# Synthesis, Flame-Retardancy Testing, and Preliminary Mechanism Studies of Nonhalogenated Aromatic Boronic Acids: A New Class of Condensed-Phase Polymer Flame-Retardant Additives for Acrylonitrile–Butadiene–Styrene and Polycarbonate

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**ABSTRACT:** This study describes the syntheses and thermal properties of aromatic boronic acids and their use as flame retardants. The possible flame-retardancy mechanisms are also discussed. The materials were synthesized from aromatic bromides using one of two procedures. The first procedure involved traditional approaches to boronic acids, using lithium–halogen exchange and quenching with trimethylborate followed by hydrolysis. The second procedure used a nickel catalyst and a dialkoxy borane to generate aromatic dialkoxyboronates that were converted to boronic acids by acid hydrolysis. The thermal properties of these aromatic boronic acids were studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). These materials were blended into acrylonitrile–butadiene–styrene (ABS) and polycarbonate (PC) resins and tested for ignition resistance, using the UL-94 flame test. A 10 wt % loading of 1,4-benzenediboronic acid in polycarbonate gave a UL-94 V-0 result. This same diboronic acid showed flame retardancy and char formation in ABS, but this result was not quantifiable by the UL-94 test. Burn times for the ABS samples often exceeded 5 min, thereby showing unusual resistance to consumption by fire. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1257–1268, 2000

**Key words:** boronic acids; polycarbonate; acrylonitrile–butadiene–styrene; flame retardants; UL-94 V-0

## INTRODUCTION

In our previous research to discover and develop new materials for fire-safe aircraft interiors, we con-

centrated on condensed-phase materials rather than the more traditional halogenated systems.[1–9] One condensed-phase mechanism to prevent flame propagation in polymers is through the use of materials that form char on exposure to high heat and flames. Char is a carbon-based soot/residue that undergoes very little oxidative degradation and prevents the passage of fuel molecules to the flame.[3–8] Sometimes the char formed is more inorganic in composition, such as carbon–inorganic oxide ceramics or glasses. Like carbon char, this ceramic or glass provides thermal insulation and acts as a physical barrier to fuel transport. Primarily, the

ceramic prevents heat from reaching the rest of the plastic, thus preventing melt, flow, and thermal decomposition.[3–8] Described here are the results from synthesizing and blending arylboronic acids into acrylonitrile–butadiene–styrene (ABS) and polycarbonate (PC) to test their efficacy as condensed-phase flame retardants in these plastics.

Boron compounds are currently used in some plastic formulations as flame retardants,[9] but they are plagued by poor melt-blendability, which weakens the polymers' mechanical properties. Borates such as zinc borate ($Zn_3B_4O_9$) are typically used. The exact mechanism of action for these borates as flame retardants is unknown, but it is believed that they form a borate glass on melting at high temperatures.[10–12] This borate glass acts as a thermally insulating layer to protect the remaining plastic from further oxidative degradation. Furthermore, it may be possible for carbon-based char or boron carbide–type char to form under the glass layer. Boronic acids are known to release water on thermolysis, thereby leading to boroxine or boronic acid anhydride formation.[13–17] These materials, if they contain more than one boronic acid functionality, may form a network polymer system. Specifically, they may form a boroxine glass that could lead to high char formation on burning. Examples of boronic acids, 1,4-benzenediboronic acid (**1**) and 1,3,5-benzenetriboronic acid (**2**), are shown forming boroxine glass networks [eqs. (1) and (2)].
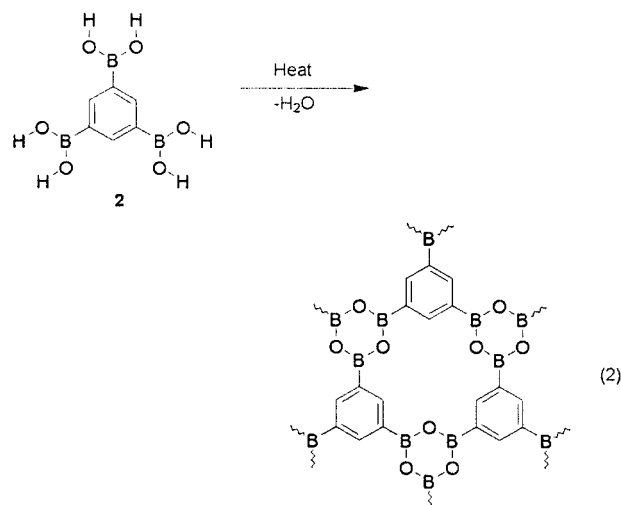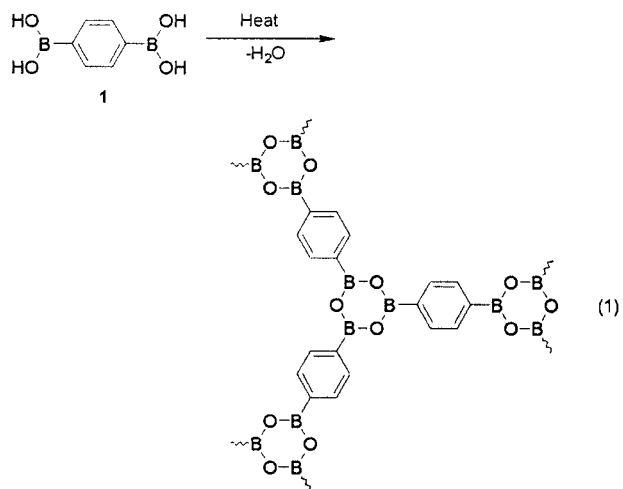


Our method of making boronic acid flame retardants uses brominated aromatics as starting materials. Brominated aromatics are currently used as flame retardants for polymers, and there are a variety of structures for these materials. Previously, we synthesized alkyne-based[1] and alkyne/phosphorus-based flame retardants[2] from commercially available brominated aromatic flame retardants. Therefore, our approach in using these starting materials is a logical one as it offers three major advantages: (1) since there is a wide variety of brominated starting materials, numerous boronic acid compounds can be prepared from those readily available compounds; (2) the reaction used to synthesize these boronic acid flame retardants is a one-pot reaction, using either organolithium reagents and trimethylborate or a nickel catalyst system with pinacol borane; and (3) since the synthesis of these boronic acids relies on brominated organics, the flame-retardant industry would not have to retool to produce these compounds. Therefore, the brominated flame retardants could be used as starting materials for halogen-free flame retardants by simply adding one step to the current process.

## EXPERIMENTAL

### Char Yield Calculation from TGA Data at 900°C

100 wt % − wt % loss at 900°C

$$= \text{char yield at } 900°C$$

### Theoretical Char Yield Calculations for Boronic Acid 1 and PC or ABS Blends at 900°C

Char yield **1** at 900°C (A*): 40 wt %; char yield ABS at 900°C (B*): 2.9 wt %; char yield PC at 900°C (C*): 24.4 wt %.

Theoretical char yield = [(wt % 1/100) × (A*)]

+ [(wt % ABS or PC/100) × (B* or C*)]

## General Procedures

^{1}H–NMR spectra were recorded at 300 MHz on a Brüker AM-300 spectrometer and at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. The ^{13}C–NMR spectra at 75 MHz was recorded on a Brüker AM-300 spectrometer, and at 100 or 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively. The ^{11}B–NMR spectra at 96 MHz was recorded on a Brüker AM-300 spectrometer. [1]H chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). [11]B resonances were recorded using $BF_3 \cdot Et_2O$ as the reference at 0 ppm and are reported as "±" in relation to this 0 ppm standard. [13]C resonances were recorded using the 77.0-ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin–Elmer 1600 Series FTIR. Thermal gravimetric analysis (TGA) was performed with a Perkin–Elmer TGA7 from 30 to 900°C at 10°C/min under $N_2$. Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC7 using a 50 to 450°C scanning window at 10°C/min under $N_2$. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head. An Atlas Electric HVUL-94 flame-test station was used for the UL-94 flame tests. Reagent grade tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled under nitrogen from sodium benzophenone ketyl. Benzene, toluene, and triethylamine were distilled over $CaH_2$ under nitrogen. Pinacol was dried and distilled prior to use. $Ni(dppm)Cl_2$, $Ni(dppe)Cl_2$, $Ni(dppp)Cl_2$, and $Ni(dppb)Cl_2$ were synthesized following or extrapolating from literature procedures.[18,19] 2,4,6-Tribromophenol and 1,4-dibromobenzene were recrystallized, respectively, from toluene and MeOH prior to use. 2,4,6-Tribromophenol (Great Lakes PH-73) was provided by Great Lakes Chemical Corporation. Polycarbonate (Dow Calibre 301-15, 891-20) and acrylonitrile–butadiene–styrene (Dow Magnum 9010) were provided by Dow Chemical Corporation. Polycarbonate and acrylonitrile–butadiene–styrene resins were dried in a vacuum oven for 24 h at 100°C before blending. Unless noted otherwise, all other reagents were used as received. Mass spectrometry work was done by the University of South Carolina mass spectrometry laboratory. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. All synthetic operations were carried out under a dry, oxygen-free, nitrogen atmosphere unless otherwise noted.

### General Procedure for NMR Sample Preparation Using Boronic Acids

All NMR analyses were performed with $CD_3OD$ as the NMR solvent, because of the solubilities of the boronic acids. To each NMR tube containing the boronic acid and $CD_3OD$ was added 3–4 drops of 20 wt % DCl in $D_2O$ (purchased from Aldrich Chemical Company, Inc.). Using DCl in $D_2O$ ensures that a single compound is observed by NMR for a pure material.[16]

### General Procedure for Synthesis of Aryl Boronic Acids Using a Transition Metal Catalyst and Pinacol Borane

To a round-bottomed flask, equipped with a water-cooled West condenser and a magnetic stir bar, were added the aryl bromide and either (1,3-diphenylphosphinopropane)nickel(II) chloride or bis(triphenylphosphine)palladium(II) chloride. The vessel was then sealed with a rubber septum under a $N_2$ atmosphere. Toluene and triethylamine (3 to 4 equiv/bromide) were then added. 4,4′,5,5′-Tetramethyl-1,3,2-dioxaborolane (pinacol borane) (1.5 equiv/bromide) was added and the mixture turned to a darker color. The reaction mixture was heated to reflux (~100°C), during which time the reaction turned a darker color with the precipitation of salts, presumably $NEt_3 \cdot HBr$. On completion of the reaction, the mixture was quenched with a saturated solution of $NH_4Cl$. The organic layer was diluted with toluene and $Et_2O$ and washed with a saturated solution of $NH_4Cl$ (1×). The combined aqueous layers were extracted with $Et_2O$ (2×). The combined organic layers were dried over $MgSO_4$, decolorized with Norit A, and filtered through Celite. The resulting solution was condensed by rotary evaporation and dried to give a solid. The solid was recrystallized from MeOH to give a white solid, to which was added MeOH and 3$M$ HCl in an Erlenmeyer flask. The reaction mixture was heated on a hot plate and stirred until all of the solid went into solution. The solution was then condensed by removal of solvent and water, and then allowed to cool in a refrigerator, yielding white crystals. The crystals were filtered and washed with cold water to give the product.

### General Procedure for Nickel Catalyst Studies Using 1,4-Dibromobenzene and Pinacol Borane

Using the procedure previously described, a nickel catalyst [Ni(dppm)Cl$_2$, Ni(dppe)Cl$_2$, Ni(dppp)Cl$_2$, or Ni(dppb)Cl$_2$] (6 mol %) was used to react 1,4-dibromobenzene (0.59 g, 2.5 mmol) with 4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane (pinacol borane; 1.1 mL, 7.5 mmol) in the presence of toluene (30 mL) and triethylamine (2.8 mL, 20 mmol). The mixture was heated to reflux (~100°C) for 1 day. On completion of the reaction, the reaction mixture was subjected to a workup as already described. The crude product was analyzed by drying *in vacuo* and then analyzed by $^1$H–NMR. Product ratios were determined by $^1$H–NMR and 1,4-benzenedipinacolboronate, if present, was isolated as indicated earlier.

### 1,4-Benzenediboronic acid[13–17] (by tert-BuLi)

A dry 500-mL round-bottomed flask, equipped with a magnetic stir bar, was purged with N$_2$ and 1,4-dibromobenzene (11.9 g, 50 mmol) was added. The flask was sealed with a rubber septum under a N$_2$ atmosphere, THF (150 mL) was added, and the mixture was cooled to −78°C. *tert*-Butyllithium (121 mL, 205 mmol, 1.69$M$ in pentane) was added dropwise, whereupon the reaction turned a lime gold in color. The reaction was allowed to stir for 2 h at −78°C, eventually becoming yellow in color. Trimethylborate (39.2 mL, 350 mmol) was added quickly and the reaction became white, then clear. The reaction was allowed to stir at −78°C for 1 h, and then allowed to warm to room temperature and stirred overnight. At the end of the reaction, the septum and stir bar were removed, and unreacted trimethylborate and THF were removed by a rotary evaporator. The resulting yellow-white solid was dissolved in MeOH and decolorized with Norit 211 (neutral) decolorizing carbon. The resulting solution was filtered through Celite to remove the charcoal, giving a clear to very light yellow solution. The solution was condensed by removal of excess MeOH, and the concentrated solution was poured into 180 mL of 1.5$M$ HCl in an Erlenmeyer flask containing a magnetic stir bar. The white reaction suspension was heated to boiling, whereupon the white suspension disappeared. The solution was heated until all the MeOH had been boiled off, and the remaining acidic solution was used to recrystallize the product. After sitting overnight in a refrigerator, white crystals precipitated that were then filtered and washed with cold water to give 6.42 g (77%) of a white solid.

$^1$H–NMR (300 MHz, CD$_3$OD, DCl in D$_2$O) δ 7.73. As stated earlier and in subsequent elemental analyses, using DCl in D$_2$O ensures that a single compound is observed by NMR for a pure material.[16]

### 1,4-Benzenediboronic Acid[13–17] (by Pd/pinacol borane)[20]

1,4-Dibromobenzene (2.36 g, 10 mmol) was reacted with 4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane (pinacol borane; 3.8 mL, 26 mmol) as described earlier, using bis(triphenylphosphine)palladium(II) chloride (0.42 g, 0.6 mmol), toluene (35 mL), and triethylamine (11.2 mL, 80 mmol). The mixture was heated to reflux (~100°C) for 18 h, during which time the reaction mixture turned black with the precipitation of gray salts, presumably NEt$_3$·HBr. On completion of the reaction, the black reaction mixture was subjected to a workup, as described, to give a light yellow solid. This solid was hydrolyzed, using MeOH and 3$M$ HCl in the method previously described, to give light yellow crystals. The crystals were filtered and washed with cold water to give 0.41 g (25%) of product.

$^1$H–NMR (300 MHz, CD$_3$OD, DCl in D$_2$O) δ 7.73.

### 1,4-Benzenediboronic Acid[13–17] (by Ni/pinacol borane)

1,4-Dibromobenzene (2.36 g, 10 mmol) was reacted with 4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane (pinacol borane; 3.8 mL, 26 mmol) as already described, using (1,3-bis(diphenylphosphino)propane)nickel(II) chloride (0.33 g, 0.6 mmol), toluene (35 mL), and triethylamine (11.2 mL, 80 mmol). The reaction mixture was heated to reflux (~100°C) for 1 day, during which time the reaction turned dark green with the precipitation of white-green salts. On completion of the reaction, the dark green reaction mixture was subjected to a workup, as described, to give a light yellow solid. This solid was recrystallized from MeOH and then hydrolyzed, using MeOH and 3$M$ HCl in the method described earlier, to give white crystals. The crystals were filtered and washed with cold water to give 1.08 g (65%) of product.

FTIR (KBr) 3394.9, 3292.3, 1589.7, 1512.8, 1379.5, 1343.6, 1256.4, 1164.1, 1117.9, 1030.8, 1005.1, 810.3, 646.2 cm$^{-1}$. $^1$H–NMR (300 MHz, CD$_3$OD, DCl in D$_2$O) δ 7.73. $^{11}$B–NMR (96 MHz, CD$_3$OD, DCl in D$_2$O) δ 29.2. $^{13}$C–NMR (100 MHz, CD$_3$OD, DCl in D$_2$O) δ 133.75. HRMS calcd for C$_6$H$_8^{11}$B$_2$O$_4$: 166.0609. Found: 166.0611.

### 1,3,5-Benzenetriboronic Acid

1,3,5-Tribromobenzene (7.87 g, 25 mmol) was reacted with 4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane (pinacol borane; 16.3 mL, 112.5 mmol) as previously described, using (1,3-bis(diphenylphosphino)propane)nickel(II) dichloride (0.68 g, 1.25 mmol), toluene (80 mL), and triethylamine (32 mL, 225 mmol). The reaction mixture was heated to reflux (~100°C) for 2 days, during which time the reaction turned dark green, then brown, with the precipitation of salts. On completion of the reaction, the reaction mixture was subjected to a workup, as described, to give a light yellow solid. This solid was recrystallized from MeOH and then hydrolyzed, using MeOH and 3$M$ HCl in the method previously described, to give white crystals. The crystals were filtered and washed with cold water to give 2.62 g (50%) of product.

FTIR (KBr) 3145.4, 3282.1, 1594.9, 1430.8, 1348.7, 1297.4, 1230.8, 1164.1, 1097.4, 1035.9, 892.3, 825.6, 774.4, 702.6 cm$^{-1}$. $^1$H–NMR (300 MHz, CD$_3$OD, DCl in D$_2$O) δ 8.18. $^{11}$B–NMR (96 MHz, CD$_3$OD, DCl in D$_2$O) δ 30.44. $^{13}$C–NMR (100 MHz, CD$_3$OD, DCl in D$_2$O) δ 140.86. LRMS calcd for C$_{12}$H$_{21}$B$_3$O$_6$: 294. (The LRMS was obtained with a direct-exposure probe, using the 1,3,5-benzene tris(dimethylboronate), synthesized by treating 1,3,5-benzenetriboronic acid with MeOH. All techniques tried for MS analysis of 1,3,5-benzenetriboronic acid failed, leading to the use of the above-mentioned methylboronate derivative.) Found: 294. ANAL. calcd. for C$_6$H$_9$B$_3$O$_6$ C, 34.38; H, 4.34; B, 15.47; O, 45.81. Found: C, 34.42; H, 4.38.

### General Procedure for Blending Boron Containing Flame-Retardant Additive and Plastic (ABS or PC) in Brabender 30-mL Type 6/2 Mixing Bowl–Prep-Center

The additive and plastic were weighed out in their respective amounts according to the wt % of additive: 25.41 g batch (PC), 22.05 g batch (ABS). The total weight of polymer/additive batch was determined as follows: 70% volume of the 30-mL Brabender mixing bowl was used, and the density of the plastic (1.21 g/mL PC, 1.05 g/mL ABS) was used to calculate the total weight of the batch. Heating temperatures for the blending bowl varied, depending on the material involved. The processing temperatures used during blending were: ABS, 225°C; PC, 270°C. After the bowl had heated to the necessary processing temperature, the sample was quickly charged through the top opening, while the blades were rotating at 50 rpm. The opening was then closed with the weighted handle and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additive were blended for 10 min at 100 rpm. If a non-melt-blendable additive was used, the plastic and additive were blended for 10 min at 150 rpm. If fibrillar PTFE was used as an antidrip additive, the resin and PTFE were blended first for 10 min at 150 rpm. (The PTFE used was DuPont PTFE 30, an aqueous suspension of small PTFE particles. The density of this suspension was 1.3 g/mL and was 60% PTFE. For ABS, the PTFE had to be blended into the resin. For PC resin, the 0.1 wt % PTFE was preblended into the resin.) Then the flame-retardant additive was added and the plastic was blended again for 10 min at 150 rpm. After blending was completed and the blades were stopped, the bowl was opened and the molten plastic removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

### General Procedure for Extruding Plastic into UL-94 Test Bars

The plastic removed from the Brabender was broken into smaller pieces and inserted into the heated blending cup of the CSI-183MMX blender until the cup was full. The plastic was heated until molten and then extruded into a heated $\frac{1}{8}''$ thick × $\frac{1}{2}''$ wide × 3″ long rectangular bar mold. Heating temperatures for the blending cup and the extrusion mold varied, depending on the material involved. The general processing temperatures for the plastics used are as follows. ABS: blending cup temperature, 225–230°C; mold temperature, 40–90°C. PC: blending cup temperature, 270°C; mold temperature, 71–93°C.

### General Procedure for Modified UL-94 Burn Test

Two $\frac{1}{8}''$ thick × $\frac{1}{2}''$ wide × 3″ long plastic (polymer + additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame-test station. The setting on the methane tank pressure regulator was set to 23 psi; the pressure regulator on the HVUL-94 test station was set to 5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. All test bars underwent two trials, each trial consisting of ignition for 10 s, followed by flame removal and the time to self-extinguishing recorded.

## RESULTS AND DISCUSSION

Aromatic boronic acids are typically synthesized by lithium–halogen exchange, using alkyllithium reagents with an aromatic halide, or by reaction with magnesium metal to generate an aromatic Grignard reagent; this aryllithium or Grignard reagent is then added to a trialkylborate to generate the aromatic dialkoxyboronate.[13–17] The boronic ester is then hydrolyzed with acid or water to generate the boronic acid. Traditional Grignard and organolithium techniques were used to generate the diboronic acid from 1,4-dibromobenzene. The use of $n$-BuLi generated only 1-halo-4-benzeneboronic acids, indicating incomplete lithiation [eqs. (3) and (4)]. Reactions attempted with Mg metal did generate the diboronic acid, but only in low yields (20–25%) . The use of *tert*-BuLi in THF at −78°C successfully generated the diboronic acid on quenching the 1,4-dilithiobenzene with trimethylborate. Hydrolysis of the 1,4-bis(boronic ester) with dilute acid gave yields ranging from 70 to 75% for diboronic acid **1**.
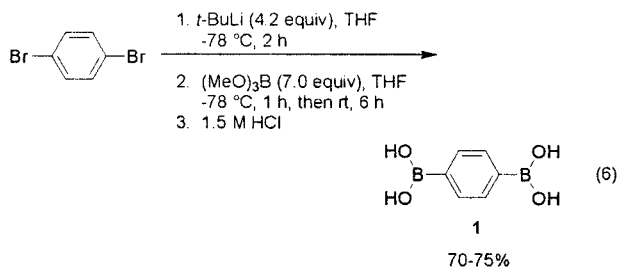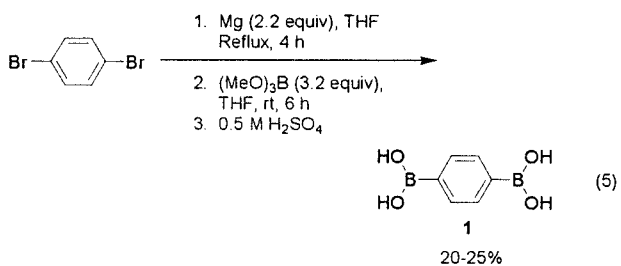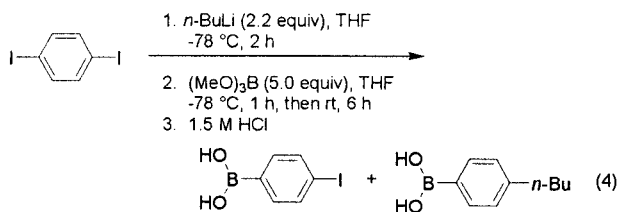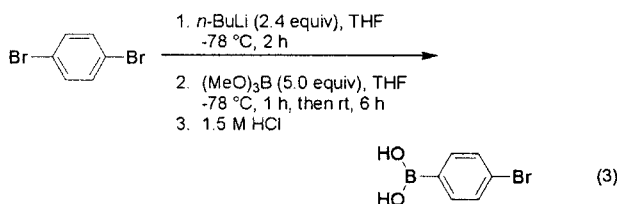


This organolithium methodology has several disadvantages. First, it does not lend itself to easy synthetic scale-up. Second, this reaction does not give the diboronic acid cleanly. In all reactions, there is a small amount of 1-bromo-4-benzeneboronic acid formed during the reaction that could not be separated from the diboronic acid. Also, small amounts of oligo(*p*-phenylene)s are seen that cannot always be removed from the recovered diboronic acid.[17] Because of these problems, we searched for other synthetic routes to the diboronic acid **1**. There are reported palladium-catalyzed reactions that convert aromatic bromides, iodides, or triflates to aromatic pinacolboronates.[21,22] One of the techniques uses bis(4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane), or pinacol diboron, to generate the pinacolboronate.[21,22] However, this reactant is very expensive and half of the boron reagent is squandered during the reaction, thereby making it a poor choice for generating commodity flame retardants. The other reaction uses 4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane, or pinacol borane, to generate the pinacolboronate.[20] This methodology was used to generate the 1,4-benzenebis(pinacolboronate) that was further hydrolyzed with 3$M$ HCl to generate the diboronic acid, albeit in a low yield.
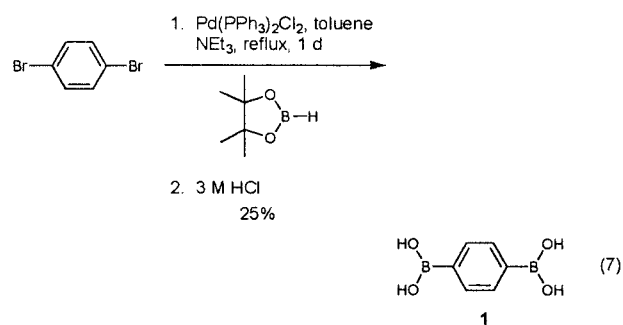


We then looked to potentially more reactive nickel catalysts to use in this reaction. Four nickel catalysts were investigated: (1,1-bis-(diphenyphosphino)methane)nickel(II) chloride (Ni(dppm)Cl$_2$), (1,2-bis(diphenyphosphino)ethane)nickel(II) chloride (Ni(dppe)Cl$_2$), (1,3-bis-(diphenyphosphino)propane)nickel(II) chloride (Ni(dppp)Cl$_2$), and (1,4-bis(diphenyphosphino)-butane)nickel(II) chloride (Ni(dppb)Cl$_2$) [eq. (8) and Table I].

**Table I   Nickel Catalyst Study Results**

| Catalyst | Ratio **3 : 4** | Yield **3** |
|---|---|---|
| Ni(dppm)Cl$_2$ | 0 : 1 | 0 |
| Ni(dppe)Cl$_2$ | 1 : 0 | 60% |
| Ni(dppp)Cl$_2$ | 10 : 1 | 65% |
| Ni(dppb)Cl$_2$ | 1 : 4 | 10% |



(8)
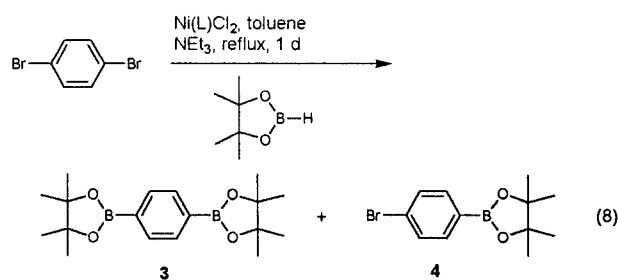
Optimal results were obtained when Ni(dppp)-Cl$_2$ was used, giving a yield of 65% after acid hydrolysis. The nickel-catalyzed reaction was cleaner than the previously reported palladium-catalyzed reactions with no oligo(p-phenylene)s formed and very little 4-bromophenylpinacolboronate (**4**) being observed. It is known that with the palladium-catalyzed reaction, the other products often obtained are dehalogenated aromatics,[20] such as benzene, or partially reacted dehalogenated aromatics, such as phenylpinacolboronate. With the nickel-catalyzed reaction, some of these products were observed in the crude reaction mixture, indicating a potentially similar reaction mechanism that would account for some of the mass loss observed with the 65% yield. Compound **4** was easily removed during crystallization of **3** from methanol. Acid hydrolysis also converts the pinacol to pinacolone by the pinacol rearrangement.[23–25]



(9)
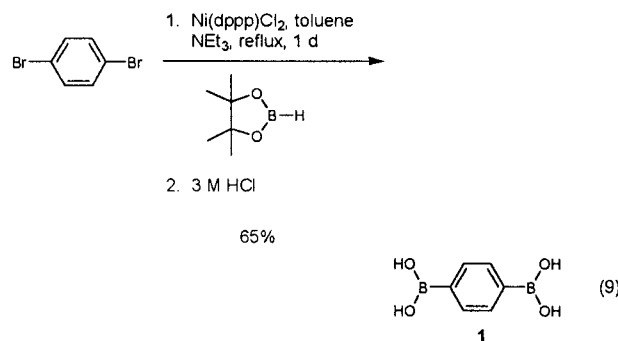
Synthesis of triboronic acids was attempted using organolithium techniques, but these failed

to give the desired products. Use of *tert*-BuLi with 1,3,5-tribromobenzene resulted in 1-bromo-3,5-benzenediboronic acid as the only isolable product. Using *tert*-BuLi with 2,4,6-tribromophenol resulted in no identifiable product. However, the nickel-catalyst reaction with pinacol borane was applicable to the synthesis of 1,3,5-benzenetriboronic acid (**2**) after hydrolysis.



(10)
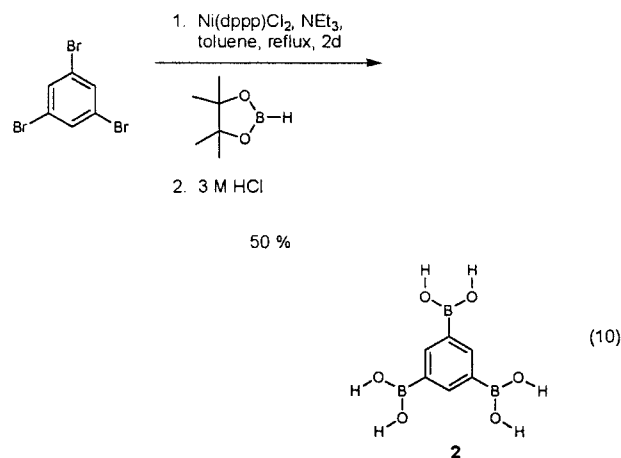
Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to analyze the synthesized boronic acids for their thermal properties. Both TGA and DSC analysis were done at 10°C/min under a N$_2$ atmosphere. With DSC analysis, an endothermic event was noted for boronic acids **1** and **2.** This event was assigned to the loss of water that occurs on transformation from the boronic acid to the corresponding boroxine network. It is noteworthy that no exothermic events were observed, indicating that crosslinking to form a network occurred as an endothermic event with boronic acids. Note that exothermic events are usually seen with other crosslinking groups such as alkynes.[1] It is this boroxine formation that leads to such high char for these materials. At first glance, TGA and DSC hint at decomposition of the potential flame retardant. This is not the case, however, as a more thermally stable material, the boroxine network, is being formed at elevated temperatures. Although the boronic acid functionality is no longer intact at temperatures above 180°C, the boroxine network formed at these temperatures shows no further decomposition until approximately 450°C by TGA. For comparison, thermal data are included for phenylboronic acid (**3**). Phenylboronic acid, having only one boronic acid group, does form a boroxine at 215–220°C, as indicated by the endothermic event observed. However, after boroxine formation, the phenylboroxine sublimes away as indicated by

**Table II    Thermal Characteristics of Boronic Acids**

| Compound | TGA Data | | | DSC Data | |
|---|---|---|---|---|---|
| | Decomposition Onset (°C) | Early wt Loss (°C) | Char Yield at 900°C (wt %)[a] | Event Ranges (°C) | Event Peaks (°C) |
| **1** | 180 | 230[b] | 40 | 180–230[c] | 210[d] |
| **2** | 180 | 230[e] | 48 | 200–260[c] | 245[d] |
| **3** | 60 | 220[f] | 0[g] | 215–220[c] | 217[d] |

[a] Char yield is 100 wt % − wt % remaining at 900°C.
[b] 20 wt % lost.
[c] Endothermic event.
[d] Maximum absorbance temperature of endothermic event.
[e] 22 wt % lost.
[f] 5 wt % lost.
[g] 100 wt % lost at 400°C.

the TGA results. This result is not surprising since the phenylboronic acid cannot form an extended network as with boronic acids **1** and **2**. The specific data for the above-mentioned compounds are shown below in Table II.

## Flame-Retardant Testing

There are a number of flame-retardancy tests used, each measuring specific flammability aspects of the material tested. Because of the limited amounts of flame-retardant additive available to us for testing, we initially chose to restrict our analysis to one test that would allow us to screen polymer/additives blends and give us a general idea of flame retardancy, that is, the industry standard UL-94 test. This test permits us to rapidly study the blends and their dripping properties. Future tests will include limiting oxygen index (LOI) and cone calorimetry to provide a clearer understanding of the potential mechanisms of action. Since many plastic components in aircraft interiors are above or on the side of the passengers,[26] ignited molten polymer becomes a major concern for fire safety, and hence our first area for analysis.

The UL-94 flame test is performed such that the plastic sample is suspended above a cotton patch.[27] The plastic is subjected to two 10-s ignitions with a calibrated methane-fueled flame in a controlled-size unit that is free of passing air currents. After the first ignition, the flame is removed, and the time for the polymer to self-extinguish is recorded. Cotton ignition is noted if polymer dripping ensues. Then the second bar ignition is performed on the same sample and the

self-extinguishing time and dripping characteristics are recorded. If the plastic self-extinguishes in less than 10 s after each ignition, with no dripping, it is considered to be a V-0 material, an industry standard for flame retardancy. Dripping is permissible if no cotton ignition results. However, we sought to achieve no dripping results, for the reasons discussed earlier. Flame-retardant testing was done with ABS and PC resins. Polycarbonate (PC) was initially chosen for study because of its use in aircraft interiors and other engineering plastic applications. ABS is another engineering plastic, lower in cost than PC, but significantly more flammable, making it a challenging target for achieving flame retardancy. The predominant boronic acid tested was diboronic acid **1**, but there was one experiment with triboronic acid **2**.

An antidrip additive is always needed with ABS. One that is commonly used is 25% chlorinated polyethylene (ClPE). Without this compound, the ABS drips excessively on burning, preventing an accurate assessment of flame retardancy. All results shown in Table II incorporate ClPE of 10 wt %, unless otherwise mentioned. Fibrillar polytetrafluoroethylene (FPTFE) was also used as an antidrip additive in some cases. All of the results for the ABS blends obtained by this test were not quantifiable by the UL-94 test, but the results observed are intriguing and promising. In all experiments, char was observed and some flame-retardant effects were seen. In most cases in which a boronic acid was used, the bar burned very slowly to the clamp by a very small flame around the exterior of the bar. Char usually remained that could not be reignited; it glowed
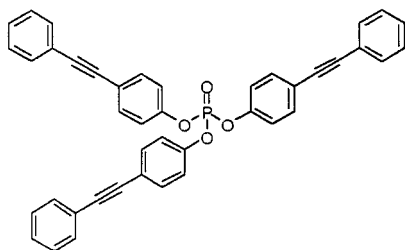
**Scheme 1**  TPEPP.

only briefly on reapplication of the flame in the second ignition attempt. It is significant that char remained after burning ABS that contained diboronic acid **1**, since ABS with no flame retarding additive leaves no char. This might indicate that the boron oxide glass/boroxine networks formed by these boronic acids are assisting in char formation and flame retardancy. Many different compounds were screened as potential synergists in an attempt to obtain a V-0 result. Magnesium hydroxide [Mg(OH)$_2$] was added as a potential synergist for the boronic acids because of its ability to decompose endothermically and release water at temperatures higher than 330°C.[28] Other materials included brominated flame retardants such as decabromodiphenyl ether (Deca) and tet-

rabromobisphenol A (TBBPA). These were chosen to see whether a low-halogen system could be created if a nonhalogenated system failed to give the desirable UL-94 result. The last additive tried was an alkyne-containing phosphate, tri[(4-phenylethynyl)phenyl]phosphate[2] (TPEPP, Scheme 1). The two condensed-phase mechanisms available to this phosphate may work in concert with the boronic acids to yield a superior flame-retardant system for ABS. The results of these tests are shown in Table III.

ABS containing the diboronic acid **1** with the ClPE antidrip additive gave very long burn times with no dripping. The flame moved very slowly along the exterior of the bar with almost no deformation of the plastic monolithic structure. ABS/**1** with FPTFE as the antidrip additive gave very similar burn times to the ClPE results. The only observed difference between the two additives was that slightly more contraction of the plastic bar occurred with FPTFE-containing bar. In contrast, boronic acid–free ABS with either antidrip additive suffered immediate contraction into a flaming wad of burning plastic. Higher weight percent loading of **1**, specifically 20 wt %, lowered the burn times as expected but still did not give a UL-94 V-0 result. The cooling effect

**Table III  UL-94 Burn Results for ABS with the Listed Additive**

| Additive | First Ignition[a] (s) | Observed Dripping[b] | Second Ignition[a] (s) | Observed Dripping[b] | UL-94 Rating |
|---|---|---|---|---|---|
| 10 wt % **1** | 335, 320 | No, No | 3,[c] 2[c] | No, No | — |
| 20 wt % **1** | 289, 295 | No, No | < 1,[c] < 1[c] | No, No | — |
| 10 wt % **1** + 10 wt % Mg(OH)$_2$ | 273, 290 | No, No | 5,[c] 5[c] | No, No | — |
| 10 wt % **1** + 20 wt % Mg(OH)$_2$ | 224, 234 | No, No | 10,[c] 10[c] | No, No | — |
| 10 wt % **1** + 5 wt % "Br" (Deca) | 113, 109 | Yes,[d] Yes[d] | X, X | X, X | — |
| 10 wt % **1** + 5 wt % "Br" (TBBPA) + 2.5 wt % Sb$_2$O$_3$ | 263, 171 | No, Yes[d] | 12,[c] 4[c] | No, No | — |
| 10 wt % **1** + 10 wt % TPEPP | 173, 203 | No, No | < 1,[c] < 1[c] | No, No | — |
| 10 wt % **1** + 0.5 wt % FPTFE | 347, 337 | No, No | < 1,[c] < 1[c] | No, No | — |
| 10 wt % **2** | 304, 293 | No, No | < 1,[c] < 1[c] | No, No | — |

[a] Time(s) to self-extinguishing after first, second, or third 10-s ignition.
[b] Indicates that molten ABS did (Yes) or did not (No) drip onto cotton patch underneath ignited bar during UL-94 test. X indicates not enough bar remaining for second ignition.
[c] Indicates time that only glowing, not flame, occurred after reapplication of flame.
[d] Indicates ignition of cotton patch underneath ignited bar of plastic.

**Table IV    UL-94 Burn Results for Polycarbonate**

| Additive | First Ignition[a] (s) | Observed Dripping[b] | Second Ignition[a] (s) | Observed Dripping[b] | UL-94 Rating |
|---|---|---|---|---|---|
| 10 wt % **1** | 40, 24 | No, No | 8, 8 | Yes,[c] Yes[c] | V-2 |
| 5 wt % **1** | 5, 7 | No, No | 9, 9 | No, No | V-0 |
| 2.5 wt % **1** | 8, 6 | No, No | 8, 16 | Yes,[d] Yes[d] | V-1 |

[a] Time(s) to self-extinguishing after 10-s ignition.
[b] Indicates that molten PC did (Yes) or did not (No) drip onto cotton patch underneath ignited bar during UL-94 test.
[c] Indicates ignition of cotton patch underneath ignited bar of plastic.
[d] Indicates dripping after extinguishing, with no ignition of cotton patch underneath bar of plastic.

provided by water release in $Mg(OH)_2$ at elevated temperatures has led to its use as a flame retardant in commercial applications, but it is also plagued with poor melt-blendability.[28] $Mg(OH)_2$ lowered the burn times but the char that remained glowed longer on removal of the flame. The brominated compounds that were tried did not improve the flame retardancy of the ABS blend containing the diboronic acid. When brominated additives were blended along with **1**, less char formed and the char that did form broke apart more easily. Even when using TBBPA, a melt-blendable additive, with a $Sb_2O_3$ synergist, less char was observed during burning and the obtained results were not impressive. This indicates that brominated aromatic flame retardants are incompatible with diboronic acids. Alkyne phosphate TPEPP, however, did show some effectiveness with **1**. The burn times dropped significantly, and the char that remained after the test ended was observed to be thicker and more profuse than the char observed without TPEPP. The two crosslinking mechanisms of this alkyne phosphate seem to work nicely with diboronic acid **1.** It is interesting to note that 10 wt % of TPEPP with only 10 wt % ClPE and no boronic acid gives no noticeable flame retardancy to ABS. Triboronic acid **2** was briefly tested, showing a slight improvement in burn times over **1**, indicating that the extra boron on **2** does seem to help with flame retardancy for the ABS system. Interestingly, from the **1**- or **2**-containing systems, a second ignition does nothing to the remaining intact charred bar; the bar simply glows momentarily before nearly immediate extinguishing. Although these boronic acid systems do not permit one to pass a V-0 UL-94 flame test, the prolonged burn times, nondeformation of the plastic on burning, and non-reignition capabilities make these additives extremely intriguing for further study.

PC was also tested using the UL-94 flame test. In all tests, 0.1 wt % fibrillar PTFE was used as an antidrip additive. Without this antidrip additive, major dripping occurs shortly after ignition, making flame retardancy difficult to assess. Since diboronic acid **1** releases water to form the boroxine network at PC processing temperatures, it was blended into PC using a Brabender mixer head. The folding action provided by the Brabender roller-type blades allowed good blending of the compound **1** into PC. Loadings of 10 wt % **1** gave a UL-94 V-2 result, little different from PC with no additives. Additive loading of 2.5 wt % **1** gave a V-1 result, and 5 wt % loading of diboronic acid **1** gave a V-0 result. In all results, however, large amounts of char were seen to form during the flame test. This indicates that the boroxine network of **1** formed during blending assisted in char formation during flame conditions. The specific burn times and data from this testing are shown in Table IV. Therefore, these compounds serve as excellent nonhalogenated flame retardants for PC when added in small loading amounts.

**Preliminary Flame-Retardancy Mechanism Studies for Boronic Acids**

The observance of char seen during the UL-94 testing of the ABS and PC blends strongly suggests a condensed-phase mechanism of flame retardancy.[3–8] Using TGA analysis of the ABS/boronic acid and PC/boronic acid blends, we observed slight increases in char yields for the blends above their theoretical char yields. The method for calculating the theoretical yields is listed in the Experimental section and the data collected are shown in Table V.

Since the boronic acid loses water to form the boroxine at the blending/processing temperatures of ABS and PC (225 and 270°C, respectively), the boronic acid is being blended into the plastics as the boroxine glass network. When the plastic begins to burn and decompose, these boroxine networks, or organoceramic layers, may be acting as a barrier to fuel transport. Specifically, they are

**Table V   TGA Char Yields for ABS/ and PC/Boronic Acid 1 Blends**

| Sample | Theoretical Char Yield (wt %) | Actual Char Yield (wt %) | Onset of Decomposition (°C) |
|---|---|---|---|
| ABS | — | 2.9 | 385 |
| PC | — | 24.4 | 475 |
| ClPE | — | 0 | 280 |
| 20 wt % **1**, 10 wt % ClPE in ABS | 10.0 | 13.5 | 350 |
| 10 wt % **1**, 10 wt % ClPE in ABS | 6.3 | 7.2 | 385 |
| 10 wt % **1** in ABS | 6.6 | 7.5 | 385 |
| 10 wt % **1**, 0.5 wt % FPTFE in ABS | 6.6 | 8.3 | 400 |
| 5 wt % **1**, 0.1 wt % FPTFE in PC | 25.2 | 30.0 | 450 |
| 10 wt % **1**, 0.1 wt % FPTFE in PC | 26.0 | 31.4 | 450 |

slowing the release of fuel from the decomposing plastic to the flame front.[3–8] Furthermore, the char formation may occur through prevention of fuel flow to the flame front. Small molecules and decomposition products containing free radicals now have longer residence times in the condensed phase and, as such, are more likely to form char.[3–8] These effects could explain the prolonged and sustained burning observed with the ABS samples. The effects are amplified depending on the antidrip additive used. For example, in ABS, ClPE does not cause much bar contraction or shape deformation during burning, but it does prevent dripping of the molten polymer. FPTFE does cause bar contraction and shape deformation on burning, and this exaggerated effect most likely draws together the boroxine networks. This action from FPTFE now forms thicker layers of organoceramic material that can create a greater barrier to fuel release. This thicker barrier could explain the slightly longer burn times observed during the UL-94 test and the increased amount of char seen with TGA. In addition, FPTFE seems to slightly increase the onset of decomposition temperatures, indicating that the thicker layer of boroxine networks may have an added thermal insulation effect as well as acting as a barrier to mass transport of fuel to the flame front. With the PC samples, increases in char yields are also observed, indicating that the boroxine networks are working in a manner similar to that proposed for ABS blends. Specifically, the boroxine networks are preventing fuel transport to the flame front and promoting char formation, thus giving flame retardancy to PC.

During the UL-94 testing of these boronic acid/polymer blends, we observed a phenomenon that qualitatively points to a condensed-phase mechanism for these aromatic diboronic acids. Initially, we tried blending phenylboronic acid (**3**) (a monoboronic acid) at 20 wt % loadings into high-impact polystyrene (HIPS) and ABS to see if any flame retardancy occurred. Both of these blends failed the UL-94 test, but a green flame was observed coming from the burning plastic. Boron compounds give off a characteristic green flame when burned[29] and this effect led us to believe that the phenylboronic acid, which at 220°C either sublimes or boils away, was entering the vapor phase and combusting, thus providing the green flame. However, when using any of the ABS blends containing diboronic acid **1**, even at loadings of 20 wt % **1**, no green flames were observed. This may result because diboronic acid **1** is forming large boroxine networks that do not sublime or boil out at elevated temperatures, as indicated by DSC and TGA analysis. Although this result is based on a rather simplistic elemental analysis flame test, it nevertheless suggests that the flame-retardancy effect of diboronic acids is the result of a condensed-phase, not vapor-phase, mechanism. Further work and more detailed analysis of the mechanisms of these materials are currently being investigated.

## CONCLUSIONS

Diboronic acid **1** was successfully synthesized in good yields, using either organolithium (*tert*-BuLi) reagents or nickel-catalyzed reactions with pinacol borane. Even though organolithium techniques failed to yield triboronic acid **2**, the nickel-catalyzed reaction with pinacol borane did give the desired compound cleanly and in a reasonable yield. DSC and TGA testing of these two boronic acids showed they were good char-yielding compounds, forming a crosslinked boroxine network through an endothermic event, specifically the loss of water. These two materials were then blended into ABS and PC res-

ins, and tested with the UL-94 flame test. Flame retardancy has been shown in PC and ABS resins with the use of 1,4-benzenediboronic acid (**1**). UL-94 V-0 results were obtained with 5 wt % of diboronic acid **1** in PC. Whereas diboronic acid **1** failed to give a quantifiable UL-94 result in ABS, the observation of char that could not be reignited is noteworthy. TGA analysis of the ABS and PC blends containing diboronic acid **1** suggested that the boronic acid mechanism of flame retardancy is related to the formation of boroxine layers, created by the heating of **1**. The increases in char yields observed by TGA suggest that the boronic acids are working to give flame retardancy to ABS and PC through char formation and the prevention of fuel molecules to the flame front. Additional research and other flame testing will be done to help determine a more precise flame-retardancy mechanism that occurs in the presence of boronic acids. As a result of the observed condensed-phase flame retardancy with these boronic acids, these materials may find further use in these two resins, or possibly in other thermoplastic resins.

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