aesar, and Fluoro Chem were used as received. 1,3,5-triphenylhexahydro-1,3,5-triazine was prepared in our laboratories following a previously described protocol [21].

2.2 Measurements

Nuclear magnetic resonance: Benzoxazines were characterized by ^{1}H, ^{19}F and ^{13}C nuclear magnetic resonance (NMR). The spectra were recorded on a Bruker Advance III AV400 spectrometer (400 MHz ^{1}H NMR; 376.3 MHz ^{19}F NMR; 100.6 MHz ^{13}C NMR), a Bruker Advance DPX360 spectrometer (360 MHz ^{1}H NMR; 90.5 MHz ^{13}C NMR), or a Bruker Advance DPX250 spectrometer (250 MHz ^{1}H NMR; 235.2 MHz ^{19}F NMR, 62.9 MHz ^{13}C NMR) spectrometer using chloroform-d ($CDCl_3$) as a solvent and tetramethylsilane as an internal standard.

Attenuated Total Reflectance Fourier Transform infrared spectroscopy (ATR-FTIR): Measurements were performed in a Bruker Tensor 27 FTIR spectrometer equipped with a MKII Golden Gate accessory, Specac, with a diamond crystal as ATR element at a nominal incidence angle 45º with a ZnSe lens. Single-beam spectra samples were obtained after averaging 16 scans in the range from 4000 to 600 cm^{-1} with resolution of 4 cm^{-1}.

High resolution mass spectra (HRMS): Some new benzoxazines were analyzed in a high resolution Bruker MicroTOF-Q with electrospray ionization (ESI).

Differential Scanning Calorimetry (DSC): The calorimetric tests were carried out in TA Instrument Q20 using Tzero™ pans and lids calibrated with indium (T_m = 429.75 K, AH_m = 3267 kJ/mol). The thermogram was recorded in a range of temperatures between 0 and 300 ºC at a heating rate 10 ºC/min, under N_2 flow. Between 2 and 5 mg of the samples were used in all of the tests.

2.3. General method A for the synthesis of benzoxazines.

0.032 mol of 1,3,5-triphenylhexahydro-1,3,5-triazine [21], 0.1 mol of phenol, and 0.1 mol of paraformaldehyde were placed in a round bottom flask and the mixture was heated provided with magnetic stirring. Once the reaction was finished, the crude was cooled and was dissolved in diethyl ether, and washed three times with 2 M NaOH and three times with water. The

organic phase was dried with anhydrous Na_2SO_4, and after filtration the solvent was removed at low pressure, and the resulting solid was purified by flash column.

2.3.1 Experimental details and spectroscopic data for previously non-reported benzoxazines synthesized by method A (descriptions for the benzoxazines already described in the literature can be found in the SI).

6-Fluoro-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***4****.* The obtained product was purified by crystallization in hexane (1,00 g, 50 % yield). Mp: 48.2 ^oC ($T_{m(onset)}$, DSC). ^1H NMR (250 MHz, $CDCl_3$) δ(ppm): 4.61 (s, 2H, C_{Ar}-C<u>H</u>$_2$-N), 5.34 (s, 2H, O-C<u>H</u>$_2$-N), 6.73-6.86 (complex abs., 3H, Ar-<u>H</u>), 6.96 (t, *J* = 7.3 Hz, 1H, Ar-<u>H</u>), 7.11 (d, *J* = 7.8 Hz, 2H, Ar-<u>H</u>), 7.28 (m, 2H, Ar-<u>H</u>). ^{13}C RMN (100.6 MHz, $CDCl_3$): δ(ppm): 50.6 (d, J_{C-F} = 1.5 Hz), 79.7, 113.0 (d, J_{C-F} = 22.9 Hz), 114.8 (d, J_{C-F} = 23.0 Hz), 118.1 (d, J_{C-F} = 7.75 Hz), 118.5, 121.8, 121.9 (d, J_{C-F} = 6.5 Hz), 129.5, 148.4, 150.5 (d, J_{C-F} = 2.1 Hz), 157.01 (d, J_{C-F} = 240 Hz). ^{19}F NMR (235.2 MHz, $CDCl_3$) δ(ppm): -123.28. IR (ATR) ν(cm^{-1}): 3068, 2989, 2910, 2862, 1603, 1487, 1431, 1364, 1217, 918, 687. HRMS (ESI/Q-TOF) m/z: [M+H^+] Calcd for $C_{14}H_{13}FNO$ 230.0976; Found 230.0971.

Ethyl 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-6-carboxylate, ***5***. The resulting yellow solid was directly subjected to flash column chromatography (silica gel, hexane: DCM = 1:1 v/v as eluent), obtaining a yellow powder (2.55 g, 85 % yield). Mp: 67.9 ^oC ($T_{m(onset)}$, DSC). ^1H NMR ($CDCl_3$, 360 MHz) δ(ppm): 1.36 (t, *J* = 7.0 Hz, 3H, C<u>H</u>$_3$-CH_2), 4.33 (q, *J* = 7.0 Hz, 2H, CH_3-C<u>H</u>$_2$-C), 4.66 (s, 2H, C_{Ar}-C<u>H</u>$_2$-N), 5.41 (s, 2H, O-C<u>H</u>$_2$-N), 6.81 (d, *J* = 8.6 Hz, 1H, Ar-<u>H</u>), 6.94 (t, *J* = 7.2 Hz, 1H, Ar-<u>H</u>), 7.09 (d, *J*= 8.6 Hz, 2H, Ar-<u>H</u>), 7.26 (t, *J* = 7.9 Hz, 2H, Ar-<u>H</u>), 7.75 (s, 1H, Ar-<u>H</u>), 7.80 (dd, *J* = 2.0 Hz, *J* = 8.5 Hz,1H, Ar-<u>H</u>). ^{13}C NMR ($CDCl_3$, 90.5 MHz) δ(ppm): 14.5, 50.6, 60.9, 80.3, 117.0, 118.7, 120.6, 122.1, 123.0, 129.0, 129.5, 129.8, 148.1, 158.5, 166.4. IR (ATR) ν(cm^{-1}): 3029, 2993, 2918, 1691, 1604, 1582, 1498, 1367, 1280, 1236, 1214, 1198, 1160, 1039, 1024, 971, 940, 914, 768, 754, 691. HRMS (ESI/Q-TOF) m/z: [M+Na^+] Calcd for $C_{17}H_{17}NNaO_3$: 306.1101; Found 306.1099.

5-Methoxy-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***9****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA = 9.5:0.5 v/v as eluent). Total yield for *m*-OCH_3(Bz): 48 % (1.15 g) (Product **<u>9</u>**: white solid 37 % yield (888 mg) and product **10**: white solid 11% yield (264 mg)). Mp: 91.2 ^oC ($T_{m(onset)}$, DSC). ^1H NMR (250 MHz, $CDCl_3$) δ(ppm): 3.81 (s, 3H, O-C<u>H</u>$_3$), 4.55 (s, 2H, Ar-C<u>H</u>$_2$-N), 5.32 (s, 2H, O-C<u>H</u>$_2$-N), 6.42 (d, *J* = 8.3 Hz, 1H, Ar-<u>H</u>), 6.46 (d, *J* = 8.5 Hz, 1H, Ar-<u>H</u>), 6.91 (t, *J* = 7.3 Hz, 1H, Ar-<u>H</u>), 7.05 (d, *J* = 8.3 Hz, 1H, Ar-<u>H</u>), 7.11 (d, *J* = 8.8 Hz, 2H, Ar-<u>H</u>), 7.13-7.29 (m, 2H, Ar-<u>H</u>). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 46.6, 55.5, 79.1, 102.3, 109.7, 109.9, 118.3, 121.4, 127.8, 129.3, 148.6, 155.3, 156.7. IR (ATR) ν(cm^{-1}): 2901, 1589, 1497, 1470, 1456, 1435, 1375, 1268, 1237, 1032, 1105, 1070, 943, 892, 780, 771, 752, 696. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67 %; H, 6.37 %; N, 5.82 %. Found: C, 74.69 %; H, 6.39 %; N, 5.74 %.

7-Methoxy-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***10****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA = 9.5:0.5 v/v as eluent). Total yield for *m*-OCH_3(Bz): 48 % (1.15 g) (Product **9**: white solid 37 % yield (888 mg)

and product **10**: white solid 11 % yield (264 mg)). Mp: 82.5 °C ($T_{m(onset)}$, DSC). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 3.73 (s, 3H, O-CH_3), 4.57 (s, 2H, Ar-CH_2-N), 5.34 (s, 2H, O-CH_2-N), 6.37 (s, 1H, Ar-H), 6.48 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.90 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.93 (app. t, *J* = 7.2 Hz, 1H, Ar-H), 7.10 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.26 (t, *J* = 7.6 Hz, 2H, Ar-H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ(ppm): 50.1, 55.4, 79.9, 101.9, 107.9, 113.1, 118.4, 121.5, 127.4, 129.4, 148.5, 155.2, 159.5. IR (ATR) υ(cm^{-1}): 3004, 2889, 2834,1620, 1591, 1501, 1442, 1405, 1363, 1269, 1246, 1203, 1145, 1077, 1030, 929, 834, 826, 814, 748, 689. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67 %; H, 6.37 %; N, 5.82 %. Found: C, 75.05 %; H, 6.48 %; N, 5.80 %.

Ethyl 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-5-carboxylate, ***13****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: DCM = 7:3 v/v as eluent). Total yield for *m*-COOEt(Bz): 76 % (0.76 g) (Product **13**: yellow oil 11 % yield (110 mg) and product **14**: yellow oil 65% yield (650 mg)). ^{1}H NMR ($CDCl_3$, 250 MHz) δ(ppm): 1.40 (t, *J* = 7.1 Hz, 3H, CH_3-CH_2), 4.36 (q, *J* =7.1 Hz, 2H, CH_3-CH_2), 5.02 (s, 2H, C_{Ar}-CH_2-N), 5.38 (s, 2H, O-CH_2-N), 6.89-7.00 (complex abs., 2H, Ar-H), 7.10-7.17 (complex abs., 3H, Ar-H), 7.20-7.29 (complex abs., 2H, Ar-H), 7.60 (dd, *J* = 1.5 Hz, *J* = 7.8 Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 62.5) δ(ppm): 14.5, 50.3, 61.1, 79.2, 118.6, 121.7, 123.6, 123.7, 127.4, 128.7, 129.4, 148.4, 155.2, 166.8. IR (ATR) ν(cm^{-1}): 2980, 2900, 1709, 1589, 1582, 1496, 1460, 1261, 1184, 1146, 1030, 947, 754, 694, 631. HRMS (ESI/Q-TOF) m/z: [M+Na^+] Calcd for $C_{17}H_{17}NNaO_3$ 306.1101; Found 306.1091.

Ethyl 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-7-carboxylate, ***14****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: DCM = 7:3 v/v as eluent). Total yield for *m*-COOEt(Bz): 76 % (0.76 g) (Product **13**: yellow oil 11 % yield (110 mg) and product **14**: yellow solid 65% yield (650 mg)). Mp: 63.6 °C ($T_{m(onset)}$, DSC). ^{1}H NMR ($CDCl_3$, 360 MHz) δ(ppm): 1.36 (t, *J* = 7.2 Hz, 3H, CH_3-CH_2), 4.33 (q, *J* = 7.2 Hz, 2H, CH_3-CH_2), 4.66 (s, 2H, C_{Ar}-CH_2-N), 5.41 (s, 2H, O-CH_2-N), 6.81 (d, *J* = 8.6 Hz, 1H, Ar-H), 6.95 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.10 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.26 (t, *J* = 8.3 Hz, 2H, Ar-H), 7.75 (s, 1H, Ar-H), 7.81 (d, *J* = 8.6 Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 90.5) δ(ppm): 14.5, 50.6, 60.9, 80.3, 116.9, 118.7, 120.6, 122.1, 123.0, 128.9, 129.5, 129.8, 148.1, 158.4, 166.4. IR (ATR) ν(cm^{-1}): 2982, 2904, 1708, 1601, 1576, 1501, 1287, 1267, 1246, 1200, 1126, 1096, 1022, 980, 969, 901, 887, 873, 873, 756, 745, 691. HRMS (ESI/Q-TOF) m/z: [M+Na^+] Calcd for $C_{17}H_{17}NNaO_3$: 306.1101; Found 306.1099.

3-Phenyl-3,4-dihydro-2H-1,3-benzoxazine-7-carbonitrile, ***16****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA = 7:3 v/v as eluent), obtaining a pale brown powder (0.04 g, 35 % yield). Mp: 94.9 °C ($T_{m(onset)}$, DSC). ^{1}H NMR ($CDCl_3$, 250 MHz) δ(ppm): 4.83 (s, 2H, C_{Ar}-CH_2-N), 5.44 (s, 2H, O-CH_2-N), 7.00-7.09 (complex abs., 2H, Ar-H), 7.17 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.23-7.26 (complex abs., 2H, Ar-H), 7.30-7.37 (complex abs., 2H, Ar- H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ(ppm): 49.3, 79.4, 110.2, 116.4, 118.3, 121.7, 122.0, 123.8, 124.9, 128.2, 129.2, 147.4, 154.6. IR (ATR) ν (cm^{-1}): 3085, 3045, 2914, 2228, 1600, 1581, 1496, 1466, 1369, 1346, 1243, 1214, 1191, 1161, 1103, 1034, 1009, 978,

941, 891, 798, 783, 778, 759, 694, 653. HRMS (ESI/Q-TOF) m/z: [M+Na$^+$] Calcd for $C_{15}H_{12}N_2ONa$ 259.0842; Found 259.0841.

2.4 General method B for the benzoxazines.

It is the same method A but using dioxane as solvent.

2.4.1 Experimental details and spectroscopic data for benzoxazines synthesized by method B.

3-Phenyl-6-(trifluoromethyl)-3,4-dihydro-2H-1,3-benzoxazine, ***6****.* The resulting residue was purified by flash column chromatography (silica gel, 5% EA in hexane as eluent), affording a white solid (0.32 g, 57% yield). Mp: 89.3 ºC ($T_{m(onset)}$, DSC). ^{1}H NMR ($CDCl_3$, 360 MHz) δ(ppm): 4.66 (s, 2H, C_{Ar}-C<u>H$_2$</u>-N) 5.40 (s, 2H, O-C<u>H$_2$</u>-N), 6.87 (d, *J* = 8.6 Hz, 1H, Ar-<u>H</u>), 6.96 (t, *J* = 7.4 Hz, 1H, Ar-<u>H</u>), 7.10 (d, *J* = 7.6 Hz, 2H, Ar-<u>H</u>), 7.24-7.30 (m, 3H, Ar-<u>H</u>), 7.35 (d, *J* = 8.6 Hz, 1H, Ar-<u>H</u>). ^{13}C NMR ($CDCl_3$, 90.5 MHz) δ(ppm): 50.6, 80.1, 117.4, 118.7, 121.1, 122.1, 123.0 (d, J_{C-F} = 32.7 Hz), 124.3 (q, J_{C-F} = 3.8 Hz), 124.4 (d, J_{C-F} = 271.2 Hz), 125.3 (q, J_{C-F} = 3.6 Hz), 129.5, 148.1, 157.2. ^{19}F NMR ($CDCl_3$, 235.2 MHz) δ(ppm): -62.09. IR (ATR) ν(cm^{-1}): 1625, 1594, 1494, 1375, 1326, 1255, 1235, 1209, 1189, 1140, 1125, 1073, 1029, 970, 937, 880, 825, 794, 760, 694. HRMS (ESI/Q-TOF) m/z: [M+Na$^+$] Calcd for $C_{15}H_{12}F_3NNaO$ 302.0763; Found 302.0753.

5-Fluoro-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***11****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA = 9.5:0.5 v/v as eluent). Total yield for *m*-F(Bz): 19 % (190 mg) (Product **<u>11</u>**: yellow oil 13 % yield (130 mg) and product **12**: yellow oil 6% yield (60 g)). ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 4.62 (s, 2H, C_{Ar}-C<u>H$_2$</u>-N), 5.38 (s, 2H, 2H, O-C<u>H$_2$</u>-N), 6.56-6.68 (complex abs., 2H, Ar-<u>H</u>), 6.94-7.02 (complex abs., 2H, Ar-<u>H</u>), 7.14 (d, *J* = 7.5 Hz, Ar-<u>H</u>), 7.31 (t, *J* = 7.5 Hz, 2H, Ar-<u>H</u>). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ(ppm): 50.4, 79.9, 104.5 (d, J_{C-F} = 24.0 Hz), 108,3 (d, J_{C-F} = 22.0 Hz), 116.8 (d, J_{C-F} = 3.8 Hz), 118.7, 122.0, 127.9 (d, J_{C-F} = 9.4 Hz), 129.6, 148.5, 155.6 (d, *J* = 12.5), 162.4 (d, J_{C-F} = 243.7). ^{19}F NMR (235.2 MHz, $CDCl_3$) δ(ppm): -114.15. IR (ATR) ν(cm^{-1}): 1622, 1599, 1500, 1436, 1264, 1135, 1103, 1031, 991, 964, 631. HRMS (ESI/Q-TOF) m/z: [M+H$^+$] Calcd for $C_{14}H_{13}FNO$ 230.0976; Found 230.0970.

7-Fluoro-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***12****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA =9.5:0.5 v/v as eluent). Total yield for *m*-F(Bz): 19% (190 mg) (Product **11**: yellow oil 13 % yield (130 mg) and product **<u>12</u>**: yellow oil 6% (60 mg)). ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 4.66 (s, 2H, C_{Ar}-C<u>H$_2$</u>-N), 5.36 (s, 2H, O-C<u>H$_2$</u>-N), 6.58-6.64 (complex abs., 2H, Ar-<u>H</u>), 6.96 (t, *J* = 7.5 Hz, 1H, Ar-<u>H</u>), 7.06 (m, 1H, Ar-<u>H</u>), 7.13 (d, *J* = 7.5 Hz, 2H, Ar-<u>H</u>), 7.29 (t, *J* = 7.7, 2H, Ar-<u>H</u>). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ(ppm): 45.7, 79.6, 107.1 (d, J_{C-F} = 21.0 Hz), 109.3 (d, *J* = 22.0 Hz), 112.6 (d, J_{C-F} = 3.5 Hz), 118.5, 121.9, 128.1 (d, J_{C-F} = 10.2 Hz), 129.5, 148.3, 155.7 (d, J_{C-F} = 7.8 Hz), 159.7 (d, J_{C-F} = 243.9 Hz) ^{19}F NMR (235.2 MHz, $CDCl_3$) δ(ppm): -119.72. IR (ATR) ν(cm^{-1}): 1623, 1598, 1495,

1467, 1369, 1345, 1256, 1234, 1160, 1020, 985, 949, 777, 754, 694, 631. HRMS (ESI/Q-TOF) m/z: [M+H$^+$] Calcd for $C_{14}H_{13}FNO$ 230.0976; Found 230.0976.

3-Phenyl-7-(trifluoromethyl)-3,4-dihydro-2H-1,3-benzoxazine, ***15***. The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: EA = 1:1 v/v as eluent), affording the desired yellow solid (0.27 g, 18 % yield). Mp: 51.3 ^{o}C ($T_{m(onset)}$, DSC). ^{1}H NMR ($CDCl_3$, 360 MHz) δ(ppm): 4.67 (s, 2H, C_{Ar}-C$\underline{H_2}$-N), 5.40 (s, 2H, O-C$\underline{H_2}$-N), 7.05 (t, *J* = 7.4 Hz, 1H, Ar-$\underline{H}$), 6.96 (s, 1H, Ar-$\underline{H}$), 7.09-7.12 (complex abs., 4H, Ar-$\underline{H}$), 7.28 (app. t, *J* = 7.7 Hz, 2H, Ar-$\underline{H}$). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ(ppm): 50.6, 80.0, 114.1 (q, J_{C-F} = 3.9 Hz), 117.2 (q, J_{C-F} = 3.7 Hz), 118.6, 121.1, 123.9 (q, J_{C-F} = 272.8 Hz), 124.8, 127.4, 129.5, 130.5 (q, J_{C-F} = 32.6 Hz), 148.1, 154.7. ^{19}F NMR ($CDCl_3$, 376.3 MHz) δ(ppm): -62.69 IR (ATR) ν(cm^{-1}): 3039, 2825, 1587, 1505, 1494, 1433, 1324, 1271, 1224, 1156, 1134, 1065, 1026, 980, 957, 826, 754, 743, 695, 680. HRMS (ESI/Q-TOF) m/z: [M+H$^+$] Calcd for $C_{15}H_{13}F_3NO$ 280.0944; Found 280.0929.

5-Nitro-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***17****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: DCM = 1:1 v/v as eluent). Total yield for *m*-NO_2(Bz): 19 % (570 mg) (Product **17**: yellow solid 11 % yield (330 mg) and product **18**: yellow solid 8 % yield (240 mg)). Mp: 94.1 ^{o}C ($T_{m(onset)}$, DSC). ^{1}H NMR (250 MHz, $CDCl_3$) δ(ppm): 4.98 (s, 2H, C_{Ar}-C$\underline{H_2}$-N), 5.41 (s, 2H, O-C$\underline{H_2}$-N), 6.96 (t, *J* = 7.5 Hz, 1H, Ar-$\underline{H}$), 7.07-7.12 (complex abs., 3H, Ar-$\underline{H}$), 7.20-7.29 (complex abs., 3H, Ar-$\underline{H}$), 7.69 (dd, *J* = 1.3 Hz, *J* = 8.0 Hz 1H, Ar-$\underline{H}$).^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 49.8, 79.4, 117.6, 117.8, 118.9, 122.4, 123.1, 127.9, 129.5, 147.5, 147.8, 155.8. IR (ATR) ν(cm^{-1}): 3101, 3059, 3013, 2908, 2850, 1597, 1514, 1477, 1450, 1342, 1331, 1298, 1240, 1225, 1181, 1163, 1152, 1029, 981, 944, 900, 830, 803, 771, 759, 736, 700, 688. HRMS (ESI/Q-TOF) m/z: [M+Na$^+$] Calcd for $C_{14}H_{12}N_2NaO_3$ 279.0740; Found 279.0729.

7-Nitro-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine, ***18****.* The resulting yellow oil was directly subjected to flash column chromatography (silica gel, hexane: DCM = 1:1 v/v as eluent). Total yield for *m*-NO_2(Bz): 19 % (570 mg) (Product **17**: yellow solid 11 % yield (330 mg) and product **18**: yellow solid 8 % yield (240 mg)). Mp.:103.4 ^{o}C ($T_{m(onset)}$, DSC). ^{1}H NMR ($CDCl_3$, 360 MHz) δ(ppm): 4.69 (s, 2H, C_{Ar}-C$\underline{H_2}$-N), 5.41 (s, 2H, O-C$\underline{H_2}$-N), 6.97 (t, *J* = 7.2 Hz, 1H, Ar-$\underline{H}$), 7.09 (d, *J* = 7.9 Hz, 2H, Ar-$\underline{H}$), 7.14 (d, *J* = 8.3 Hz, 1H, Ar-$\underline{H}$), 7.27 (t, *J* = 7.9 Hz, 2H, Ar-$\underline{H}$), 7.64 (d, *J* = 2.2 Hz, 1H, Ar-$\underline{H}$), 7.71 (dd, *J* = 8.6 Hz, *J* = 2.2 Hz, 1H, Ar-$\underline{H}$). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ (ppm): 50.7, 80.2, 112.4, 115.8, 118.6, 122.3, 127.5, 128.3, 129.5, 147.7, 147.8, 154.8. IR (ATR) ν(cm^{-1}): 3072, 2912, 1598, 1520, 1493, 1434, 1353, 1331, 1227, 1192, 1158, 1032, 961, 946, 898, 871, 814, 765, 737, 698. HRMS (ESI/Q-TOF) m/z: [M+Na$^+$] Calcd for $C_{14}H_{12}N_2NaO_3$ 279.0740; Found 279.0736.

3. Results and Discussion

3.1 Synthesis of monomers

In this work, we have synthesized a wide set of 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine derivatives, including 13 previously non reported products (**1**-**18**, Table 1). They were prepared

according to the methods described in the literature by Ronda *et. al.* [20]. In all cases the reaction of commercially available monosubstituted phenols, with paraformaldehyde and 1,3,5-triphenylhexahydro-1,3,5-triazine was performed. The use of solvent was not required in most of the cases (method A), however when uncontrolled polymerization of benzoxazines occurred during their synthesis, this process could be minimized working under reflux of 1,4-dioxane (method B); these conditions allowed working at lower reaction temperatures compared to bulk methodology, however lower yields were obtained at longer reaction times. Most compounds were purified by flash column chromatography, except **3**, and **4** that were recrystallized. Previously reported compounds (**1**-**3**, **7**, and **8**) were obtained in yields similar to the ones reported [20,22].

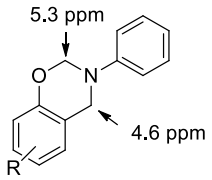


Figure 1. Identification of signals by ^{1}H NMR in $CDCl_3$.

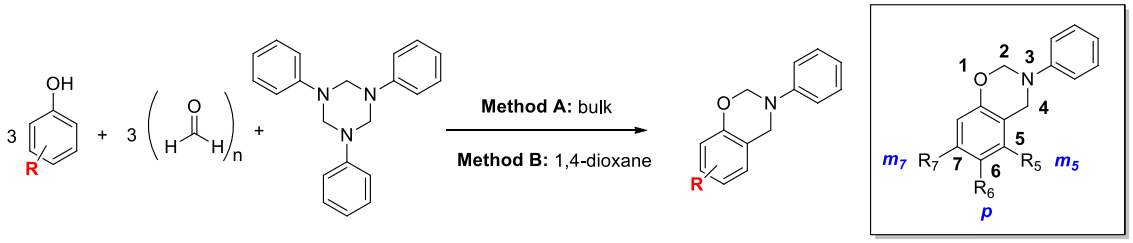
We identify benzoxazine monomers with the nomenclature *p*-R(Bz), m_5-R(Bz) and m_7-R(Bz), where *p*, m_5 and m_7 refer to the position of the substituent R, in *para* or *meta* positions of the benzoxazine alkoxyphenyl ring, respectively. Non-substituted 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine, is designed as Bz.

The reactions were monitored by ^{1}H NMR following the disappearance of the signal of 1,3,5-triazine reagent, through $C\underline{H}_2$ protons at 4.9 ppm in $CDCl_3$. All synthesized compounds were characterized by ^{1}H NMR and FTIR. The benzoxazines exhibit characteristic signals by ^{1}H NMR, two singlet peaks of the methylene groups of 1,3-oxazine ring are observed around 4.6 ppm and 5.3 ppm in $CDCl_3$, corresponding to Ar-$C\underline{H}_2$-N and O-$C\underline{H}_2$-N, respectively (**Figure 1**). The IR spectra showed the characteristic absorptions of benzoxazines structures at 1235 cm^{-1} (asymmetric stretching of C-O-C), and at 1035 cm^{-1} (symmetric stretching of C-O-C). In addition, the new benzoxazines were analyzed by ^{13}C NMR and elemental analysis or high resolution mass spectra confirming their structures. Full description of new benzoxazines is included in the experimental section and spectra are gathered in the supporting information.

When *m*-monosubstituted phenols were selected as reactants, two positional isomers could be obtained, *m_5 and m_7-R(Bz)* (**Table 1)**. In most of the reactions where both isomers appeared, their separation by column chromatography was difficult reducing the isolated yields of pure compounds. For that reason, yields of the *m*-R(Bz) are generally lower than the *p*-R(Bz). When *m*-NO_2(Bz) were purified, the yields obtained were really low. We could observe that m_7-NO_2(Bz) was unstable to column chromatography and starting phenol (3-nitrophenol) was mainly recovered. In the preparation of compounds **15** and **16**, containing $–CF_3$ and –CN substituents in *meta* position of alkoxyphenyl moiety, only one isomer was obtained. When the reaction was attempted with 3-methylphenol, both isomers were obtained, however their

separation couldn't be achieved. The mixture was considered not useful for this type of study. To identify each *meta* isomer, 2D NMR (COSY, HSQC, HMBC) experiments were performed (see SI).

Table 1.
Benzoxazines: synthetic methods and yields.



Entry	Benzoxazine	R_5	R_6	R_7	Method	Yield(%)[a]	Ref.
1	Bz, **1**	H	H	H	A	60	20
2	*p*-OCH_3(Bz), **2**	H	OCH_3	H	A	71	20
3	*p*-CH_3(Bz), **3**	H	CH_3	H	A	71	20
4	*p*-F(Bz), **4**	H	F	H	A	50	-[b]
5	*p*-COOEt(Bz), **5**	H	COOEt	H	A	85	-[b]
6	*p*-CF_3(Bz), **6**	H	CF_3	H	B	57	-[b]
7	*p*-CN(Bz), **7**	H	CN	H	A	28	22
8	*p*-NO_2(Bz), **8**	H	NO_2	H	A	53	20
9	m_5-OCH_3(Bz), **9**	OCH_3	H	H	A	37	-[b]
10	m_7-OCH_3(Bz), **10**	H	H	OCH_3		11	-[b]
11	m_5-F(Bz), **11**	F	H	H	B	13	-[b]
12	m_7-F(Bz), **12**	H	H	F		6	-[b]
13	m_5-COOEt(Bz), **13**	COOEt	H	H	A	11	-[b]
14	m_7-COOEt(Bz), **14**	H	H	COOEt		65	-[b]
15	m_7-CF_3(Bz), **15**	H	H	CF_3	B	18	-[b]
16	m_7-CN(Bz), **16**	H	H	CN	A	35	-[b]
17	m_5-NO_2(Bz), **17**	NO_2	H	H	B	11	-[b]
18	m_7-NO_2(Bz), **18**	H	H	NO_2		8	-[b]

[a] Isolated yield. [b] New compounds

3.2 Effect of substituents on the polymerization temperature

Differential Scanning Calorimetry (DSC) was used to determine the polymerization temperature of monofunctional benzoxazine monomers in order to study the electronic effects of the substituents in this thermally induced process. The thermograms of solid benzoxazines show a typical profile during heating, with two thermal transitions, first an endothermic signal that corresponds to melting and a second exothermic peak assigned to the polymerization reaction. In **Figure 2** the thermogram of *p*-CH_3(Bz), **3**, is shown as an example (the rest are included in the supporting information). It can be observed that this compound melts at 47 ºC ($T_{m(onset)}$) and polymerizes around 260 ºC ($T_{p(onset)}$ = 257 ºC and $T_{p(peak)}$ = 265 ºC).

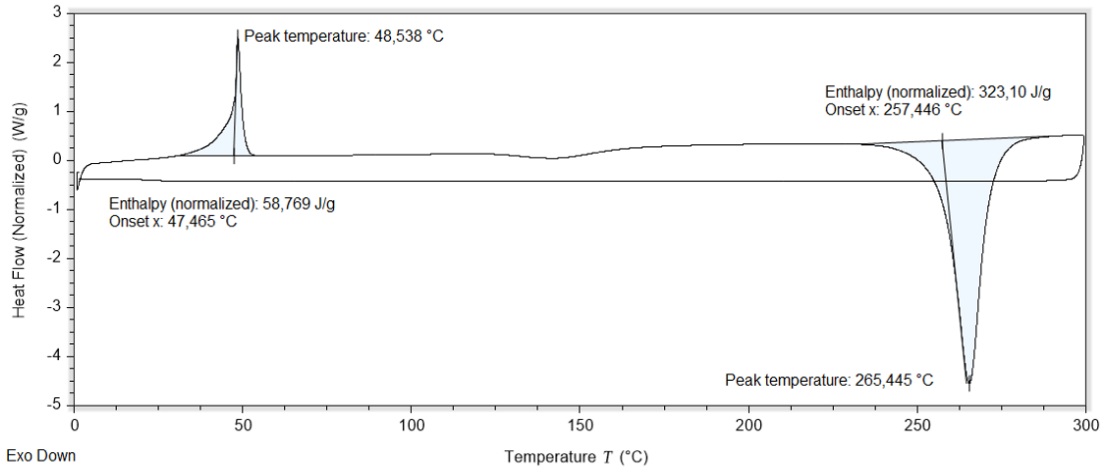


Figure 2. DSC thermogram of benzoxazine **3** at heating rate 10 ºC/min from 0 to 300 ºC.

In Table 2 temperatures obtained for both thermal processes from the DSC thermograms of the different studied benzoxazines are gathered. Transition enthalpies for polymerization reactions are also indicated. The results for *p*-R(Bz) compounds confirm the studies previously described by Ronda *et al.* [20]. Thus, a decrease in polymerization temperature with increase of electron-withdrawing character of the substituent is observed. The *p*-NO_2(Bz) shows the lowest polymerization temperature, around 208ºC. However, when *p*-electron-donor and *meta*-substituents are included in the picture no clear pattern can be easily envisaged. In order to help with a possible interpretation, the corresponding Hammett's parameters have been also included in Table 2; compounds have been ordered in the table by increasing valor of Hammett sigma constants in both positions (*p* and *m*).

Table 2.
Melting and polymerization temperatures obtained by DSC, and Hammett sigma constants

	DSC Thermogram[a]					
Benzoxazine	**$T_{m(onset)}$ (°C)[b]**	**$T_{p(onset)}$ (°C)[c]**	**$T_{p(peak)}$ (°C)[d]**	**ΔH (kJ·mol^{-1})[e]**	**σ_{para}[23]**	**σ_{meta}[23]**
p-OCH_3(Bz), **2**	oil	249.9	259.3	-77.6	-0.268	
p-CH_3(Bz), **3**	47.5	257.4	265.4	-72.8	-0.170	
Bz, **1**	57.4	263.5	267.9	-85.1	0	
p-F(Bz), **4**	48.2	270.6	276.2	-72.7	0.062	
p-COOEt(Bz), **5**	67.9	240.8	246.7	-89.4	0.450	
p-CF_3(Bz), **6**	89.3	246.9	252.5	-142.7	0.540	
p-CN(Bz), **7**	116.8	220.7	225.1	-84.4	0.660	
p-NO_2(Bz), **8**	128.4	203.0	207.7	-83.0	0.778	
m_5-OCH_3(Bz), **9**[f]	91.2	250.3	254.9	-68.5		0.115
m_7-OCH_3(Bz), **10**[f]	82.5	226.8	231.1	-69.5		0.115
m_5-F(Bz), **11**[f]	oil	225.8	230.5	-90.0		0.337
m_7-F(Bz), **12**[f]	oil	231.4	236.5	-99.6		0.337
m_5-COOEt(Bz), **13**	oil	254.4	260.8	-66.1		0.370
m_7-COOEt(Bz), **14**	63.6	264.0	271.6	-60.7		0.370
m_7-CF_3(Bz), **15**	51.3	267.7	273.4	-51.8		0.430
m_7-CN(Bz), **16**	94.9	225.0	230.5	-102.4		0.560
m_5-NO_2(Bz), **17**	94.1	242.7	248.0	-75.3		0.710
m_7-NO_2(Bz), **18**	103.4	230.4	236.7	-114.9		0.710

[a] Conditions: *v* = 10 °C/min from 0 to 300 °C. [b] Melting temperature ($T_{m(onset)}$). [c] Onset of polymerization of exotherm. [d] Peak maximum of polymerization exotherm. [e] Polymerization heat. [f] Non included in representation, Figure 3.

3.3 Hammett analysis of the effects of the substituents on the polymerization temperature ($T_{p(peak)}$) obtained by DSC.

Hammett equation has been used to get some insight on the benzoxazines polymerization mechanism. As it is well known, the Hammett equation is a linear free energy relationship that allows to quantify the electronic effects of the substituents on one particular reaction (Equation 1) [24]

Equation 1

$$log\left(\frac{k_R}{k_H}\right) = \rho \cdot \sigma$$

The rate constant (k_R or k_H), according to Arrhenius's law (Equation 2).

$$k(T) = A\ exp\left(-\frac{E_a}{RT}\right) \qquad \textbf{Equation 2}$$

From equation 1 and equation 2 the following proportionality can be obtained, Equation 3.

$$\frac{1}{T_R} - \frac{1}{T_H} \propto \rho \cdot \sigma \qquad \textbf{Equation 3}$$

Where T_R and T_H are the polymerization temperatures of substituted and unsubstituted benzoxazines, respectively. The parameter σ is a measure of the total polar effect exerted by substituent R with respect to H on a model reaction (ionization equilibrium of benzoic acids). Its value gives the direction and magnitude of the effect: a negative value indicates a prevailing electron-donor effect, while a positive value indicates an electron-withdrawing effect. The values are tabulated for the different substituents in different relative positions of the aromatic ring (σ_{para} and σ_{meta}) [23]. On the other hand, ρ is a measurement of the response of a particular reaction to the electronic effects (σ values). The sign of ρ indicates the development of charge in the rate determining step.

In Figure 3, a representation of $\frac{1}{T_R} - \frac{1}{T_H}$ vs. σ is shown. From there, apparent ρ values can be obtained.

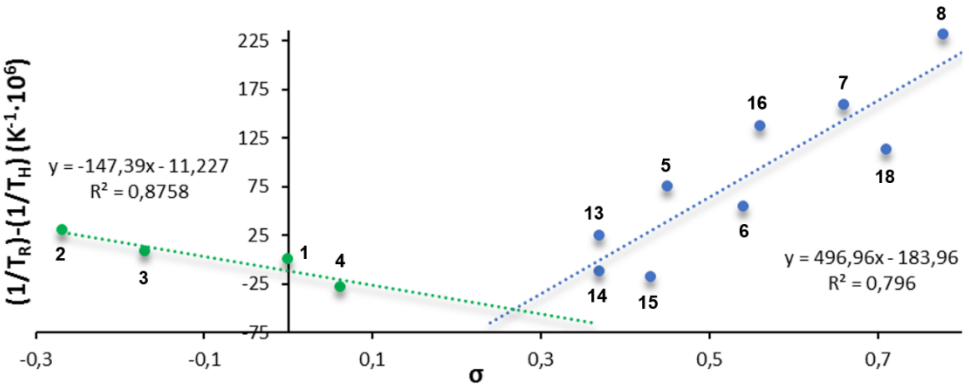


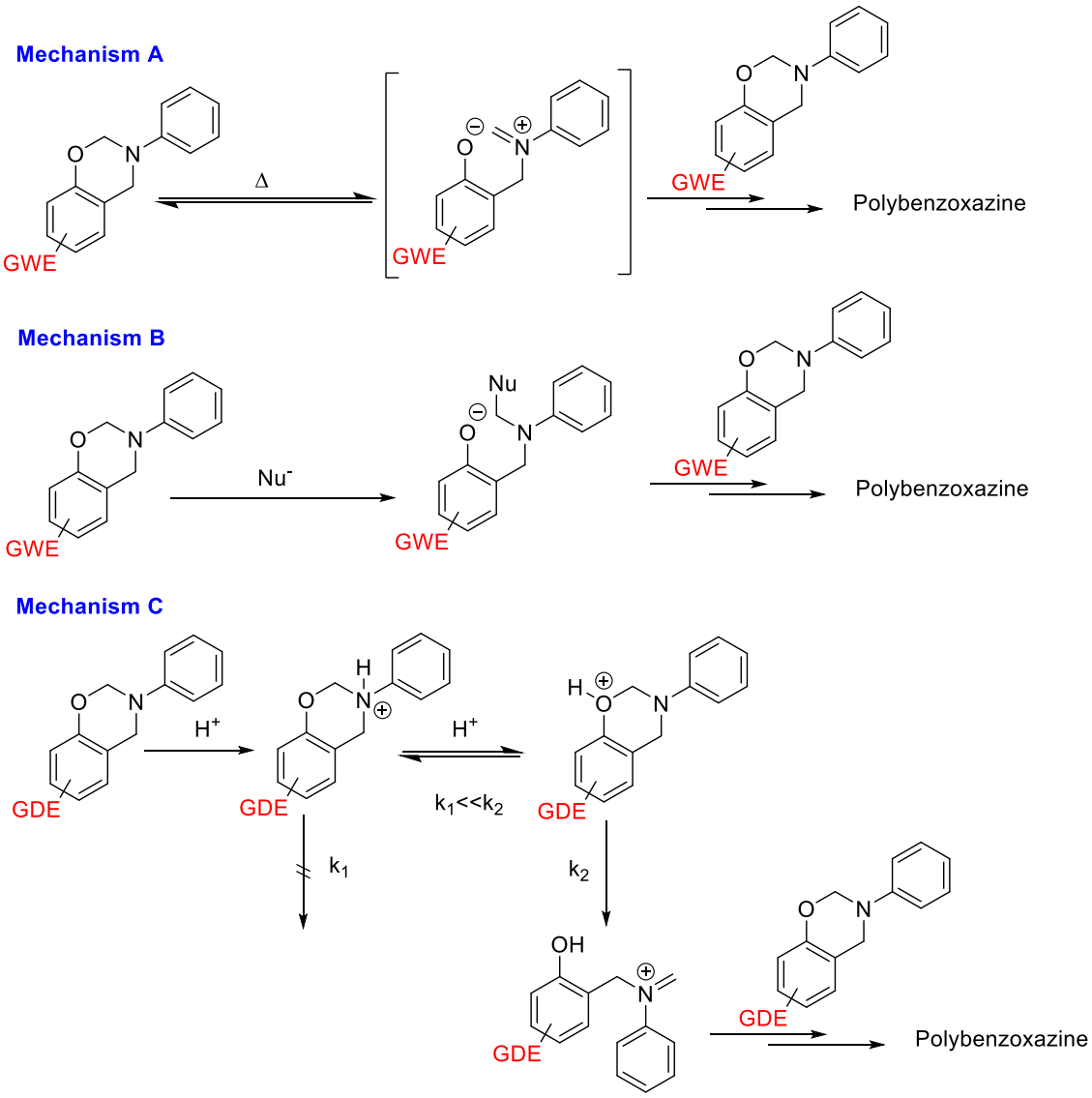
Figure 3. Hammett representation of $\frac{1}{T_R} - \frac{1}{T_H}$ vs. σ.

The nonlinear plot obtained is a composite of two straight lines, one with negative and the other with positive ρ value. This type of behavior is characteristic of a change in reaction mechanism of a reaction upon changing the substituents [24]. A negative ρ value (left side of the Figure 3) indicates a generation of positive charge in the transition state of the rate-limiting step or before. Thus, in this case the polymerization temperature is lower (higher rate) when electron-donating groups (EDG) are present. On the other hand, a positive ρ value (right side of the Figure 3) indicates a generation of negative charge in the transition state of the rate-limiting

step or before. Thus, the polymerization temperature is lower (higher rate) when electron-withdrawing groups (EWG) are present in the structure (aprox. $\sigma > 0.28$).

These results can be interpreted deeming a change in the mechanism of the initial and crucial ring opening step. Hence, electron-withdrawing groups (Table 2 and Figure 3) seem to induce a spontaneous or nucleophilically promoted ring opening of the oxazine (Scheme 2). In this mechanism, the high temperatures and the presence of electron-withdrawing groups would result in a ring opening step with concomitant generation of negative charge in the oxygen atom ($\rho > 0$, right straight line in Figure 3). If this process happens spontaneously, we will be in the presence of a zwitterionic chain growth mechanism (Mechanism A in Scheme 2). On the other hand, if this ring opening step takes place with the help of an external nucleophile (i.e. water), we will be in the presence of a nucleophilically initiated chain growth mechanism or step growth mechanism (Mechanism B in Scheme 2), depending on the existence, or not, of discrete long living intermediates. These mechanistic alternatives have been previously proposed but only in studies using catalysts and initiators [25]

On the other hand, when electron-donor groups are present in the alkoxyphenyl ring, the opposite behavior is observed (Figure 3 and Table 2). In these cases, a development of positive charge is observed before or in the rate determining step ($\rho < 0$). This behavior can be explained considering that in these cases the oxazine ring will be less prone to spontaneous opening (lower polarization of the O-C bond in the aminal [O-CH_2-N] structure). However, this fact is compensated by the higher basicity of the oxygen atom compared with benzoxazines with EWD substituents. The Hammett analysis in this case ($\rho < 0$), suggests that protonation happens in the oxygen atom before ring opening (Mechanism C in Scheme 2). Thus, we are here in the presence of the cationic ring opening polymerization chain mechanism, deemed in most of the publications on the topic as the standard mechanism for the polymerization of benzoxazines [17].



Scheme 2. Proposed mechanisms for the thermal polymerization of benzoxazines depending on the substituent in the alkoxyphenyl ring.

In Table 2, the values of polymerization enthalpies are also shown. It is difficult to take any useful information from them, since most are rather similar. However, there are three values over 100 kJ/mol, and all belong to compounds placed on the right side of the representation in Figure 3 (Mechanisms A or B, Scheme 2). Perhaps those high values could be associated to the participation of an external nucleophile on the ring opening step (Mechanism B). However, we have not elaborated on this hypothesis.

From the correlations shown in Figure 3, two very different behaviors of substituted benzoxazines appear depending on the electronic properties of the substituents. However, there is still a third group of compounds (benzoxazines **9-12**, Table 2). Those four benzoxazines are not included in the correlation due to their anomalous behavior. Deeming their σ values,

they should be the borderline cases; however, they show an anomalous rather low polymerization temperature (faster polymerization than expected). From data gathered in Table 3 it comes that those four benzoxazines share the feature of producing rather acidic phenols while the polymer is forming. The most probable interpretation for their anomalous behavior would be that in those cases we are in the presence of an auto-catalyzed polymerization process through Mechanism C (Scheme 2), the cationic ring opening chain polymerization. Very probably this autocatalysis is present in all the benzoxazines that follow Mechanism C (Scheme 2), producing a flattening of the graphic and a reduced ρ value, but it becomes more extreme in the 4 borderline cases (m_7-OMe, m_5-OMe, m_7-F, m_5-F, Table 3).This effect could justify the low temperatures observed for previously reported bifunctional benzoxazine monomers based on resorcinol previously reported by some of us [27]. For benzoxazines following mechanisms A and **B**, the autocatalytic effect is not be observed although the phenols are quite acidic (pKa for HOPh-*p*-NO_2 ~ 7.9), because the ring opening process is spontaneous.

Table 3.
Polymerization temperatures, $T_{p(peak)}$, of different benzoxazines and pKa values of the corresponding phenols (benzoxazines that show anomalous behavior shaded in the table)

Entry	Benzoxazine	$T_{p(peak)}$	σ_{para} or σ_{meta}	pKa (phenol) [26]
1	Bz, **1**	266.7	0	9.98
2	*p*-OMe, **2**	259.3	-0.268	10.21
3	*p*-F, **4**	276.2	0.062	9.95
4	m_5-OMe, **9**	254.9	0.115	9.65
5	m_7-OMe, **10**	231.1	0.115	9.65
6	m_5-F, **11**	230.5	0.337	9.28
7	m_7-F, **12**	236.5	0.337	9.28

4. Conclusions

Thermal analysis of the polymerization of differently substituted 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazines by DSC shows an apparent random behavior. However, analysis of the data with the help of the Hammett equation shows some clear trends that can be summarized as follows: 1) Both electron-withdrawing groups and electron-donor groups accelerate the polymerization process. 2) The Hammett plot shows an upward bended shape that indicates a change of mechanism. 3) Electron-withdrawing groups seem to promote a spontaneous (or nucleophilically assisted) ring opening of the oxazine ring. 4) With electron-donor substituents the opening of the benzoxazine ring seems to happen through previous protonation. 5) A few compounds, placed in the mechanistic borderline, don't fit in the Hammett representation indicating that another effect must be taken into account, very probably an autocatalysis effect due to the acidity of the phenols formed in the process of polymerization. For this work eighteen benzoxazines have been studied, thirteen of them were new compounds that have been

completely characterized. Several of them have substituents in the *meta* position of the phenolic ring. This type of benzoxazines has been very scarcely studied in the literature.

Considering that polymerization temperature is a key element that prevents a wider commercial use of thermosetting benzoxazine resins, a proper knowledge of the different factors that affect the polymerization temperature seems crucial. Our work provides some mechanistic clues for the previous apparent unpredictable effects of the substituents, making in principle now possible to design thermosetting benzoxazine resins, that with the help of the appropriate catalysts and initiators [18] will cure at significantly lower temperatures.

Acknowledgments

This work was financially supported by the Spanish Government (CTQ2015-65439-R, CTQ2014-51912-REDC). We also acknowledge support from the Generalitat de Catalunya (2017SGR1105). We are grateful to H. Ishida and P. Froimowicz for helpful discussions.

Data availability

The raw data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)]. The processed data required to reproduce these findings are available to download from [INSERT PERMANENT WEB LINK(s)].

References

[1] D. Ratra, *Handbook of Thermoset Resins.* Smithers Rapra: Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK, 2009.

[2] M. Arslan, Y. Y. Kiskan, *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons: Hoboken, NJ, USA, 2015; pp 1-23.

[3] N. N. Ghosh, B. Kiskan, Y. Yagci, Prog. Polym. Sci. 32 (2007) 1344-1391.

[4] T. Takeichi, T. Kawauchi, T. Agag, Polym. J. 40 (2008) 1121-1131.

[5] H. Ishida, T. Agag, *Handbook of benzoxazine resins*. Elsevier: Amsterdam; Boston, 2011.

[6] M. A. Espinosa, V. Cádiz, M. Galià, J. Appl. Polym. Sci. 90 (2003) 470-481.

[7] H. D. Kim, H. Ishida, J. Phys. Chem. A. 106 (2002) 3271-3280.

[8] H. D. Kim, H. Ishida, Macromolecules 36 (2003) 8320-8329.

[9] S. Wirasate, S. Dhumrongvaraporn, D. J. Allen, H. Ishida, J. Appl. Polym. Sci. 70 (1998) 1299-1306.

[10] T. Takeichi, T. Agag, High Perform. Polym. 18 (2006) 777-797.

[11] Y. Yagci, B. Kiskan, N. N. Ghosh, J. Polym. Sci., Part A: Polym. Chem. 47 *(2009)* 5565-5576.

[12] X. Liu, Y. Gu, Sci. China, Ser. B. 44 (2001) 552−560.

[13] Y. X. Wang, H. Ishida, *Macromolecules* 33 (2000) 2839-2847.

[14] A. Sudo, L.-C. Du, S. Hirayama, T. Endo, J. Polym. Sci., Part A: Polym. Chem. 48 (2010) 2777-2782.

[15] W. M. Wang, R. J. Jeng, C. H. Lin, *Macromolecules* 48 (2015) 530-535.

[16] Y. Prostata, P. J. Coelho, Dyes and Pigments 98 (2013) 93-99.

[17] C. Liu, D. Shen, R. M. Sebastian, J. Marquet, R. Schönfeld, Macromolecules 44 (2011) 4616-4622, and references therein.

[18] C. Liu, D. Shen, R. M. Sebastián, J. Marquet, R. Schönfeld, Polymer 54 (2013) 2873-2878.

[19] G. P. Moloney, D. J. Craik, M. G. Iskander, J. Pharm. Sci. 81 (1992) 692-697.

[20] R. Andreu, J. A. Reina, J. C. Ronda, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 3353-3366.

[21] Z. Brunovska, J. P. Liu, H. Ishida, Macromol. Chem. Phys. 200 (1999) 1745-1752.

[22] H. Qi, H. Ren, G. Pan, Y. Zhuang, F. Huang, L. Du, Polym. Adv. Technol. 20 (2009) 268-272.

[23] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 91 (1991) 165-195.

[24] E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*. University Physical Books: United States of America, 2005; pp 421-488.

[25] H. Y. Wang, R. Zhu, P. Yang, Y. Gu, Polym. Chem. 7 (2016) 860-866.

[26] M. D. Liptak, K. C. Gross, P. G. Seybold, S. Feldgus, S. F. Shields, J. Am. Chem. Soc. 124 (2002) 6421–6427.

[27] H. Schäfer, A. Arnebold, J. Stelten, J. Marquet, R. M. Sebastián, A. Hartwig, K. Koschek,. J. Polym. Sci. Part A: Polym. Chem., 54 (2016) 1243-1251.