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- + Control of the reaction direction in the polycondensation process of the pyrocatechol phenyl borate with paraformaldehyde by the solvent used;
- + Thermal stability and thermo oxidative destruction properties of new type of oligomers;

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# Pyrocatechol borates: synthesis, reaction with formaldehyde, and solvent effect on polycondensation process

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# ABSTRACT

Pyrocatechol (I) and dipyrocatechol (II) borates were synthesized by esterification between pyrocatechol (1,2-dihydroxybenzene) and boric acid in *o*-xylene with azeotropic distillation of water. The co-esterification between pyrocatechol and boric acid with added equimolar quantities of phenol or 2,6-di-*tert*-butylphenol was studied, and pyrocatechol phenyl (III) and pyrocatechol-(2,6-di-*tert*-butyl)phenyl (IV) borates were prepared. The reaction of the resultant esters with formaldehyde in the presence of boron trifluoride etherate as a catalyst was examined. The coupling of the methylene moiety in several position of molecule III was found to be dependent on the solvent used. The electrophilic substitution on the phenol substituent took place in *o*-xylene, while the reaction in either benzene or molten monomer proceeded to substitute the methylene moiety for the proton on the catechol moiety. The molecular weights of the compounds were measured. Some properties of the synthesized oligomers were determined and thermal and thermooxidative destruction was examined.

# Keywords: Esterification; Polycondensation; Boric acid

## 1. Introduction

Esters of organoboron compounds finding increased use in modern organic synthesis and in catalysis [1-3], components for the synthesis of modified phenolic and epoxy resins [4-6] and as effective ablative thermal protection materials [7]. Nowadays, boron-containing phenolic resins are preferred materials for thermostructural composites with respect to their high flame retardancy, thermo-oxidative resistance and anti-neutron radiation compared to the traditional phenolic resins. They are interest as components of synthetic transmission oils [8], and as complexing agents for antibodies immobilized on heteroaromatic compounds [9].

Boron-containing phenolic resins and ways to synthesize them have been reported in the literature before [4-6, 10, 11]. Those compounds are usually synthesized by the Formaldehyde method, in which phenol borate synthesized from phenol and boric acid is followed by the reaction with poly-formaldehyde [4-6]. An another approach to the synthesis of boron-containing phenolic resins has been done using the Formalin method [10, 11], that consists in the initial formation of alcohols (reaction of phenols with formaldehyde) that followed the reaction with boric acid. However, the reaction of phenols with formaldehyde usually produced a mixture of several compounds in the first step.

Our research interests include the design of convenient ways to access esters and polyesters based on phenol, resorcinol, hydroquinone, bisphenol A, and boric acid, the assessment of their interaction with formaldehyde under conditions of water azeotropic distillation, and the characterization of the obtained derivatives [12-14].

The aim of this work was to development ideas about boron-containing phenolic resins based on diatomic phenol - pyrocatechol and boric acid. Thus, we describe the co-esterification between pyrocatechol and boric acid with added equimolar quantities of phenols, synthesis of pyrocatechol phenyl and pyrocatechol-(2,6-di-*tert*-butyl)phenyl borates, reactions with formaldehyde and also the study of the properties of the so formed oligomers.

# 2. Experimental section

# 2.1. General

NMR spectra were recorded on Bruker AV-300 (300.13 MHz for <sup>1</sup>H), DRX-500 (500.13 for <sup>1</sup>H, 125.76 for <sup>13</sup>C, 160.46 MHz for <sup>11</sup>B), and AV-600 (600.13 MHz for <sup>1</sup>H,

150.90 MHz <sup>13</sup>C and 192.55 MHz for <sup>11</sup>B) spectrometers. Chemical shifts were measured relative to residual solvent signals: CDCl<sub>3</sub> ( $\delta_H$  7.24 ppm and  $\delta_C$  76.90 ppm), CD<sub>3</sub>OD ( $\delta_H$  3.34 ppm and  $\delta_C$  47.66 ppm) or DMSO-d<sub>6</sub> ( $\delta_H$  2.50 ppm, and  $\delta_C$  39.50 ppm).

IR spectra were measured on a Bruker Vector 22 spectrometer in KBr pellets.

Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer (Italy). The ash content was measured after a sample was incinerated in oxygen.

The Vicat softening temperature was determined by the V50 method (50 N load, 50  $^{\circ}$ C/h temperature increment rate).

The number-average molecular weight was measured by acetylating the terminal hydroxyls with acetic anhydride [15].

The thermal destruction was studied by differential thermogravimetric analysis on a Mettler Toledo TGA SDTA 851E instrument. Samples were heated to 900°C under dry nitrogen and to 600°C under dry air: 30 mL/min purge gas flow rate, 10 /min heating rate, an Al<sub>2</sub>O<sub>3</sub> crucible.

## 2.2. Synthesis

## 2.2.1. Pyrocatechol borate (benzo[d][1,3,2]dioxaborol-2-ol) (I)

Into a three-neck round-bottom flask fitted with a mechanical stirrer, a thermometer, a Dean-Stark trap, a reflux condenser and a chlorocalcium tube were put boric acid (17.16 g, 0.278 mol), catechol (30.56 g, 0.278 mol) and *o*-xylene (77 mL). The whole was heated to a boil and boiled for 13 min until an estimated amount of water was liberated. *o*-Xylene was withdrawn *in vacuo*. The reaction mixture was recrystallized from dry benzene in inert atmosphere. Yield 34.64 g (92%). Mp = 74-79°C (Lit. m. p. 70-75 °C [16]). Found (%): C 53.34; H 4.14; ash (B<sub>2</sub>O<sub>3</sub>) 21.09. Calcd. (%): C 53.02; H 3.72; ash (B<sub>2</sub>O<sub>3</sub>) 25.61. <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 6.68 m (1H, H<sup>3.6</sup>); 6.81 m (1H, H<sup>4.5</sup>). <sup>11</sup>B NMR ( $\delta_{B}$ , ppm): 18.49 s. <sup>13</sup>C NMR ( $\delta_{C}$ , ppm): 117.35 (C<sup>3.6</sup>); 119.96 (C<sup>4.5</sup>); 151.53 (C<sup>1.2</sup>). IR ( $\lambda$ , cm<sup>-1</sup>): 742; 1281; 1365; 1470; 1514; 1602; 2963; 3453. *2.2.2. Dipyrocatechol borate (2,2'-oxydibenzo[d][1,3,2]dioxaborol, bis(benzo-1,3,2-*

dioxaborolanyl)oxid) (**II**)

A three-necked round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capping with a drying tube was changed with boric acid (13.74 g, 0.222 mol), catechol (24.47 g, 0.222 mol) and *o*-xylene (77 mL). The mixture was heated for 5 h under reflux until the water was

separated. The solvent was removed and dipyrocatechol borate was distilled *in vacuo* (1 mm Hg) at 198°C in a argon stream. Yield 25.33 g (90%). Mp = 150–155°C. (Lit. b. p. 160°/0.1 mm [16]; 146-147 °C [17]). Found (%): C 56.34; H 3.2; ash (B<sub>2</sub>O<sub>3</sub>) 22.12. Calcd. (%): C 56.79; H 3.18; ash (B<sub>2</sub>O<sub>3</sub>) 27.43. <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 6.68 m (1H, H<sup>3,6</sup>); 6.80 m (1H, H<sup>4,5</sup>). <sup>11</sup>B NMR ( $\delta_{B}$ , ppm): 19.04 s. <sup>13</sup>C NMR ( $\delta_{C}$ , ppm): 117.44 (C<sup>3,6</sup>); 120.01 (C<sup>4,5</sup>); 151.60 (C<sup>1,2</sup>). IR ( $\lambda$ , cm<sup>-1</sup>): 742; 1280; 1364; 1470; 1514; 1602; 1620; 2965.

# 2.2.3. Pyrocatechol phenyl borate (2-phenoxybenzo[d][1,3,2]dioxaborol) (III)

A three-necked round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capped with a drying tube was charged with boric acid (34.32 g, 0.555 mol), catechol (61.12 g, 0.555 mol), phenol (52.21 g, 0.555 mol) and o-xylene (200 mL). The mixture was heated for 3 h under reflux until the water was separated. o-Xylene was removed *in vacuo*. The pyrocatechol phenyl borate was distilled *in vacuo* (1 mm Hg) at 150°C in a argon stream. Yield 95.56 g (81%). Mp = 62–65°C. [Lit m. p. 44°C [16]). Found (%): C 68.31; H 4.57; ash (B<sub>2</sub>O<sub>3</sub>) 19.61. Calcd. (%): C 67.98; H 4.29; ash (B<sub>2</sub>O<sub>3</sub>) 16.42. <sup>1</sup>H NMR (δ<sub>H</sub>, ppm): 6.68 m (2H, H<sup>3,6</sup>, J<sub>3-4, 6-5</sub> 7.2 Hz, J<sub>3-5, 6-4</sub> 2.4 Hz); 6.78 t (1H, H<sup>4'</sup>, J<sub>4'-3'</sub>, 4<sup>1.5</sup>, 7.2 Hz); 6.85 m (2H, H<sup>2',6'</sup>, J<sub>2'-3', 6'-5'</sub> 6.0 Hz); 6.85 m (2H, H<sup>4,5</sup>, J<sub>4-3, 4-5, 5-6</sub> 7.8 Hz, J<sub>4</sub>. 6, 5-3 2.4 Hz); 7.13 t (2H, H<sup>3',5'</sup>, J<sub>3'-2', 3'-4', 5'-6'</sup> 7.8 Hz). <sup>11</sup>B NMR (δ<sub>B</sub>, ppm): 18.52 s. <sup>13</sup>C NMR (δ<sub>C</sub>, ppm): 115.87 (C<sup>2',6'</sup>); 116.21 (C<sup>3,6</sup>); 120.6 (C<sup>4'</sup>); 121.08 (C<sup>4,5</sup>); 130.15 (C<sup>3',5'</sup>); 145.4 (C<sup>1,2</sup>); 157.23 (C<sup>1'</sup>). IR (λ, cm<sup>-1</sup>): 648; 742; 1242; 1364; 1470; 1514; 1601; 1620; 2959.</sub>

# 2.2.4. Pyrocatechol-2,6-(di-tert-butyl)phenyl borate {2-(2,6-di-tertbutylphenoxy)benzo[d][1,3,2]dioxaborol} (**IV**)

A three-necked round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capped with a drying tube was charged with boric acid (34.32 g, 0.555 mol), catechol (61.12 g, 0.555 mol), 2,6-di-*tert*-butylphenol (114.53 g, 0.555 mol) and *o*-xylene (200 mL). The mixture was heated for 5.5 h until the water was separated. *o*-Xylene was removed under reduced pressure. The pyrocatechol-2,6-(di-*tert*-butyl)phenyl borate was distilled *in vacuo* (1 mm Hg) at 180°C. Yield 152.51 g (85%). Mp = 143–155°C. Found (%): C 74.42; H 8.15; ash (B<sub>2</sub>O<sub>3</sub>) 12.31. Calcd. (%): C 74.09; H 7.79; ash (B<sub>2</sub>O<sub>3</sub>) 10.74. <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 1.42 s (18H, C<u>H</u><sub>3</sub>); 6.69 m (2H, H<sup>3,6</sup>, J<sub>3-4, 6-5</sub> 7.5 Hz, J<sub>3-5, 6-4</sub> 2.1 Hz); 6.76 t (1H,

H<sup>4'</sup>, *J*<sub>4'-3', 4'-5'</sub> 7.8 Hz); 6.83 m (2H, H<sup>4,5</sup>, *J*<sub>4-3, 4-5, 5-6</sub> 7.2 Hz, *J*<sub>4-6, 5-3</sub> 2.4 Hz); 7.13 d (2H, H<sup>3',5'</sup>, *J*<sub>3'-4', 5'-4'</sub> 7.8 Hz). <sup>11</sup>B NMR (δ<sub>B</sub>, ppm) 22.38 s. <sup>13</sup>C NMR (δ<sub>C</sub>, ppm): 29.73 (<u>C</u>H<sub>3</sub>); 34.20 (<u>C</u>Me<sub>3</sub>); 115.30 (C<sup>3,6</sup>); 119.92 (C<sup>4'</sup>); 124.51 (C<sup>4,5</sup>); 126.28 (C<sup>3',5'</sup>); 137.41 (C<sup>2',6'</sup>); 144.97 (C<sup>1,2</sup>); 153.94 (C<sup>1'</sup>). IR (λ, cm<sup>-1</sup>): 741; 770; 1280; 1365; 1470; 1514; 1601; 1619; 2917.

2.2.5. Polymethylene pyrocatechol borate (V)

Pyrocatechol borate I (34.64 g, 0.255 mol) and o-xylene (77 mL) were placed into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capped with a drying tube, under an argon flow. The mixture was heated under stirring to 80°C, boron trifluoride etherate (BF<sub>3</sub>•Et<sub>2</sub>O) (3.09 g, 0.022 mol) was added and the stirring was continued for 15 min. Paraformaldehyde (6.38 g, 0.213 mol) was then added portionwise (0.5–1.0 g each) at such a rate that the temperature of the mixture did not exceed 110°C. After all the paraformaldehyde had been added, the reaction mixture was stirred at 90°C for 1 h. The solvent was removed in vacuo, and the residue was dried at 90°C for 2 h under an argon flow. The resultant oligomer was dissolved in a fivefold volume of ethanol and filtered. Ethanol was evaporated under reduced pressure and the residue was dried in vacuo at 150°C for 1 h. Yield 29.88 g (79%). Found (%): C 58.04; H 4.16; ash (B<sub>2</sub>O<sub>3</sub>) 19.66. Calcd. (%): C 56.84; H 3.38; ash (B<sub>2</sub>O<sub>3</sub>) 23.54. <sup>1</sup>H NMR (δ<sub>H</sub>, ppm): 3.81 m (2H, CH<sub>2</sub>); 6.68 m (2H, H<sup>3,6</sup>, J<sub>3-4, 6-5</sub> 7.2 Hz, J<sub>3-5, 6-4</sub> 2.4 Hz); 6.78 m (1H, H<sup>4,5</sup>, J<sub>4-3, 4-5, 5-6</sub> 7.2 Hz, J<sub>4-6, 5-3</sub> 2.4 Hz). <sup>11</sup>B NMR (δ<sub>B</sub>, ppm): 18.46 s. IR (λ, cm<sup>-1</sup>): 854; 1277; 1354; 1443; 1473; 1600; 2965; 3000-3638.

## 2.2.6. Polymethylene dipyrocatechol borate (VI)

Dipyrocatechol borate II (72.0 g, 0.284 mol) and o-xylene (250 mL) were placed into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capped with a drying tube, under a nitrogen flow. The mixture was heated under stirring to 80°C, BF<sub>3</sub>•Et<sub>2</sub>O (5.7 g, 0.04 mol) was added and the stirring was continued for 15 min. Paraformaldehyde (14.2 g, 0.473 mol) was then added portionwise (0.5–1.0 g each) at such a rate that the temperature of the mixture did not exceed 110°C. After all the paraformaldehyde had been added, the reaction mixture was stirred at 90°C for 1 h. The solvent was then removed *in vacuo*, and the residue was dried at 90°C for 2 h under a nitrogen flow. The resultant oligomer was dissolved in a fivefold volume of ethanol and

filtered. Ethanol was evaporated under reduced pressure and the residue was dried *in vacuo* at 150°C for 1 h. Yield 26.54 g (78%). Found (%): C 59.42; H 3.16; ash (B<sub>2</sub>O<sub>3</sub>) 22.96. Calcd. (%): C 60.53; H 2.91; ash (B<sub>2</sub>O<sub>3</sub>) 25.06. <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 3.80 m (2H, CH<sub>2</sub>); 6.66 m (2H, H<sup>3,6</sup>); 6.78 m (1H, H<sup>4,5</sup>). <sup>11</sup>B NMR ( $\delta_{B}$ , ppm): 18.43 s. IR ( $\lambda$ , cm<sup>-1</sup>): 853; 1277; 1358; 1473; 1508; 1600; 2965; 3000–3662.

2.2.7. Polymethylene pyrocatechol phenyl borate (VIIa)

Pyrocatechol phenyl borate III (78.94 g, 0.378 mol) and o-xylene (250 mL) were placed into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and a reflux condenser capped with a drying tube, under a nitrogen flow. The mixture was heated under stirring to 80°C, BF<sub>3</sub>•Et<sub>2</sub>O (2.28 g, 0.016 mol) was added and the stirring was continued for 15 min. Paraformaldehyde (9.5 g, 0.317 mol) was then added portionwise (0.5–1.0 g each) at such a rate that the temperature of the mixture did not exceed 110°C. After all the paraformaldehyde was added, the reaction mixture was stirred at 90°C for 1 h. The solvent was then removed in vacuo, and the residue was dried at 90°C for 2 h under a nitrogen flow. The resultant oligomer was dissolved in a fivefold volume of ethanol and filtered. Ethanol was evaporated and the residue dried in vacuo at 150°C for 1 h. Yield 68.8 g (83%). Found (%): C 70.52; H 4.06; ash (B<sub>2</sub>O<sub>3</sub>) 18.41. Calcd. (%): C 69.70; H 4.06; ash (B<sub>2</sub>O<sub>3</sub>) 15.54. <sup>1</sup>H NMR (δ<sub>H</sub>, ppm): 3.84 m (1H, CH<sub>2</sub>); 6.69 m (1H, H<sup>3',6'</sup>, J<sub>3'-4', 6'-5'</sub> 6.9 Hz, J<sub>3'-5', 6'-4'</sub> 2.4 Hz); 6.81 m (1H, H<sup>4',5'</sup>, J<sub>4'-3', 4'-5', 5'-6'</sub> 7.2 Hz, J<sub>5'-3', 4'-6'</sub> 2.4 Hz); 7.05 m (1H, H<sup>3,5</sup>). <sup>11</sup>B NMR ( $\delta_B$ , ppm): 18.41 s. <sup>13</sup>C NMR ( $\delta_C$ , ppm): 29.59 (CH<sub>2</sub>); 34.41 (CH<sub>2</sub>); 115.01 (C<sup>3',6'</sup>); 119.68 (C<sup>4',5'</sup>); 126.92 (C<sup>3,5</sup>); 129.39 (C<sup>2,6</sup>); 133.60  $(C^4)$ ; 144.56  $(C_{1',2'})$ ; 153.80  $(C^1)$ . IR  $(\lambda, \text{ cm}^{-1})$ : 747; 853; 1270; 1357; 1441; 1509; 1569; 2965; 3000-3613.

# 2.2.8. Polymethylene pyrocatechol phenyl borate (VIIb in molten monomer)

Pyrocatechol phenyl borate **III** (98.56 g, 0.465 mol) was placed into a fourneck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and a reflux condenser capped with a drying tube. After stirring for 2 min at 80°C borate **III** was fully dissolved and  $BF_3 \cdot Et_2O$  (2.28 g, 0.016 mol) was added under argon flow. The mixture was stirred for 15 min, then paraformaldehyde (11.69 g, 0.39 mol) was added portionwise (0.5–1.0 g each) at such a rate that the temperature of the mixture did not exceed 110°C. After all the paraformaldehyde was added, the reaction mixture was stirred at 90°C for 1 h under a nitrogen flow. The resultant oligomer was dissolved in a fivefold volume of ethanol and filtered. Ethanol was evaporated under reduced pressure and the residue was dried *in vacuo* at 150°C for 1 h. Yield 85.27 g (82 %). <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 3.67 m (2H, CH<sub>2</sub>); 6.60 m (2H, H<sup>3,6</sup>); 6.66 m (1H, H<sup>4'</sup>); 6.73 m (1H, H<sup>4,5</sup>); 6.78 m (2H, H<sup>2',6'</sup>), 6.98 m (2H, H<sup>3',5'</sup>). IR ( $\lambda$ , cm<sup>-1</sup>): 640, 754, 817, 1243, 1358, 1454, 1512, 1608, 2916, 3000–3750.

2.2.9. Polymethylene pyrocatechol phenyl borate (VIIb in benzene)

Pyrocatechol phenyl borate **III** (77.17 g, 0.364 mol) and benzene (250 mL) were placed into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser capped with a drying tube. The mixture was heated to 78°C, BF<sub>3</sub>•Et<sub>2</sub>O (2.28 g, 0.016 mol) was added under argon flow. The mixture was stirred at that temperature for 15 min, then paraformaldehyde (11.69 g, 0.39 mol) was added portionwise (0.5–1.0 g each). After all the paraformaldehyde was added, the reaction mixture was stirred at 78°C for 1 h. The solvent was then removed *in vacuo*, and the reaction mixture was dried at 90°C for 2 h under a argon flow. The resultant oligomer was dissolved in a fivefold volume of ethanol and filtered. Ethanol was evaporated under reduced pressure and the residue was dried *in vacuo* at 150°C for 1 h. Yield 66.85 g (82 %). Found (%): C 70.15; H 4.21. Calcd. (%): C 69.70; H 4.02. <sup>1</sup>H NMR (δ<sub>H</sub>, ppm): 3.67 m (2H, CH<sub>2</sub>); 6.61 m (2H, H<sup>3,6</sup>); 6.67 m (1H, H<sup>4</sup>); 6.71 m (1H, H<sup>4,5</sup>); 6.79 m (2H, H<sup>2,6'</sup>); 6.99 m (2H, H<sup>3',5'</sup>). <sup>11</sup>B NMR (δ<sub>B</sub>, ppm): 18.04 s. IR (λ, cm<sup>-1</sup>): 647, 753, 814, 1231, 1358, 1454, 1511, 1600, 2921, 2958–3733.

# 2.2.10. Polymethylene pyrocatechol-2,6-(di-tert-butyl)phenyl borate (VIII)

Pyrocatechol aryl borate **IV** (78.0 g, 0.241 mol) and o-xylene (250 mL) were placed into a four-neck round-bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser, capped with a drying tube. The mixture was heated to 80°C, BF<sub>3</sub>•Et<sub>2</sub>O (7.14 g, 0.5 mol) was added under argon flow. The mixture was additionally stirred at that temperature for 25 min and paraformaldehyde (6.02 g, 0.201 mol) was added portionwise (0.5–1.0 g each) at such a rate that the temperature of the mixture did not exceed 110°C. After all the paraformaldehyde was added, the reaction mixture was stirred at 90°C for 1 h. The solvent was then removed *in vacuo*, and the residue was dried at 90°C for 2 h. The resultant oligomer was dissolved in a fivefold volume of ethanol and filtered. Ethanol was evaporated under reduced pressure and the residue was dried *in vacuo* at

150°C for 1 h. Yield 62.58 g (77%). Found (%): C 75.61; H 7.66; ash (B<sub>2</sub>O<sub>3</sub>) 12.78. Calcd. (%): C 75.02; H 7.51; ash (B<sub>2</sub>O<sub>3</sub>) 10.35. <sup>1</sup>H NMR ( $\delta_{H}$ , ppm): 1.19 s (18H, CH<sub>3</sub>); 3.69 m (2H, CH<sub>2</sub>); 6.65 m (2H, H<sup>3,6</sup>); 6.80 m (1H, H<sup>4,5</sup>); 6.99 m (2H, H<sup>3',5'</sup>); 7.18 m (1H, H<sup>4'</sup>). <sup>11</sup>B NMR ( $\delta_{B}$ , ppm): 18.41 s. IR ( $\lambda$ , cm<sup>-1</sup>): 752; 817; 1265; 1363; 1436; 1506; 1604; 2963; 3013–3675.

# 3. Results and discussion

The reaction between 1,2-aromatic diols and boric acid is known to furnish esters [18]. Different methods for the formation of the oxoborolane ring have been reported, for example, the exchange reaction of boron halides with pyrocatechol in methylene chloride [16], the reaction between various boron hydrides and catechol [17, 19], the transesterification of catechol borates [20], and the reaction of catechol with boron anhydride [21, 22], boric acid [17, 23] or boronic acid [24]. The most convenient method is the reaction of pyrocatechol with boric acid in xylene with azeotropic distillation of water. The reaction between stoichiometric quantities of catechol and boric acid yielded pyrocatechol borate **I**. Borate **I** underwent degradation by further heating to give bis(benzo-1,3,2-dioxaborolanyl)oxid **II** which was isolated in the yield about 90% by distillation in vacuo in inert atmosphere (Scheme 1). None formation of  $B_2cat_3$  (2-(o-hydroxyphenyloxy)-benzo-1,3,2-dioxaborolan) or (cat)B(catH) [17] in this conditions was observed.

The formation of I was complete after 13 min, with the loss of water in the amount close to the estimated. Compound I was refined by recrystallization from absolute benzene under dry argon. Distillation of I also furnished dipyrocatechol borate II.



Scheme 1. Esterification of pyrocatechol and boric acid in o-xylene

Compounds I and II are well known compounds and its physico-chemical characteristics were compared with the literature date [16, 17].

The reaction of boric acid (1 mol) with catechol (1 mol) afforded dipyrocatechol **II**, which was refined by vacuum distillation under argon. The formation reaction of the ester was complete in 5 hrs. The NMR spectra of **I** and **II** are identical.

The addition of equimolar quantities of phenol or 2,6-di-*tert*-butylphenol to the reaction between pyrocatechol and boric acid delivered the respective mixed esters: pyrocatechol phenyl borate **III** or pyrocatechol-2,6-(di-*tert*-butyl)phenyl borate **IV**, respectively (Scheme 2). The resultant esters were refined by vacuum disttillation.



Scheme 2. Co-esterification of catechol, boric acid and phenol or 2,6-di-*tert*butylphenol in *o*-xylene

The <sup>1</sup>H NMR spectrum of **III** is made up of the multiplet centered at 6.68 ppm typical of H<sup>3,6</sup> atoms of the catechol ring. The triplet with a peak at 6.78 ppm is characteristic of the phenolic H<sup>4'</sup> atom. The complex multiplet centered at 6.85 ppm is attributed to catecholic H<sup>4,5</sup> atoms and phenolic H<sup>2',6'</sup> atoms. The triplet with a peak at 7.13 ppm is representative of phenolic H<sup>3',5'</sup> atoms.

The <sup>1</sup>H NMR spectrum of **IV** shows the singlet at 1.42 ppm typical of methyl H atoms of the *tert*-butyl group. The multiplet centered at 6.69 ppm pertains to  $H^{3,6}$  atoms. The triplet centered at 6.76 ppm is characteristic of  $H^{4'}$  atoms, and the multiplet centered at 6.83 ppm is typical of  $H^{4,5}$  atoms. The doublet centered at 7.13 ppm is representative of  $H^{3'5'}$  atoms.

All the synthesized monomers (I–IV) entered into a reaction with paraformaldehyde under conditions as described [12-14] using *o*-xylene as the solvent and boron trifluoride etherate as the catalyst to furnish oligomeric compounds.

The reaction between **I** and formaldehyde afforded polymethylene pyrocatechol borate **V** (Scheme 3).



Scheme 3. Polycondensation of I with formaldehyde in o-xylene

The <sup>1</sup>H NMR spectrum of **V** shows the multiplet centered at 6.68 ppm typical of  $H^{3,6}$  atoms and the multiplet centered at 6.78 ppm typical of  $H^{4,5}$  protons. The multiplet signal at 3.81 ppm relates to the methylene protons. The signal intensity of  $H^{4,5}$  protons is much lower than that of  $H^{3,6}$  protons, suggesting the electrophilic substitution of the catecholic  $H^{4,5}$  protons by the methylene group.

The reaction of **II** with formaldehyde resulted in polymethylene pyrocatechol borate **VI** (Scheme 4). The <sup>1</sup>H NMR spectra of **VI** and **V** are alike.



Scheme 4. Polycondensation of II with formaldehyde in o-xylene

The reaction of **III** with formaldehyde proceeded to yield polymethylene pyrocatechol phenyl borate **VII** (Scheme 5).



Scheme 5. Polycondensation of III with formaldehyde in o-xylene

The <sup>1</sup>H NMR spectrum of **VIIa** shows the multiplet centered at 6.69 ppm typical of  $H^{3',6'}$  atoms. The multiplet centered 6.78 ppm refers to  $H^{4',5'}$  protons. The signal centered at 7.05 ppm pertains to phenolic  $H^{3,5}$  protons. The multiplet signal at 3.84 ppm corresponds to methylene protons.

It follows from the comparison between <sup>1</sup>H NMR spectra of **III** and **VIIa** that the electrophilic substitution took place on the phenolic ring. Along with that, the catecholic ring had a higher electron density than the phenolic one. The reason behind the electrophilic substitution on a ring with a lower electron density could probably be steric hindrances and the solvent effect.

The spatial structure of **III** consists of two planes in one of which there lies the sp<sup>2</sup>-hybrid residue of boric acid and the catecholic ring, and the flat phenolic ring is attached to this plane at 120° [25]. Thus, the spatial structure of **III** cannot explain the presence of steric hindrances of the electrophilic attack on the catechol aromatic ring.

Fukin et al. [25] noted the possible reaction of similar boron-containing esters, in particular the pyrocatechol phenyl boronic ester, with methyl protons through means of hydrogen-bonding of the latter with oxygen atoms of the dioxaborolane fragment. Thus, *o*-xylene having two methyl groups may generate hydrogen bonds with the oxoborolane ring oxygen of **III**, shielding the catechol ring.

To experimentally confirm the ability of *o*-xylene methyl protons to form a hydrogen bond with the oxygen atom of the oxaborolan ring of compound III, we studied the changes in the <sup>1</sup>H NMR spectra of compound III in  $C_6D_6$  recorded with *o*-

xylene additives (0.052 equiv) relatively pure xylene signals. We found, that the singlet signal of xylene methyls is shifted to the low magnetic field ( $\Delta\delta$  0.01 ppm). Also the multiplisity of the aromatic protons have some changers including the integral intencity and the form of the multiplet at 7.11-7.17 ppm. This data are confirmed the propose of the posibility of *o*-xylene hydrogen bonding to the oxygen atoms of the compound III.

To corroborate the above assumption, the polycondensation of **III** using benzene as the solvent and reaction without the solvent (in molten monomer) was examined herein (Scheme 6). We found, that the result of interaction of III with formaldehyde strongly depends on the solvent used. If VIIa can be obtained from III and formaldehyde in xylene, the contact of neat III with formaldehyde caused vigorous reaction and formation of VIIb. In addition, formation of VIIb occurred when formaldehyde was added to molten III. The obtained picture reveals the signifcant diference of reactivity of compounds on the reaction conditions.



Scheme 6. Polycondensation of III with formaldehyde in benzene or molten monomer

The <sup>1</sup>H NMR spectrum of **VIIb** has a signal centered at 6.60 ppm typical of H<sup>3,6</sup> atoms. The signal at 6.73 ppm pertains to phenolic H<sup>4,5</sup> and H<sup>2',6'</sup> protons. The signal centered at 6.98 ppm refers to phenolic H<sup>3',5'</sup> protons. The signal at 6.66 ppm is attributed to phenolic H<sup>4'</sup> protons. The multiplet signal at 3.67 ppm corresponds to methylene protons. It follows from the comparison between <sup>1</sup>H NMR spectra of **III** and

**VIIb** that the integral intensity of catecholic H<sup>4,5</sup> protons declined, that is, the substitution of catecholic aromatic protons occurred.

Thus, the solvent had a determining influence on the direction of electrophilic substitution in the polycondensation reaction between pyrocatechol phenyl borate **III** and formaldehyde.

The reaction of IV with formaldehyde led to the formation of VIII (Scheme 7).



Scheme 7. Polycondensation of IV with formaldehyde in o-xylene

The <sup>1</sup>H NMR spectrum of **VIII** shows the multiplet centered at 6.65 ppm representative of H<sup>3,6</sup> atoms. The signal at 6.99 ppm pertains to phenolic H<sup>3',5'</sup> protons. The signal at 7.18 ppm is attributed to the phenolic H<sup>4'</sup> proton. The multiplet signal at 3.69 ppm corresponds to methylene protons. The singlet at 1.19 ppm refers to the methylene protons of 2,6-di-*tert*-butylphenol. It is seen from the spectral data that the integral intensity of the H<sup>4,5</sup> protons is much lower than that of the H<sup>3,6</sup> protons, suggesting the electrophilic substitution of the catecholic H<sup>4,5</sup> protons by the methylene group.

The basic properties of the synthesized compounds with a polymeric structure are summarized in Table 1 wherein it is seen that the molecular weight of the listed compounds is not high, that is, compounds V–VIII are oligomers themselves and have a relatively moderate Vicat softening temperature. All the compounds are well soluble in polar organic solvents. The number-average molecular weight is not high, and is equivalent approximately to 8–14 units.

# Table 1

Some	pro	perties	of	synthe	sized	oligon	ners

Entry	Vicat tamp $(^{\circ}C)$	N/	Solubility (g/dL)			
	vicat temp ( C)	IVIN	Alcohol	Acetone	DMF	
V	103	1780	26.2	36.6	readily	
V	105				soluble	
VI	105	2210	28.4	34.9	readily	
	100				soluble	
VIIa	85	2550	15.7	20.0	readily	
	00				soluble	
VIIb	90	3190	11.3	16.7	readily	
					soluble	
VIII	92	4090	11 1	13.9	readily	
	52				soluble	

# 3.1. Thermal destruction and stability

The thermal destruction curves of the oligomers (V, VI, VIIa, VIIb, VIII) are displayed in Fig. 1. It was shown, that the thermal destruction of the oligomers has the same nature.



Fig. 1. Weight loss during thermal destruction of oligomers under nitrogen

The degradation occurred in two stages. The first stage was high-speed and ranged from 100 to 370°C, the destruction being 37 to 47.5% for all the oligomers. The second stage started at 370°C and the destruction rate declined. The residual weights were 38% for **V**, 44.5% for **VI**, 42.5% for **VIIa**, 39% for **VIIb**, and 20% for **VIII**.

The thermal oxidation graphs of the oligomers are given in Fig. 2. It is seen that the stability of the oligomers in oxidizing medium was nearly the same. The stages of thermal oxidation nearly coincided those of thermal destruction. The residual weights at 600°C were 49% for **V**, 44% for **VI**, 49% for **VIIa**, 38% for **VIIb**, and 39.5% for **VIII**.





As can be seen from the presented data, the kinetics of destruction both in an inert atmosphere and during thermal oxidation is almost the same. In this case, the mass of the residue during thermal oxidation is much less.

Compound VI is showed the maximum heat resistance, probably due to the fact that both pyrocatechol residues are fixed by methylene bounds, which reduces their mobility with increasing temperature. Compound V during the destruction after 100°C with the loss of water is converted to compound VI. The lowest heat resistance, both in an oxidizing medium and in an inert atmosphere, is shown by compound VIII. It is evidently, that this fact is due to the large number of *tert*-butyl radicals, which are less resistant to temperature.

When studying the thermal and thermooxidative degradation of compounds VIIa and VIIb, it can be seen that, at the initial stages of destruction from 100 to 300°C, compound VIIb is showed higher heat resistance than VIIa. The stability of both compounds during thermal degradation is almost the same. In this case, VIIb is less stable during thermal oxidation. Accordingly, additional binding of the phenyl ring in the structure of the oligomer reduces its mobility (ring) and leads to an increase in heat resistance.

#### 4. Conclusions

In summary, mixed boric acid esters were synthesized on the basis of pyrocatechol in this study. The interaction between the resultant esters and formaldehyde using boron trifluoride etherate as the catalyst was examined. The reaction of 2-phenoxybenzo[d][1,3,2]dioxaborol **III** with formaldehyde in *o*-xylene was found to occur on the catechol ring, while the reaction proceeded on the phenolic ring when benzene or molten monomer was used. The structures of all the synthesized compounds were resolved by IR, <sup>1</sup>H-, <sup>13</sup>C- and <sup>11</sup>B spectroscopies and elemental analysis. The thermal stability of the oligomers in both inert atmosphere and oxidizing medium was studied by the TGA technique. Results from the studies shown that the thermal and thermooxidative destruction of the oligomers, apparently, are of the same nature. The obtained data allow us to consider new oligomers as promising additives to polymer composite materials based on rubbers and epoxy resins.

## Notes

The authors declare no competing financial interest.

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