



A new boronic acid and boronate esters containing polymer groups: Synthesis and investigation of their spectroscopic properties

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ARTICLE INFO

Article history:

Received March 25, 2022

Accepted July 10, 2022

Available online September 30, 2022

Research Article

DOI: 10.30728/boron.1093323

Keywords:

Boronate ester
Boron containing polymer
Spectroscopy
Synthesis

ABSTRACT

In this study, new boronic acid and boronate ester-based polymers were synthesized by the reaction of methoxypolyethylene glycol amine and 4-formylphenylboronic acid for the first time. As a result of the dehydration reaction of the new boronic acid-based polymer with various diols, the boronate ester-based polymers were obtained. The structures of these polymers were elucidated by NMR (¹H, ¹³C and ¹¹B), LC-MS/MS spectrometer, FT-IR, UV-Vis absorbance spectroscopy and fluorescence spectroscopy. The FT-IR spectra results showed that characteristic stretching and bending vibrations peaks belonging to the functional groups are in harmony with the proposed structures. The ¹¹B NMR broad signal were observed in 29.72-28.60 ppm due to the similar chemical environment for the boron center, indicating that they are in trigonal structure. It was observed that the emission spectra of the boronate ester-based polymers have a bigger redshift, compared to boronic acid-based polymers.

1. Introduction

Boron-containing chemicals in various forms have recently received increasing attention in organic, material, polymers, catalysis, and pharmaceuticals chemistry thanks to their rich and multifaceted reactivity patterns that possess unique and attractive properties. [1-3]. This has led many scientists to investigate how boron-containing chemical compounds can be synthesized. Boron compounds have a tremendous effect, especially in the synthesis of new organic compounds [4]. Structurally, three-coordinated boron compounds have an empty p-orbital, are electron-deficient by nature, and therefore are a strong electron pair acceptor. Boronic acids, one of the important compounds of boron chemistry, constitute an important part of synthetic intermediates due to their chemical decisiveness and Lewis acid properties, and have been in the literature since 1860 [5]. Boronic acids contain trivalent boron atoms with the binding of two hydroxyl groups to an alkyl or aryl substitution [6]. Recently, studies involving the interactions between boronate esters, different boronic acids and diol-containing compounds, which are dec of the precursors of compounds containing boronic acid, have gained more and more attention every day. Boron esters are synthesized as a result of dehydration of boronic acid with diols. Since ester formation can be achieved with high efficiency, multipurpose boronic acids and different diol derivatives have been used to prepare various structures [7,8].

Also, extended stability obtained under various alcohol and water conditions provides a platform for the boron-containing chemicals to sustain and conformationally survive during synthesis.

Recently, a number of issues have been addressed, including mixing polymers containing boronic acid with diols or mixing small molecules with multifunctional polymers [9,10]. In the family of organoboron polymers, it has been proven that polymers containing boronic acid have several potential areas of application due to their unique reactivity and stimuli sensitive behavior. [11]. The boron-containing polymers are generally advantageous over free boronic acids or boronate esters due to their cyclic rigidity and enhanced solubility. Boron-containing polymers could also be potential chemical reagents to develop new materials due to their high thermodynamic and thermal stability [12]. In addition, these polymers have a variety of biomedical applications, such as optical, electronic, and sensory applications, self-regulating drug delivery systems, and the treatment of bone tumors [13-16]. Therefore, research on the synthesis and properties of well-defined new boronic acid and boronate ester containing polymer groups is an emerging field that has attracted the attention of chemists and materials scientists. Until this time, boron-containing polymers could not be synthesized sufficiently because it was deemed that the synthesis of boron-containing polymers is difficult and that these compounds are not stable enough.

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Nowadays, boron-containing polymers of high molecular weight can be obtained readily through controlled/living polymerization techniques such as ring-opening polymerization (ROP) or other polymerization techniques and many of these new compounds are perfectly stable for extended periods under suitable or even harsh conditions [14]. Therefore, choosing functional polymers containing boron groups will remove some restrictions in boron chemistry and will be an essential research topic. For this reason, we investigated the synthesis and spectroscopic properties of the novel boronic acid and boronate ester containing polymer groups. In this study, the synthesis of a new boronic acid and boronate ester-based polymers with trigonal geometry and their structure was elucidated using NMR (^1H , ^{13}C , and ^{11}B), FT-IR, UV-Vis absorbance, fluorescence, and LC-MS/MS spectrometer.

2. Materials and Methods

2.1. General Remarks

The solvents and chemicals were purchased from commercial firms such as Merck or Sigma and used as received. The toluene and tetrahydrofuran (THF) solvents were dried by distilling over the proper drying agents under N_2 before use. All chemical reactions were carried out under reflux at room temperature (RT). FT-IR data were obtained by ATR technique in wavenumbers from 4000 to 400 cm^{-1} on a Perkin-Elmer Two-UATR-FT spectrometer. The UV-Vis spectra were recorded on a Perkin-Elmer model Lambda 25 UV spectrometer at a range of 200-1100 nm. A Perkin-Elmer model LS-55 spectrometer was used to record Fluorescence spectra in a 1 cm quartz cuvettes spectrophotometer at room temperature and in ethanol solvent. The ^1H , ^{13}C , and ^{11}B NMR spectra were recorded using an Agilent Technologies instrument operating at 400 MHz (^1H), 100 MHz (^{13}C), or 192.5 MHz (^{11}B) in deuterated chloroform (CDCl_3). Chemical shifts (δ) were expressed in ppm downfield from tetramethylsilane (TMS) as an internal reference and coupling constants (J values) are given in Hertz. LC-MS/MS spectra were performed using the electrospray positive mode (ESI^+) technique on a Shimadzu LCMS-8030 series spectrometer system and samples were diluted ($\sim 1:1000$) in methanol.

2.2. Synthesis

2.2.1. Synthesis of new boronic acid-based polymer (1)

Methoxypolyethylene glycol amine (mPEG-NH₂) (2.0 g, 2.66 mmol) and 4-formylphenylboronic acid (4-FPBA) (0.4 g, 2.66 mmol) were placed in a 50 mL round-bottomed flask containing 35 mL ethanol with a ratio of 1:1. After the reaction was stirred at room conditions for 1 h, 1-2 drops of acetic acid were added as organic catalyst. Followed by, the round-bottomed flask was connected to a refrigerant assembly and the reaction was refluxed for 18 h. Afterwards, the reaction

was cooled to RT and the solvent was rotary evaporated and a yellow oily product was obtained. The product was recrystallized twice with a $\text{CHCl}_3/\text{C}_2\text{H}_5\text{OH}$ (1/2) mixture, but it could not be obtained in crystalline form.

Polymer (1): Color: yellow. F.W: 881.92 g/mol. FT-IR (ATR, $\nu_{\text{max}}-\text{cm}^{-1}$): 3591-3107 $\nu(\text{O-H}\dots\text{O})$, 3041 $\nu(\text{Ar-CH})$, 2989-2814 $\nu(\text{Aliph-CH})$, 1664 $\nu(\text{C=N})$, 1566-1503 $\nu(\text{C=C})$, 1351 $\nu(\text{B-O})$, 1102 $\nu(\text{C-O})$ and 836 $\nu(\text{B-C})$. LC-MS/MS (Scan ES^+): $m/z = 881.92$ [M]⁺ and 882.93 [$\text{M}+\text{H}$]⁺. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 9.98 (s, 2H, -OH), 8.25 (s, 1H, -HC=N), 7.99 (d, 2H, $J = 7.2$ Hz, Ar-CH), 7.11 (d, 2H, $J = 7.6$ Hz, Ar-CH), 3.72 (s, 2H, N-CH₂), 3.59 (s, 4H, [O-CH₂-CH₂]_n), 3.33 (s, 2H O-CH₂), and 2.29 (s, 3H, -CH₃). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 169.23 (CH=N), 139.81, 134.81, 128.64, and 125.94 (Ar-CH), 76.71, 71.80, 70.36, 69.89 and 58.93 (Aliph-CH). UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 206, 254 and 295 ($\text{C}_2\text{H}_5\text{OH}$).

2.2.2. Synthesis of new boronate ester-based polymers (2-5)

The boronate ester-based polymers (2-5) were added by reacting the corresponding 4-*tert*-butylcatechol (0.07 g, 0.45 mmol) for compound (2), 4-methylcatechol (0.06 g, 0.45 mmol) for compound (3), 3,5-Di-*tert*-butylcatechol (0.10 g, 0.45 mmol) for compound (4), and 3,5-Diisopropylcatechol (0.09 g, 0.45 mmol) for compound (5) with new boronic acid-based polymer (1) (0.4 g, 0.45 mmol) in 60 mL of dry toluene/THF at room temperature. Next, the reactions were stirred for 18 h at reflux temperature using a Dean-Stark condenser for the formation of new boronate ester-based polymers (2-5). Then, the excess solvent was evaporated under low pressure and the resulting products were purified by recrystallization technique from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ (1/3) after washing with *n*-hexane. But, all boronate ester-based polymers (2-5) could not be obtained in crystalline form.

Polymer (2): Color: brown, F.W: 1012.10 g/mol. FT-IR (ATR, $\nu_{\text{max}}-\text{cm}^{-1}$): 3066 and 3037 $\nu(\text{Ar-CH})$, 2956-2871 $\nu(\text{Aliph-CH})$, 1695 $\nu(\text{C=N})$, 1602-1520 $\nu(\text{C=C})$, 1361 $\nu(\text{B-O})$, 1094 $\nu(\text{C-O})$ and 825 $\nu(\text{B-C})$. LC-MS/MS (Scan ES^+): $m/z = 1012.10$ [M]⁺ and 1013.10 [$\text{M}+\text{H}$]⁺. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 8.16 (s, 1H, -HC=N), 7.79-7.72 (dd, 2H, $J = 7.6$ Hz, Ar-CH), 7.13 (d, 2H, $J = 7.6$ Hz, Ar-CH), 6.97 (d, 1H, $J = 8.4$ Hz, Ar-CH), 6.88 (s, 1H, Ar-CH), 6.72 (d, 1H, $J = 7.0$ Hz, Ar-CH), 3.70 (s, 2H, N-CH₂), 3.54 (s, 4H, [O-CH₂-CH₂]_n), 3.34 (s, 2H O-CH₂), 2.29 (s, 3H, -CH₃), and 1.21 (s, 9H C-(CH₃)₃). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 162.37 (CH=N), 145.90, 140.08, 134.77, 132.16, 128.98, 128.75, 128.55, 125.91, 123.21, 119.34 and 116.94 (Ar-CH), 71.80, 70.31, 69.98, 69.96, 58.94, 46.03, 31.72 and 31.49 (Aliph-CH). ^{11}B NMR (CDCl_3 , 192.5 MHz, 23°C, δ ppm): 28.88. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 205, 259, and 285 ($\text{C}_2\text{H}_5\text{OH}$).

Polymer (3): Color: brown. F.W: 970.02 g/mol. FT-IR (ATR, $\nu_{\text{max}}-\text{cm}^{-1}$): 3072 and 3030 $\nu(\text{Ar-CH})$, 2952-2824

$\nu(\text{Aliph-CH})$, 1687 $\nu(\text{C=N})$, 1598-1497 $\nu(\text{C=C})$, 1356 $\nu(\text{B-O})$, 1099 $\nu(\text{C-O})$, and 822 $\nu(\text{B-C})$. LC-MS/MS (Scan ES+): $m/z = 970.02 [\text{M}]^+$ and $971.01 [\text{M+H}]^+$. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 8.03 (s, 1H, $-\text{HC=N}$), 7.78 (d, 2H, $J = 6.0$ Hz, Ar-CH), 7.11 (d, 2H, $J = 7.6$ Hz, Ar-CH), 6.68-6.46 (m, 3H, Ar-CH), 3.68 (s, 2H, N-CH₂), 3.53 (s, 4H, [O-CH₂-CH₂]_n), 3.31 (s, 2H O-CH₂), 2.31 (s, 3H, -CH₃) and 2.11 (s, 3H Ar-CH₃). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 161.16 (HC=N), 143.9, 134.94, 134.05, 132.47, 132.07, 128.63, 128.40, 125.96, 123.23, 120.30 and 111.34 (Ar-CH), 71.51, 70.10, 69.84, 66.70, 58.88 and 21.34 (Aliph-CH). ^{11}B NMR (CDCl_3 , 192.5 MHz, 23°C, δ ppm): 28.60. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 206, 257 and 290 ($\text{C}_2\text{H}_5\text{OH}$).

Polymer (4): Color: brown. F.W: 1068.20 g/mol. FT-IR (ATR, $\nu_{\text{max}}-\text{cm}^{-1}$): 3075 and 3022 $\nu(\text{Ar-CH})$, 2956-2865 $\nu(\text{Aliph-CH})$, 1687 $\nu(\text{C=N})$, 1594-1486 $\nu(\text{C=C})$, 1357 $\nu(\text{B-O})$, 1101 $\nu(\text{C-O})$ and 821 $\nu(\text{B-C})$. LC-MS/MS (Scan ES+): $m/z = 1068.20 [\text{M}]^+$ and $1069.20 [\text{M+H}]^+$. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 8.10 (s, 1H, $-\text{HC=N}$), 7.77 (d, 2H, $J = 7.6$ Hz, Ar-CH), 7.10 (d, 2H, $J = 8.0$ Hz, Ar-CH), 6.55 (s, 1H, Ar-CH), 6.54 (s, 1H, Ar-CH), 3.70 (s, 2H, N-CH₂), 3.56 (s, 4H, [O-CH₂-CH₂]_n), 3.33 (s, 2H O-CH₂), 2.32 (s, 3H, -CH₃) and 1.48 (s, 9H C-(CH₃)₃) and 1.33 (s, 9H C-(CH₃)₃). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 157.42 (HC=N), 143.16, 135.35, 134.59, 134.01, 132.32, 128.83, 123.22, 120.06, 111.59 and 107.03 (Ar-CH), 71.62, 69.98, 58.92, 31.87, 31.57, 29.77 and 29.69 (Aliph-CH). ^{11}B NMR (CDCl_3 , 192.5 MHz, 23°C, δ ppm): 28.87. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 207, 260, and 293 ($\text{C}_2\text{H}_5\text{OH}$).

Polymer (5): Color: brown. F.W: 1040.15 g/mol. FT-IR (ATR, $\nu_{\text{max}}-\text{cm}^{-1}$): 3068 and 3024 $\nu(\text{Ar-CH})$, 2956-2815 $\nu(\text{Aliph-CH})$, 1694 $\nu(\text{C=N})$, 1595-1508 $\nu(\text{C=C})$, 1358 $\nu(\text{B-O})$, 1100 $\nu(\text{C-O})$, and 832 $\nu(\text{B-C})$. LC-MS/MS (Scan ES+): $m/z = 1040.15 [\text{M}]^+$ and $1041.15 [\text{M+H}]^+$. $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 8.20 (s, 1H, $-\text{HC=N}$), 7.94 (s, 1H, Ar-CH), 7.76 (d, 2H, $J = 8.0$ Hz, Ar-CH), 7.12 (d, 2H, $J = 7.6$ Hz, Ar-CH), 6.82 (s, 1H, Ar-CH), 3.78 (s, 2H, N-CH₂), 3.60 (s, 4H, [O-CH₂-CH₂]_n), 3.35 (s, 2H O-CH₂), 3.06 and 2.92 (s, 2H, -CH(CH₃)₂), 2.31 (s, 3H, -CH₃) 1.35 (d, 6H, $J = 6.4$ Hz, CH-(CH₂)₂) and 1.24 (d, 6H, $J = 7.2$ Hz, CH-(CH₃)₂). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 161.82 (HC=N), 141.28, 135.35, 135.16, 132.07, 128.97, 128.53, 125.99, 118.59, 112.78 and 107.61 (Ar-CH), 71.82, 70.36, 69.98, 69.66, 58.95, 34.28, 29.39, 24.23 and 22.56 (Aliph-CH). ^{11}B NMR (CDCl_3 , 192.5 MHz, 23°C, δ ppm): 29.72. UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 205, 258 and 287 ($\text{C}_2\text{H}_5\text{OH}$).

3. Results and Discussion

3.1. Synthesis and Characterization

Synthesis of new boronic acid-based polymers (**1**) was achieved as a result of the condensation reaction of 4-formylphenylboronic acid and methoxypolyethylene glycol amine. The condensation reaction was carried out using ethanol as the solvent at the reflux

temperature, and the targeted boronic acid-based polymers was obtained (Figure 1). The boronic acid-based polymers (**1**) were then transformed into the boronate esters-based polymers (**2-5**) by functionalization with catechol utilizing the predetermined procedure [17].

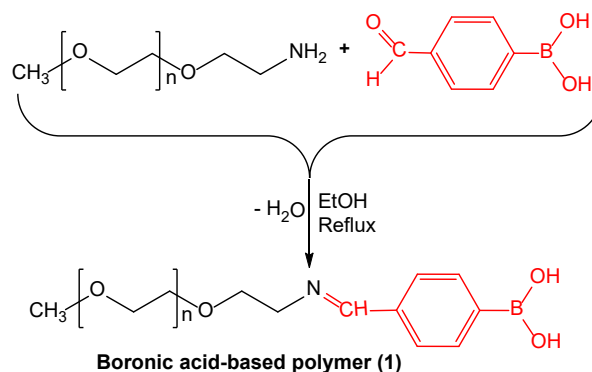


Figure 1. The structure of the proposed boronic acid-based polymer (**1**).

The boronate esters-based polymers (**2-5**) were obtained by mixing them under reflux for 18 hours at RT (Figure 2). Formation of the boronic acid-based polymers (**1**) and boronate ester-based polymers (**2-5**) was confirmed by NMR (^1H , ^{13}C , and ^{11}B) spectra, IR spectra, UV-Vis absorbance spectra, fluorescence spectra, and LC-MS/MS spectrometry techniques.

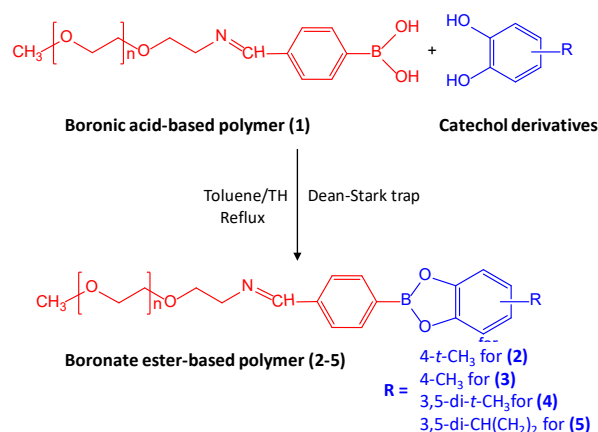


Figure 2. The structure of the proposed boronate ester-based polymers (**2-5**).

3.2. Spectroscopic Properties

FT-IR measurements were used to elucidate the structures of boronic acid-based polymer (**1**) and boronate ester-based polymers (**2-5**). When the FT-IR data of the entire polymer (**1-5**) were examined, they showed similar stretching vibrations to each other, this similarity is probably due to the similar chemical environment of the boron center. The characteristic band that indicates the boronic acid-based polymer (**1**) is formed in the FT-IR spectrum can be assigned the imine $\nu(\text{C=N})$ stretching band, which comes out at 1664 cm^{-1} [18,19]. The

typical hydroxyl group band of the 4-FPBA backbone is clearly visible at $3591\text{-}3107\text{ cm}^{-1}$ in the FT-IR spectrum as shown in the experimental part. The formation of boronate ester-based polymers (**2-5**) was achieved by the disappearance of $\nu(\text{-OH})$ vibrations after esterification between the boronic acid-based polymer (**1**) and diols by dehydration by heating at reflux with a Dean Stark trap. In the spectrum of the obtained boronate ester-based polymers (**2-5**), the disappearance of $\nu(\text{-OH})$ vibrations after esterification and the formation of a new peak in the range of $1361\text{-}1356\text{ cm}^{-1}$ revealed the presence of $\nu(\text{B-O})$ groups in the polymer chain [7,20-22]. However, in the FT-IR spectra of all polymers (**1-5**) it was observed it appears that characteristic peaks belonging to the aromatic and aliphatic $\nu(\text{C-H})$ groups in intervals $3072\text{-}3024$ and $2989\text{-}2814\text{ cm}^{-1}$, respectively, and the synthesized polymers are in harmony with the proposed structures.

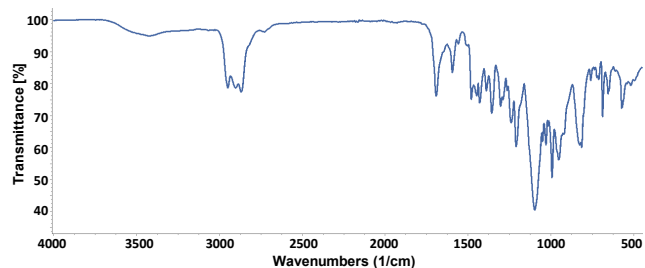


Figure 3. FT-IR spectra of boronate ester-based polymer (**4**).

Since all polymers (**1-5**) carry an aromatic ring, an imine (CH=N) group, or an empty p orbital of a boron atom, UV-Vis measurements were recorded to confirm that these groups were successfully inserted into the chain ends. All the UV-Vis measurements of synthesized boronic acid-based polymer (**1**) and the boronate ester-based polymers (**2-5**) were recorded in ethanol solvent at room temperature and the results are presented in the experimental part and Figure 4a. When the UV-Vis absorption spectra of boronic acid-based polymer (**1**) and corresponding boronate ester-based polymers (**2-5**) are examined, it was shown that λ_{max} value was between $205\text{-}295\text{ nm}$. According to the results obtained, these absorption bands can be attributed to the $\pi \rightarrow \pi^*$ transitions ($205\text{-}207\text{ nm}$) in the aromatic ring and $n \rightarrow \pi^*$ transition ($254\text{-}260\text{ nm}$) of nonbonded electrons of the imine (CH=N) group or π -to-vacant B p-orbital transition ($285\text{-}295\text{ nm}$) [20,23]. Fluorescence spectrum values, emission spectra obtained for boronic acid-based polymer (**1**) and boronate ester-based polymers (**2-5**) in ethyl alcohol are given in Figure 4b. Fluorescence spectrum revealed that the emission values of boronic acid-based polymer (**1**) were observed at 392 and 438 nm (λ_{em}) when the emission spectrum was excited at 350 nm (λ_{ex}). In the same way, the emission value (λ_{em}) observed when the boronate ester-based polymers (**2-5**) is excited at 327 nm (λ_{ex}) is in the range of 363 and 515 nm .

The boronate ester-based polymers (**2-5**) obtained as a result of bond formation between boronic acid-based

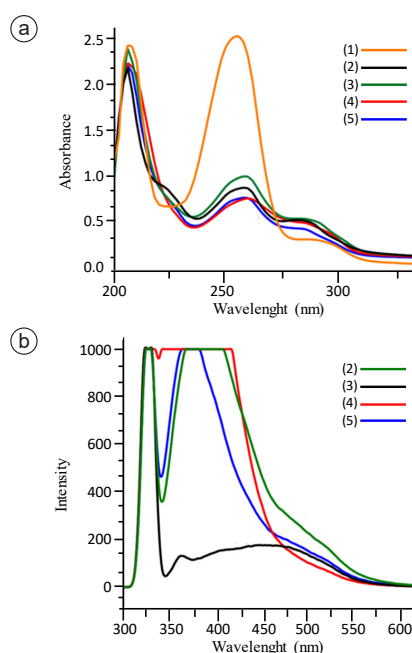


Figure 4. UV-Vis and fluorescence spectra spectra of the all boron polymers (**1-5**) in $\text{C}_2\text{H}_5\text{OH}$.

polymer (**1**) and 1,2-diol groups were investigated by NMR. The solution of the polymers obtained by this process in CDCl_3 was prepared and determined by ^1H , ^{13}C , and ^{11}B NMR technique (Figure 5). The specific difference between boronic acid-based polymer (**1**) and corresponding catechol functionalized boronate ester-based polymers (**2-5**) ^1H NMR spectrum, new chemical shift values originating from catechol group were detected in NMR time scale at RT. The formation of the boronic acid-based polymer (**1**) was proven by conversion the (C=O) bands into imine (C=N) groups of both ^1H and ^{13}C NMR as a result of the reaction of 4-FPBA with the methoxypolyethylene glycol amine. As a result of the formation of the boronic acid-based polymer (**1**), it was observed that the chemical shift of the carbonyl group in the 4-formylphenylboronic acid was lost due to the formation of the imine group (HC=N) at 8.25 ppm [19]. On the other hand, proton signals in the range of $\delta=9.98$ and $3.72\text{-}2.29\text{ ppm}$ corresponding to Ar-B(OH)_2 and the other aliphatic group, confirm that the structure was formed respectively. The ^{13}C NMR spectrum of boronic acid-based polymer (**1**) showed a characteristic signal due to the carbon of the imine group (CH=N) in $\delta=169.23\text{ ppm}$ and which confirmed the formation of the boronic acid-based polymer (**1**) [19,24]. Boronic acid-based polymer (**1**) ^{13}C NMR spectra, for 4-formylphenylboronic acid and methoxyglycolamine all aromatic and aliphatic carbons signal appeared in the range of $139.81\text{-}125.94$ (Ar-CH) and $76.71\text{-}58.93\text{ ppm}$ (Alif-CH), respectively. As a result, it seems that structure of the synthesized polymer was in agreement with the proposed structure. In the ^1H NMR spectra of catechol functionalized boronate ester-based polymers (**2-5**), the absence of 1,2-diol proton signal indicates the formation of B-O bond as a result of the reaction. Furthermore, the presence of new Ar-CH chemical resonances of singlet, doublet, or multiple signals observed at around $\delta=7.94\text{-}6.46$

ppm originating from different catechol groups indicates the formation of boronate ester-based polymers (**2-5**) as expected. The chemical shift values of aliphatic protons in the catechol groups appeared in the range of 3.06 to 1.21 ppm as singlet or doublet [20]. In addition, in boronate ester-based polymers (**2-5**), chemical shifts originating from other groups are present in their expected positions and were found to be in good agreement with the proposed structures. ^{13}C NMR spectra of trigonal planar boronate ester-based polymers (**2-5**) showed resonances in the expected region. In the ^{13}C NMR spectra of boronate ester-based polymers (**2-5**), signals for all aromatic carbons of different catechol and boronic acid-based polymer (**1**) appeared in the range of 145.90-107.03 ppm and also aliphatic carbon resonances were observed in the range of 71.82-21.34 ppm. Analysis of ^{11}B NMR results was also performed, as it gives a strong indication that all boronate ester-based polymers (**2-5**) are trigonal planar in the ^{11}B NMR spectrum (Figure 5). In

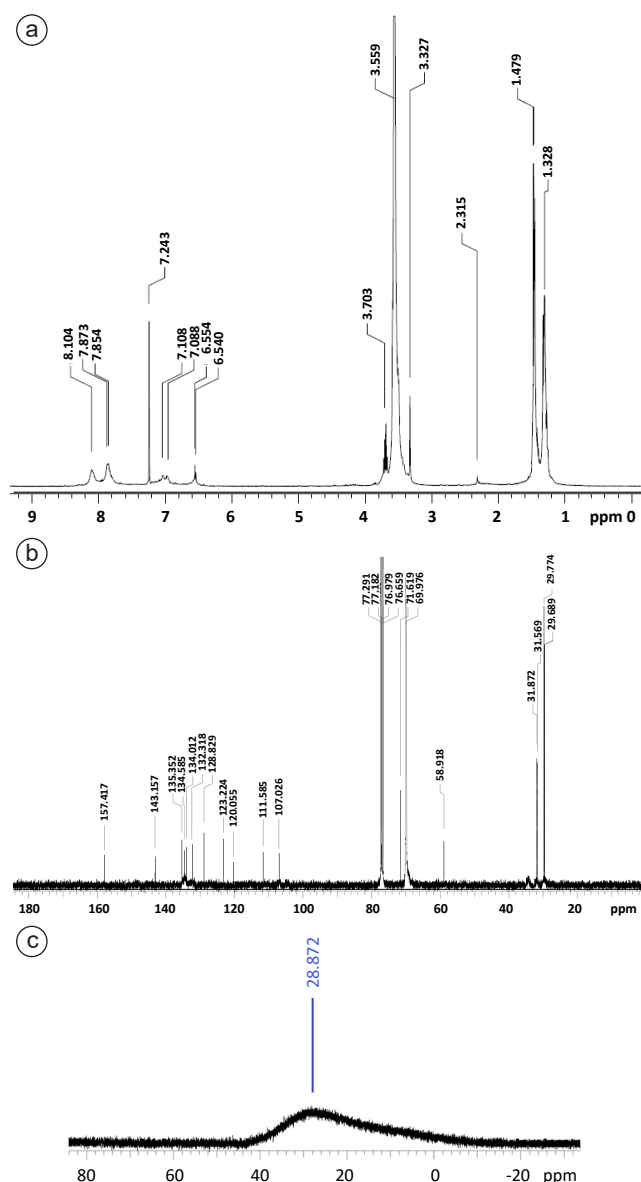


Figure 5. ^1H , ^{13}C and ^{11}B NMR spectra of the boronate ester-based polymers (**4**) in CDCl_3 .

the ^{11}B NMR spectrum of boronate ester-based polymers (**2-5**) in CDCl_3 , the only broad signal in the range of 29.72-28.60 ppm, due to the similar chemical environment for the boron center, indicates that they are in trigonal structure [25].

Analysis of the LC-MS/MS spectra recorded after the reaction of the boronic acid-based polymer (**1**) with the different catechol group shows that the proposed structures for all polymers (**1-5**) are formed (Figure 6). The presence of all synthesized polymers was also proved by LC-MS/MS analysis in accordance with the data showing molecular $[\text{M}]^+$ and $[\text{M}+1]^+$ ions, since the natural boron atom has two isotopes, respectively. In the LC-MS/MS spectra, molecular ion peaks of boronic acid-based polymer (**1**) and boronate ester-based polymers (**2-5**) were found at $m/z = 881.92 [\text{M}]^+$ and $882.93 [\text{M}+\text{H}]^+$ for (**1**), at $m/z 1012.10 [\text{M}]^+$ and $1013.10 [\text{M}+\text{H}]^+$ for (**2**), at $m/z 970.02 [\text{M}]^+$ and $971.01 [\text{M}+\text{H}]^+$ for (**3**), at $m/z 1068.20 [\text{M}]^+$ and $1069.20 [\text{M}+\text{H}]^+$ for (**4**), and at $m/z 1040.15 [\text{M}]^+$ and $1041.15 [\text{M}+\text{H}]^+$ for (**5**), respectively.

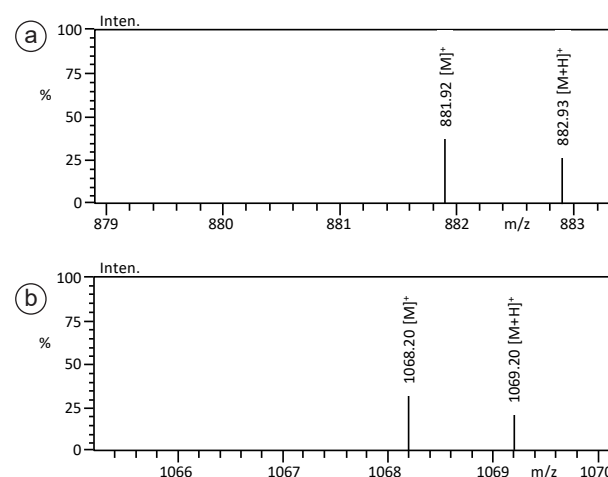


Figure 6. LC-MS/MS spectrum of the boronic acid-based polymer (**1**) (a) and the boronic acid-based polymer (**4**) (b).

4. Conclusions

In this study, preparation and spectroscopic properties of boronate ester-based polymers (**2-5**) functionalized with different catechol derivatives produced from a boronic acid-based polymer (**1**). Structures of the obtained products were examined with NMR (^1H , ^{13}C , and ^{11}B), LC-MS/MS spectrometer, FT-IR, UV-Vis absorbance spectroscopy, and fluorescence spectroscopy. This paper shows that boronic acid and boronate ester-based polymers can be conveniently synthesized and indicates that they are in trigonal structure. These boron polymers, whose structures are explained in detail, can have the potential to be used in different application areas in the future.

Acknowledgement

This work was supported by the Research Fund of Harran University (HUBAP).

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