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Synthesis and Flame Retardant Testing of New Boronated and Phosphonated Aromatic Compounds

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Abstract: The present report describes the preparation and use of some dimethyl terephthalate derivatives in transition metal-catalyzed coupling reactions to produce new reactive flame retardants. Dimethyl iodoterephthalate and dimethyl 2,5-diiodoterephthalate were successfully employed in the preparation of phosphonic and boronic esters and acids. The latter were tested for heat release with a micro combustion calorimeter (ASTM D7309) to determine the potential for heat release reduction of these flame retardant molecules. The results showed that the addition of boronic or phosphonic acids greatly lowered the heat release, due to a condensed phase (char formation) mechanism. Adding ester groups to the boronic acids or phosphonic acids could either completely remove all flame retardant effects or make the molecule act more like a vapor phase flame retardant. Finally, the various potential flame retardants were solvent blended with a thermoplastic polyurethane to assess their flammability reduction effects by micro combustion calorimetry. The results of these experiments found that the molecules that reduced heat release the most by themselves showed the greatest reduction in heat release in a polyurethane as well, with the boronic acids yielding the greatest reduction in heat release.

Introduction

While modern polymeric materials bring many benefits by their use in society, they typically suffer from flammability / fire risk issues, and so they may be flame retarded to provide fire protection in a variety of fire risk scenarios. Wood is certainly a flammable material, but there are commodity plastics in use today in furniture, consumer goods, and clothing that have heat releases and fire risk potentials far greater than that of cellulosic matter.[1-5] When a polymeric material requires a flame retardant to be used/sold in a particular application, one can use a non-reactive flame retardant molecule/polymer, which is blended into the polymer, or one can use a reactive flame retardant molecule, which bonds directly to the polymer during polymerization or *via* side-chain/grafting reactions.[6, 7] With concerns about environmental persistence of some flame retardant additives that are not bound to the polymer which may leach out over time[8-13], the use of reactive flame retardants becomes more attractive. Further, there is a desire to develop condensed phase (char forming) reactive flame retardants, so more of the polymer fuel can be converted into low-flammability carbon char (graphite/glassy carbon) rather than the polymer mass being pyrolyzed as high heat release decomposition products.[3, 6] To that end, we have proposed the synthesis of boron and phosphorus functionalized reactive molecules which could co-polymerize with thermoset-type polymers such as epoxy and polyurethane. Boron has shown some interesting condensed phase activity when available in a boronic acid / boroxine structure[14, 15], and phosphorus-based structures are well known for creating char in polymers containing heteroatoms such as nitrogen and oxygen in the polymer structure.[6, 16] Due to the efficacy of boron and phosphorus in flame retardancy, we have focused on the use of catalytic processes to add boron and phosphorus based groups to aromatic compounds such as terephthalates and phenols. This has been done since these compounds could in turn act as

reactive flame retardants which could address some of the environmental/leaching issues that affect flame retardant materials.

Establishing the chemical structure-property relationships prior to scale-up of a new flame retardant is very important, and goes back to the case of considering reactive vs. additive flame retardants. Making reactive flame retardants is not a trivial activity, since those same reactive groups may lead to short shelf lives for the flame retardants, or, high cost of synthesis due to protection/deprotection schemes needed in the synthesis of those molecules. Therefore, knowing *what* to scale up is of as much importance as discovering a possible compound for flame retardant evaluation. If funding is limited for discovery or scale-up, and not both, one needs good measurement tools to ensure the right molecule is made for evaluation. This becomes difficult when the success of flame retardancy is determined by larger scale regulatory pass/fail tests, and so a much smaller scale test is needed to quantify the effectiveness of the flame retardant prior to scale-up. There is a wealth of organic chemistry available which can identify how to make the target flame retardant molecule, but without confirmation from a small-scale test, one may have to expend large amounts of resources to make enough material for the regulatory pass-fail tests if the chemistry is difficult or low-yielding. Therefore we believe that studying flammability of small molecules themselves, followed by simple experiments of mixing the potential flame retardants into a polymer, is a reasonable approach to take for identifying and screening flame retardant potential prior to scale-up, and that is the key concept behind this paper.

In the current report, we wish to provide some details of their use in the generation of phosphonic and boronic esters and acids. The target phosphonic and boronic esters and acids were tested for heat release/char formation potential with a pyrolysis combustion flow

calorimeter (PCFC), a small scale standard method which mimics flammability phenomena of pyrolysis and oxidation quite well.[17-21] In order to compare the charring and lowered heat release potential of these new structures, we also measured the heat release of terephthalic acid, dimethyl terephthalate, and hydroquinone, which served as non-flame retardant standards, thus allowing us to study structure/property relationships prior to scale-up and incorporation of these molecules into polymers for larger scale flammability testing. We then combined these flame retardants into a thermoplastic polyurethane (TPU) which could serve as a small-scale mimic for a polymer with a high need for new flame retardant chemistry; polyurethane. Because polyurethane foams can be difficult to synthesize at small scale, trying a small scale mimic test makes them an excellent candidate for this study. More importantly though, polyurethanes, especially flexible polyurethane foams, represent a notable fire threat in the home which requires new flame retardants that lower heat release while enhancing char formation to slow down flame spread and time to flashover (total fire loss) conditions.[22-24]

Results and Discussion

The research was composed of three parts. The first was the synthesis of potential reactive flame retardants. The second part was studying these potential flame retardants by themselves *via* PCFC to see what their potential for heat release and char formation would be. Finally, these substances were combined with a thermoplastic polyurethane (TPU) and tested again *via* PCFC to see if the findings from the 2nd part justified the synthesis of the materials in the 1st part. If successful, this approach would begin to help solidify a testing scheme and screening criteria for new potential flame retardants, thus telling the chemist what to focus on from a resource perspective.

Part I. A. Preparation of monophosphonic and monoboronic esters/acids. Several structures containing a single phosphonic or boronic ester (or acid) functionality were prepared using dimethyl iodoterephthalate **1.** Although the latter has been mentioned in the scientific literature[25], no particular reference provides explicit protocol for its preparation and characterization. We prepared it in a single step, from commercially available dimethyl aminoterephthalate (Scheme 1). The latter was diazotized in H_2O/H_2SO_4 mixture, followed by treatment with aqueous KI solution.[26] Compound **1** was subjected to transition metal-catalyzed coupling reactions in order to introduce phosphonic or boronic ester functionality.
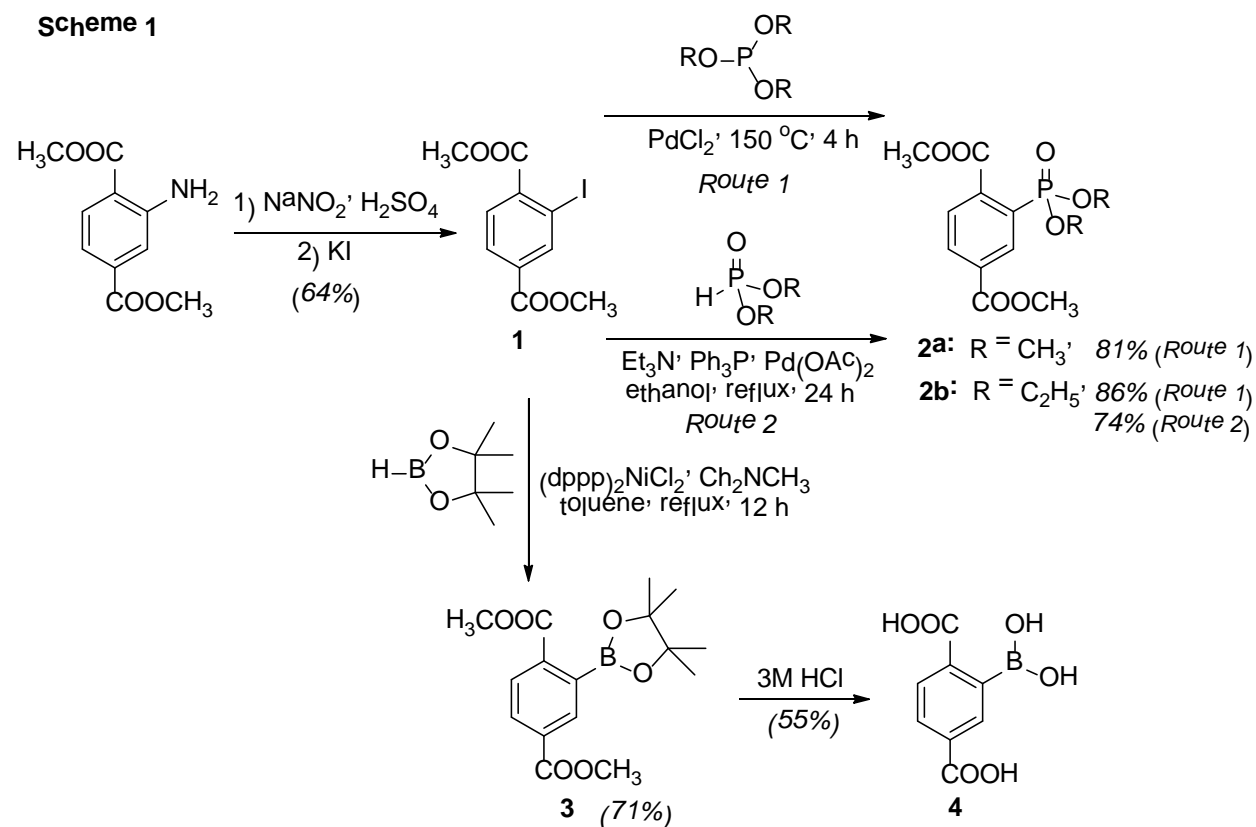
Scheme 1

The preparation of phosphonic esters was successfully accomplished following one of two general strategies, utilizing a trialkyl- or a dialkylphosphite correspondingly (*Route 1* and *Route 2*, Scheme 1). Thus trimethylphosphite and triethylphosphite were successfully employed in the

preparation of compounds **2a,b** (*Route 1*). The protocol was adapted from a patented work of Hashiba *et al.* and involves reaction of **1** with a large excess of the trialkylphosphite (also used as a solvent in these conditions), at elevated temperature, in the presence of $PdCl_2$ as a catalyst.[27]

The generation of phosphonate esters with dialkylphosphites as starting materials was accomplished following the procedure of Dezfuli and Goosen (*Route 2*).[28] The reactions were conducted in ethanol as a solvent, in the presence of base (triethylamine or dicyclohexylmethylamine) and $Pd(OAc)_2/Ph_3P$.

Iodoterephthalate **1** proved to be also an excellent starting material for the introduction of a boronic ester moiety. In particular, the cyclic boronic ester **3** was prepared in good yield, using $(dppp)_2NiCl_2$ as a catalyst (Scheme 1).[29] The reaction was carried out in the presence of triethylamine or dicyclohexylmethylamine, as a base, leading to the product in similar yields. Finally, pinacolboronate **3** was hydrolyzed in acidic conditions (3M HCl) to yield the boronoterephthalic acid **4**. Earlier attempts to prepare **4** from 2-bromo-*p*-xylene, using Grignard chemistry followed by permanganate oxidation, were not successful. We demonstrated that in basic conditions a novel dimeric sodium salt of **4** was isolated, instead of the free acid.[30]

Part I. B. Preparation of diboronic esters/acids. *p*-Xylene was diiodinated by using periodic acid/iodine, in a mixture of acetic acid, sulfuric acid and water, to yield 2,5-diiodo-*p*-xylene **5** (Scheme 2).[31] Compound **5** was subjected to oxidation, using $KMnO_4$ in a *t*-butanol/water solvent mixture, followed by acidification, to yield 2,5-diiodoterephthalic acid **6**. Fischer esterification of the acid in excess methanol, using sulfuric acid as a catalyst, generated the dimethyl ester **7**. Compound **7** was then subjected to transition metal catalyzed coupling, utilizing two different methods: 1) Use of pinacolborane, with $(Ph_3P)_2PdCl_2$ as a catalyst and Et_3N as a base, in toluene[29], or 2) Use of bis(pinacolato)diboron, with $(dppf)_2PdCl_2$ as a catalyst

and KOAc as a base in DMF. The cyclic diboronic ester **8** was generated following either route, although in both cases significant amounts of bi-products were generated. Method (1) yielded consistently mixtures of the target **8**, the monoboronic ester **3**, and dimethyl terephthalate, i.e. bi-products of hydrodeboronation. Following Method (2) the main impurity was a highly insoluble, likely polymeric material, whose formation could speculatively be based on a Suzuki coupling reaction between the starting diiodide **7** and the product **8**.

Diboronic ester **8** was successfully hydrolyzed to 2,5-diboronoterephthalic acid **9**, using conditions similar to those employed in the preparation of **4** (3M HCl).

Scheme 2
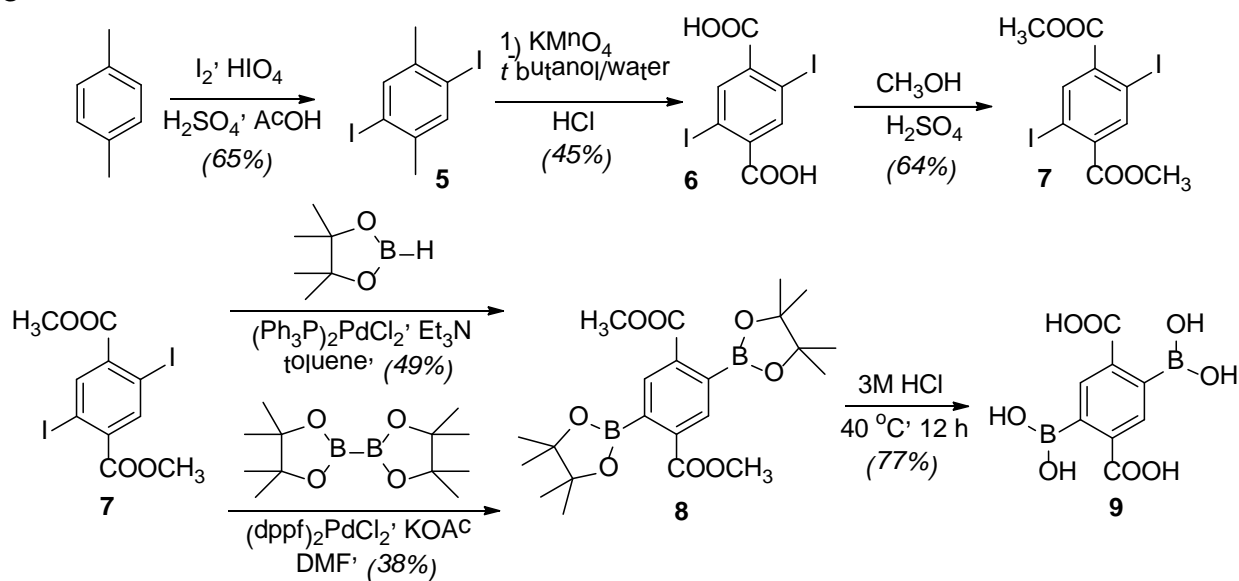
Part II. Thermal Analysis and Micro Combustion Calorimeter Studies. To understand the ability of these molecules to serve as flame retardants, we chose to study their inherent heat release *via* the use of a microscale combustion calorimetry technique. This technique, known as pyrolysis combustion flow calorimetry (PCFC) is an ASTM standard method for measuring the heat release of organic materials *via* oxygen consumption calorimetry. The method is a standard technique under ASTM D7309, and has been successfully used to measure the heat release

(inherent flammability) of a wide range of polymers, flammable solids & liquids, and small molecules.[17,18.19,29,21]   In this study we investigated the target molecules described above (Structures **2 – 4** and **9**, Figure 1), using the PCFC method. Also included in the study were 2-phosphonoterephtahlic acid **11**, whose preparation we recently reported[32], and hydroquinone **14**, with a cyclic phosphonate ester functionality.[33] It was found that a significant portion of the studied structures did show reductions in their inherent flammability (heat release) but the amount of reduction is very chemical structure-dependent.
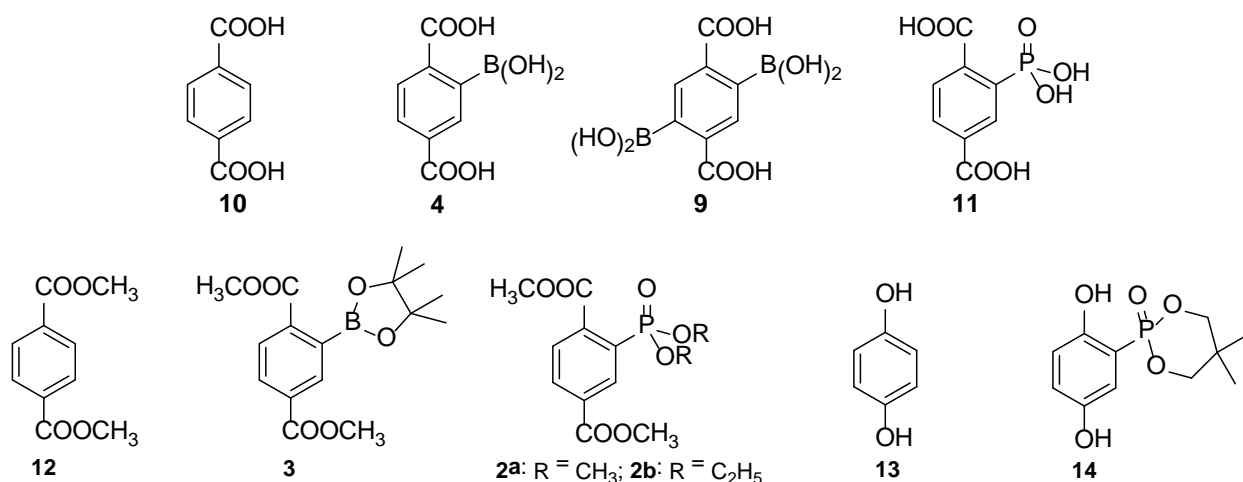

Figure 1. Structures of several flame retardants, studied by pyrolysis combustion flow calorimetry (PCFC).

Typical results from the PCFC focus on heat release measurements and the results that were recorded from each of the materials are shown in Table 1. The data in the table covers the following measurements:

- Char yield: Obtained by measuring the sample mass before and after pyrolysis. The higher the char yield, the more carbon/inorganic material left behind. As more carbon is left behind, the total heat release should decrease.

- HRR Peak(s): The recorded peak maximum of heat release rate (HRR), found during each experiment. The higher the HRR value, the more heat given off at that event. This value

roughly correlates to peak heat release rate that would be obtained by a cone calorimeter. The temperatures at which the peak HRR was detected are listed as well.

- Total HR: This is the total heat release (HR) for the sample, which is the area under the curve(s) for each sample analysis. The % reduction in total heat release is also given.

- Char Notes: Description of the sample residues collected from each test.

Table 1. PCFC summary data for compounds **2 – 4**, and **9 - 14**.

Compound	Char Yield (wt%)	HRR Peak Value (W/g)	HRR Peak Temps (°C)	Total HR (kJ/g)	% HR Reduction	Char Description
10	0.0	450	378	19.3	0	none visible
	0.0	441	382	19.4	0	
	0.0	501	380	19.4	0	
4	41.2	181, 89	355, 481	9.6	50.5	1/2 pan of black foamy residue
	41.5	160, 91	355, 483	9.4	51.5	
	35.3	180, 83	355, 481	9.6	50.5	
9	66.1	5, 21	365, 407	0.7	96.4	dark brown powder
	66.0	5, 20	365, 406	0.7	96.4	
	65.9	5, 21	365, 407	0.7	96.4	
11	43.2	69	475	4.3	77.8	pan full of black shiny foamy residue
	44.6	65	477	4.1	78.9	
	45.1	59	475	4.1	78.9	
12	0.0	613	247	16.8	0	none visible
	0.0	611	249	22.7	0	
	0.0	619	248	19.5	0	
3	2.0	710	295	23.3	-18.9	black shiny oil film on bottom
	3.2	838	292	22.9	-16.8	
	2.6	782	294	22.6	-15.3	
2a	0.0	402	326	17.9	8.7	very thin gray film on bottom
	0.0	390	323	17.5	10.7	
	0.0	399	324	17.6	10.2	
2b	0.0	44, 345	175, 312	18.1	7.7	none visible
	0.0	44, 333	183, 315	18.4	6.1	
	0.0	41, 341	184, 314	18.3	6.6	
13	0.1	652	261	24.4	0	none visible
	0.1	712	259	24.5	0	
	0.0	684	259	24.6	0	
14	42.19	817	321	9.0	63.3	pan full of black shiny foamy residue
	48.11	875	319	8.2	66.5	
	38.17	837	320	8.8	64.1	

In Table 1, compounds **10**, **12** and **13** are control samples as they represent the molecular cores, without the flame retardant (boron- or phosphorus-containing) functionalities. From the data we can clearly see that the addition of boron or phosphorus lowers the total HR of the molecule, sometimes as much as 96%. Reductions in HRR peak values are noted as well. If we focus on the addition of boronic acid moiety to the terephthalic acid structure (compare compounds **4** and **9** to structure **10**) we can see that the addition of boronic acid greatly increases char yield and results in significant reductions in heat release. However, we see a two peak heat release behavior for these materials when compared to the control sample (compare Figures 2b and 2c to Figure 2a) and the heat release rate profile for the monoboronic acid **4** is very different from that seen for the diboronic acid **9** (compare Figures 2b and 2c).
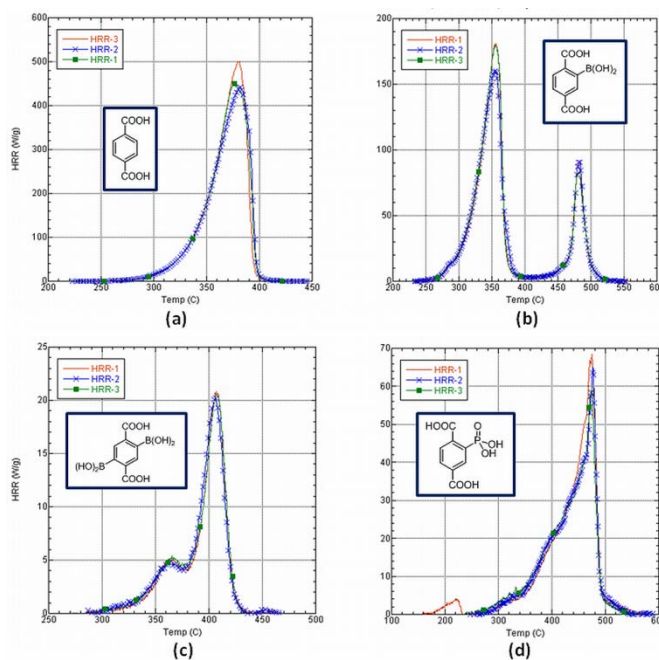

Figure 2. HRR curves for terephthalic acid (**a**), boronoterephthalic acid **4** (**b**), 2,5-diboronoterephthalic acid **9** (**c**), and phosphonoterephthalic acid **11** (**d**).

The likely reason for this different heat release behavior is the formation of boroxine structures as the boronic acids are heated. Boronic acids are well known to form boroxine structures

around 180 – 200 °C, and once this network is in place, it has a strong tendency to char rather than burn.[14] Very likely, the monoboronic acid **4** forms a single boroxine, and then, when this is heated further, the carboxylic acid groups become involved, which in turn creates a complex boron oxycarbide structure (Figure 3). The first peak of HRR is probably from some initial combustion of the monomeric boroxine, and the 2nd peak of HRR is probably from thermal decomposition of the boron oxycarbide as it forms.
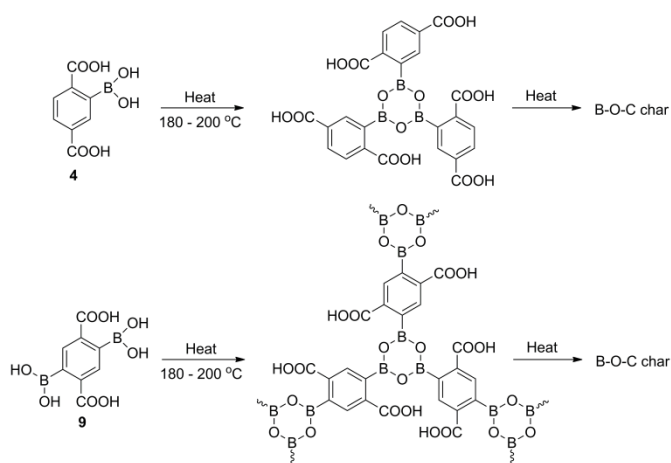

Figure 3. Proposed mechanisms for the thermal decomposition of boronoterephthalic acid (**4**) and 2,5-diboronoterephthalic acid (**9**).

In the case of the diboronic acid **9**, a boroxine network must be formed right away, which could then form faster a thermally stable boron oxycarbide char, thus resulting in a much lower peak HRR, and smaller secondary peak of heat release at lower temperature. While the formation of the boroxine is pretty clear, the mechanism of condensation between the boroxine and carboxylic acid groups (or thermal decomposition of the carboxylic acids into additional cross-linked structures) is not clear and is likely a complex thermal condensation reaction.

DSC of compound **9** shows two endothermic events for this material, one probably for loss of water, hydrated/complexed with the boronic acid, at 112 °C, and then a conversion of the boronic acid to boroxine at 166 °C (Figure 4).
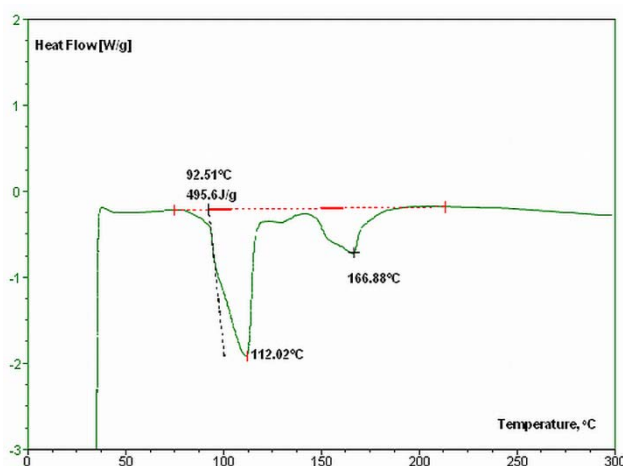

Figure 4. DSC curve of 2,5-diboronoterephthalic acid **9**.

The phosphonic acid functionalized molecule[32] (Compound **11**, Figure 2d) also shows high char yields and low heat release rates, as would be expected, since it is well known that phosphonic acids can condense with carbon-oxygen bonds to form polyphosphate cross-links which rapidly lead to char.[6] The results become very interesting when studying the pinacol boronate (Compound **3**, Figure 5b) and dimethyl phosphonate (Compound **2a**, Figure 5c) when compared to the control sample of dimethyl terephthalate **12** (Figure 5a). By capping the boronic acid with a pinacol functionality, no boroxine network can form and so heat release actually increases for this molecule relative to the control. This makes sense in that there is more carbon present on the boronate to be combusted, and since the boroxine cannot form, the molecule is free to pyrolyze completely and burn to completion. Indeed, the HRR profile for this molecule is sharper indicating a rapid pyrolysis and combustion.
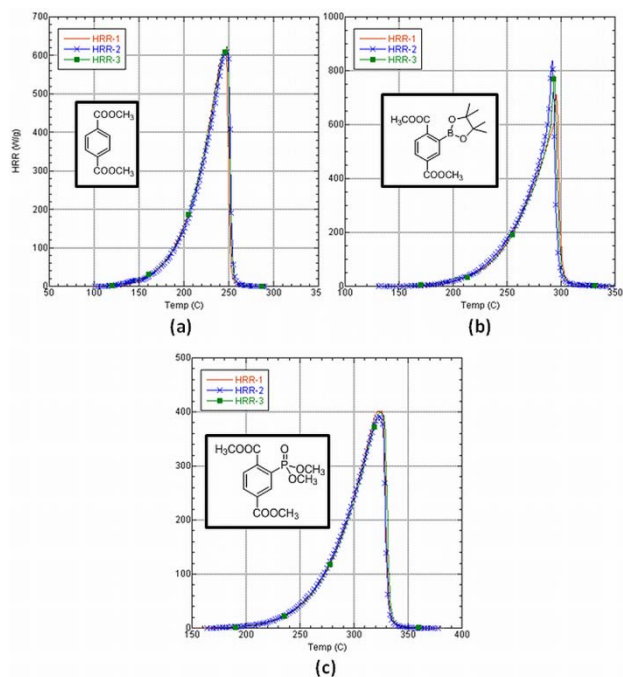
Figure 5. HRR curves for dimethyl terephthalate (**a**), and its pinacolboronate (**b**) and dimethylphosphonate derivatives (**c**).

The dimethyl phosphonate functionalized terephthalate shows no char indicating that the molecule was fully pyrolyzed, but it does show a reduction in heat release. This suggests that the molecule may be a vapor phase flame retardant such that the phosphonate breaks off from the terephthalate after the molecule is pyrolyzed and pushed into the instrument's 900 °C combustion furnace. Phosphorus in some forms is known to be a vapor phase flame retardant which inhibits combustion[6], and so it seems likely that while the reduction in total HR is modest for this molecule, the phosphonate functionality has the strong potential to be a vapor phase flame retardant while the pinacol boronate has no vapor phase activity. However, one must look to the rest of the structure in this analysis. Since phosphorus reacts with other oxygen atoms to form polyphosphate linkages which lead to char, we can state that compound **2a** volatilizes before any phosphorus and oxygen can react. Structure **14** (Figure 6b), which is also a

phosphonate ester[34], but has free hydroxyl groups, shows an effect opposite to compound **2a**. Specifically, it shows high char yields and lowered heat release, indicating that it is a condensed phase/char forming flame retardant despite the alkyl phosphonate. Therefore, in the case of compound **14**, the phosphorus and oxygen react first, before volatilizing, while compound **2a** volatilizes first and then reacts. Sample **2b** (HRR curve not shown) behaves similarly to **2a**. Changing the chemical structure of the phosphonate to a diethyl phosphonate results in a decrease in total HR reduction and a small heat release event at lower temperature, but otherwise the heat release behavior is the same, further indicating that this type of functionality leads to more vapor phase behavior.
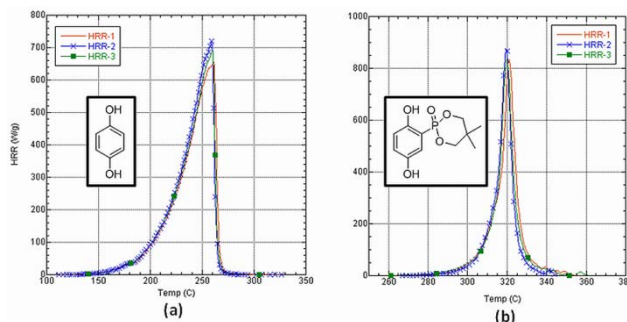

Figure 6. HRR curves for hydroquinone (**a**), and its cyclic phosphonate ester **14** (**b**).

From these results we can conclude that the boronic acids are high char forming materials, and when combined with a polymer where they can form boroxine networks, they will serve as condensed phase flame retardants. Likewise, the phosphonic acid functionality will serve as a condensed phase flame retardant as well. The boronate ester functionality appears to have no affect on flammability at all, and would likely make flammability worse in the presence of a polymer, while the organophosphonates may have some vapor phase activity depending upon the polymer they are compounded into. In a polymer with no oxygen in the backbone, this

molecule is likely to be a vapor phase flame retardant, while in a polymer with oxygen present, the phosphonate could work in both vapor phase and condensed phase[6], unless it pyrolyzes out of the polymer before getting a chance to crosslink/char. Obviously the flame retardant will have to be tested in an actual polymer matrix to determine its flame retardant mechanism in that particular polymer, but from the data collected here, we can infer how the molecules are likely to behave if particular chemical groups are present for interaction between flame retardant molecule and polymer during polymer thermal decomposition.

Table 2. PCFC heat release data for PU foam and Texin 990R (TPU).

Sample	Char yield (wt%)	HRR Peak(s) Value (W/g)	Total HR (kJ/g)	Char Notes
polyurethane foam-5	0.91	217, 366	25.5	light black residue all over pan, 1 small dot on bottom
polyurethane foam-6	0.82	213, 367	25.6	
polyurethane foam-7	0.93	215, 415	25.8	
Texin 990R-1	1.14	169, 176, 332	27.5	black thin fine film all over inside of pan and top part of outside
Texin 990R-2	0.53	203, 346	27.2	
Texin 990R-3	0.95	184, 361	27.5	

Part III: TPU + Flame Retardant Blends and PCFC Testing. As mentioned in the introduction, polyurethane foam is a target for the development of new flame retardant chemistry, but as also mentioned, making a small scale polyurethane foam is not a trivial exercise. Therefore we sought to see if we could use a thermoplastic polyurethane (TPU) as a screening matrix to mix the flame retardants into for PCFC testing. The advantage of a TPU over a PU foam is that solvent blending of flame retardants and TPU is possible at 1 gram batch scales, something not possible if one were to try and make a homogenous flexible PU foam. However, we first had to determine if the TPU was a reasonable mimic for small scale polymer +

flame retardant blend tests, and we conducted PCFC tests on PU foam and a TPU (Texin 990R). From the heat release rate data collected (Table 2, Figure 7), we can conclude that the TPU chosen is not a perfect mimic for a polyurethane foam, but it is still a reasonable choice when one compares the HRR curves (Figure 7).
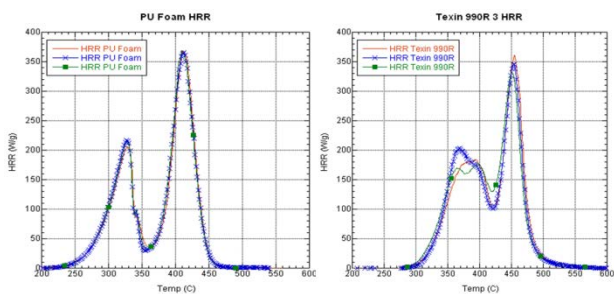

Figure 7. HRR curves for PU foam and Texin 990R.

So with this information we studied the effect of the most promising flame retardants from section II in the TPU matrix. Figure 8 shows the relevant data for compounds **11** and **14**.
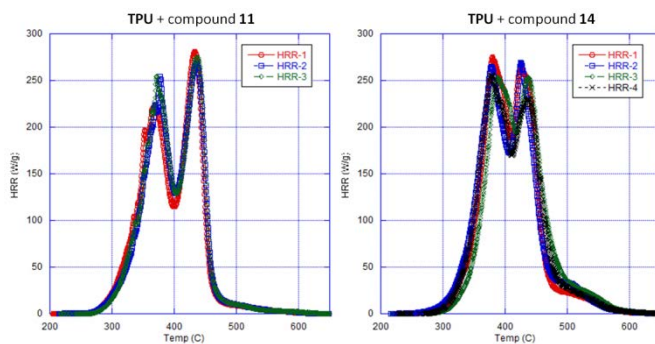
Figure 8. HRR curves for **TPU** + compound **11** (left), and **TPU** + compound **14** (right).

The phosphonate ester (Compound **14**) showed good flame retardancy when tested by itself, but when mixed into the TPU, it was not as effective and appears instead to make flammability worse. It still helps with char yield but does raise total heat release. Only the free phosphonic acid (**11**) increases char yield and lowers heat release.
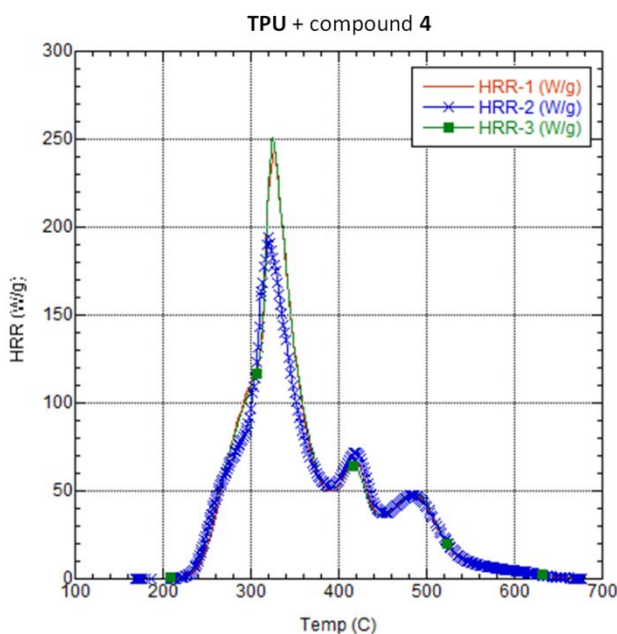
Figure 9. HRR for **TPU** + boronoterephthalic acid (**4**).

The monoboronic acid **4**, however, lowers heat release greatly in the TPU (Figure 9, Table 3) and was noted to keep the char mostly intact (did not flow into the corners of the crucible, Figure 10). The HRR shape for the TPU is greatly changed in the presence of **4** (Figure 9) which suggests that the monoboronic acid is chemically reacting with the TPU during decomposition and likely is assisting in char formation through potential crosslinking reactions between polyurethane and boronic acid groups. While we have not isolated chemical species to assign a mechanism of flammability reduction, it is likely that the boronic acid first forms a boroxine network around 180-200 °C, as verified by DSC (Figures 3, 4) and then this boroxine begins to complex with urethane linkages. Boron is pre-disposed to form complexes with the free electron pair on nitrogen and therefore it is likely that the boroxine intermediate is complexing with decomposing urethane groups which in turn serves as crosslinking sites for char formation. Overall, the higher char yield, reduction in total HR, and change in HRR behavior suggests that

the monoboronic acid, with its inherently high char yield, is a suitable candidate for PU foam flammability studies along with the phosphonic acid. Additionally, the monoboronic acid **4** is likely to bring some enhanced char formation and possibly even prevent dripping during burning since the (TPU + compound **4**) did not flow during thermal decomposition. Obviously this must be verified with larger scale experiments, but still, the change in char structure may be a promising one and would be an additional benefit of the small scale PCFC testing if such char structure was found to correlate to larger scale flammability behavior.

Table 3. HRR data for TPU and TPU + FR blends.

Sample	Char yield (wt%)	HRR Peak(s) Value (W/g)	Total HR (kJ/g)	% THR Reduction	Char Notes
Texin 990R-1	1.14	169, 176, 332	27.5	0.00	black thin fine film all over inside of pan and top part of outside
Texin 990R-2	0.53	203, 346	27.2	0.00	
Texin 990R-3	0.95	184, 361	27.5	0.00	
TPU 990 + 10% FR #11-1	11.78	22, 281	24.9	9.12	black all over inside of pan with some flakey residue
TPU 990 + 10% FR #11-2	11.12	251, 268	25.1	8.39	
TPU 990 + 10% FR #11-3	10.27	254, 275	25.5	6.93	
TPU 990 + 10% FR #14-1	4.81	274, 262, 19	27.5	-0.36	black all over inside of pan, no flakes, small residue around edge
TPU 990 + 10% FR #14-2	4.91	265, 269, 32	27.5	-0.36	
TPU 990 + 10% FR #14-3	5.51	253, 253, 19	27.3	0.36	
TPU 990 + 10% FR #14-4	5.61	256, 230	27.4	0.00	
TPU 990 + 10% FR4-1	15.09	244, 67, 48	21.9	20.07	small ball of ash in center of pan, no film on rest of pan
TPU 990 + 10% FR4-2	15.11	195, 72, 47	21.9	20.07	
TPU 990 + 10% FR4-3	14.98	251, 63, 49	22.2	18.98	

Figure 10. Final chars for TPU + compound **11** (left) and TPU + compound **4** (right).

Conclusions

This report has outlined the preparation and use of some dimethyl terephthalate derivatives in various transition metal-catalyzed coupling reactions. Dimethyl iodoterephthalate and dimethyl 2,5-diiodoterephthalate have been successfully used in the generation of phosphonic and boronic esters, using Pd- or Ni-containing catalysts. The boronic esters have been utilized further to generate the previously unknown mono- and diboronoterephthalic acids.

When studying the heat release of these molecules and their potential as flame retardants, we see that groups capable of crosslinking and condensed phase char formation yield the greatest reduction in heat release. The boronic and phosphonic acid groups reduced heat release the most, followed by the phosphonates. However, if the boronic acid group is present as an ester (such as the pinacol ester in this paper), heat release is increased, indicating that this material would make a poor flame retardant additive. When comparing this result to the dimethyl phosphonate, which also does not form any char, some heat release reduction is observed and so this molecule may have some value as a vapor phase flame retardant. When the flame retardants are combined with a TPU polymer, some similar effects of heat release reduction are noted, but the boronic acid and phosphonic acid containing molecules show the greatest reduction in heat release which roughly correlates to their effectiveness found when the FR additives were tested alone. Of course the correlation is not perfect, but for screening purposes to identify what

materials are worth scaling up for additional work, the use of PCFC to screen flame retardant performance prior to scale-up appears to be justified. Obviously more work is needed to verify the screening criteria that we outline in this paper and further justify the use of this tool for flame retardant material development. To that end, we intend to study this metrology need further via studies of existing commercial flame retardants and flame retardant polyurethanes.

Experimental Section

Pyrolysis combustion flow calorimetry (PCFC) was accomplished with an MCC-1 (Govmark Inc, USA) at 1 °C/sec heating rate under nitrogen from 150 to 900 °C using method A of ASTM D7309 (pyrolysis under nitrogen). Each sample was run in triplicate to evaluate reproducibility of the flammability measurements. Differential scanning calorimetry was accomplished with a Q1000 DSC (TA Instruments, USA), under nitrogen from 25 to 300 °C at 5 °C/min.

^{1}H and ^{13}C spectra were recorded at 300 MHz and 75 MHz respectively and referenced to the solvent (CDCl$_3$: 7.27 ppm and 77.0 ppm). Elemental analysis was provided by Atlantic Microlab, Norcross, GA. HRMS data was provided by the Mass Spectrometry and Proteomics facility at the Ohio State University.

Dimethyl iodoterephthalate **1** has been reported previously, but we could not find an actual synthetic procedure in any of the available references. Thus, the full details of its preparation are reported here, along with pertinent NMR data. Literature search yields a single reference for each of the phosphonates **2a** and **2b**[35], and details on the preparation, or NMR data, of **2a** are not available. Taking into account that a different synthetic protocol was used in the current work, we have found it justified to list preparation details and NMR data for both

phosphonates. Dimethyl aminoterephthalate was purchased from Acros Organics. Phosphonoterephthalic acid (**11**)[32], 2,5-diiodoterephthalic acid (**6**)[31], and 2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)hydroquinone (**14**)[33] were prepared using previously published synthetic protocols.

Dimethyl iodoterephthalate (1). A mixture of dimethyl aminoterephthalate (10.50 g, 50.0 mmol), water (10 mL), ice (40 g) and 98% sulfuric acid (15 mL) was cooled in an ice – water bath. Solution of $NaNO_2$ (3.65 g, 50.0 mmol) in water (10 mL) was added dropwise at the same temperature, over 0.5 h period. The reaction mixture was allowed to stir for additional 30 min at 0 – 5 °C, then poured slowly into a solution of KI (9.96 g, 60.0 mmol) in water (10 mL), at ambient temperature. The resultant mixture was stirred for additional 20 min at 60 °C, then cooled and the excess iodine quenched with aqueous $NaHSO_3$. The product precipitate was filtered, washed with water and dried to yield an orange-brown solid. Recrystallization from methanol yielded a yellow solid (10.24 g, 64%). ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H), 3.87 (s, 3H), 7.80 (d, J = 8.1, 1H), 8.02 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 1H), 8.56 (d, J = 1.5 Hz, 1H).

Preparation of phosphonate esters 2 (*Route 1*). A mixture of dimethyl iodoterephthalate (1 eqv.), trialkyl phosphite (4 eqv.) and $PdCl_2$ (0.1 eqv.) was purged with nitrogen, and then stirred for 5 h at 150 °C, in nitrogen atmosphere. Water and 1,2-dichloroethane were added after cooling to ambient temperature. The organic layer was separated, washed two times with water, dried ($MgSO_4$) and the volatile components removed under reduced pressure. The residue was purified on a silica gel column, using methylene chloride, followed by CH_2Cl_2 : EtOAc = 3 : 1, followed by pure EtOAc. The last two fractions were combined, solvent removed under reduced pressure, to yield the product.

Preparation of phosphonate esters 2 (*Route 2*). A mixture of dimethyl iodoterephthalate (1 eqv.), dialkyl phosphite (1.2 eqv.), triethylamine (1.5 eqv), triphenylphosphine (0.06 eqv.) and Pd(OAc)$_2$ (0.02 eqv.) in ethanol (4 mL per 1 mmol of terephthalate) was purged with nitrogen, then refluxed for 18 h under nitrogen atmosphere. After cooling to ambient temperature the solvent was removed under reduced pressure. The residue was dissolved in a small amount of CH$_2$Cl$_2$ and purified on a silica gel column, using methylene chloride, followed by CH$_2$Cl$_2$: EtOAc = 3 : 1, followed by pure EtOAc. The last two fractions were combined, solvent removed under reduced pressure, to yield the product.

Dimethyl (dimethylphosphono)terephthalate (2a). Yield: 81%. Colorless oil. ^{1}H NMR (CDCl$_3$) δ 3.83 (d, J = 11.4 Hz, 6H), 3.96 (s, 3H), 3.97 (s, 3H), 7.79 (dd, J$_1$ = 4.9 Hz, J$_2$ = 8.0, 1H), 8.25 (dt, J$_1$ = 1.5 Hz, J$_2$ = 8.0 Hz, 1H), 8.56 (dd, J$_1$ = 1.6 Hz, J$_2$ = 14.3 Hz, 1H).

Dimethyl (diethylphosphono)terephthalate (2b). Yield: 86%. Colorless oil. ^{1}H NMR (CDCl$_3$) δ 1.34 (t, J = 7.5 Hz, 6H), 3.96 (s, 3H), 4.08 – 4.22 (m, 4H), 7.76 (dd, J$_1$ = 4.8 Hz, J$_2$ = 7.8 Hz, 1H), 8.24 (dt, J$_1$ = 1.5 Hz, J$_2$ = 7.8 Hz, 1H), 8.56 (dd, J$_1$ = 1.5 Hz, J$_2$ = 14.1 Hz, 1H).

Dimethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate (3). A mixture of dimethyl iodoterephthalate (3.53 g, 11.02 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaboralane (1.76 g, 13.78 mmol, 2.00 mL), dicyclohexylmethylamine (4.05 g, 20.75 mmol, 4.41 mL) and (dppp)$_2$NiCl$_2$ (0.17 g, 0.32 mmol) in toluene (20 mL) was purged with nitrogen and refluxed for 12 h in inert atmosphere. TLC analysis (CH$_2$Cl$_2$) indicated the presence of two main components: the target material (slower running) and dimethylterephthalate. The contents were poured into dilute HCl, stirred for 5 min and the layers separated. The organic layer was dried (MgSO$_4$) and the solvent removed under reduced pressure. The residue was purified on a silica gel column (hexane : CH$_2$Cl$_2$ = 1 : 1), the solvent removed under reduced pressure and the

product was isolated as a white solid (2.51 g, 71%). Additional purification via recrystallization from pentane. Mp 69 – 71 °C. ^{1}H NMR (CDCl$_3$) δ 1.44 (s, 12H), 3.94 (s, 6H), 7.99 (dd, J_1 = 8.1 Hz, J_2 = 0.6 Hz, 1H), 8.08 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 8.16 (dd, J_1 = 1.7 Hz, J_2 = 0.6 Hz, 1H). ^{13}C NMR (CD$_3$CN) δ 24.9, 52.4, 52.6, 84.3, 128.7, 130.2, 132.7, 133.4, 137.3, 166.4, 167.8; Anal. Calcd. for C$_{16}$H$_{21}$BO$_6$: C, 60.03; H, 6.61. Found: C, 59.93; H, 6.78.

Boronoterephthalic acid (4). Hydrochloric acid (3M, 10 mL) was added to boronic ester **3** (1.50 g, 4.68 mmol) and the mixture was stirred for 4 h at 60 °C, then cooled to room temperature and the solvent was evaporated. The residue was dissolved in water upon heating, the solution was cooled and the crystallized impurity (terephthalic acid) was vacuum filtered. The mother liquor was evaporated to dryness, and the resultant solid was subjected two more times to the same purification protocol, but with diminishing amounts of water. Purity was monitored by NMR. Yield: 0.54 g (55%, off-white solid). Mp 305 °C (dec). ^{1}H NMR (D$_2$O) δ 7.57 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.97 (s, 1H). ^{13}C NMR (D$_2$O, indirectly referenced to acetone-d_6 in D$_2$O) δ 127.2, 132.3, 135.9, 141.4, 173.1, 177.5; Anal. Calcd. for C$_8$H$_7$BO$_6$: C, 45.77; H, 3.36. Found: C, 45.34; H, 3.26.

Dimethyl 2,5-diiodoterephthalate (7). Although previously reported[31], compound **7** was prepared by us using Fischer esterification, instead of intermediate conversion of the starting acid to the corresponding acid chloride. Its synthesis is therefore described in detail: 2,5-Diiodoterephthalic acid **6** (3.00 g, 7.18 mmol) was dissolved in methanol (40 mL), conc. H$_2$SO$_4$ (4 mL) was added, and the solution was refluxed for 5 h. The reaction mixture was cooled in the refrigerator overnight, the product was filtered and washed with small amount of cold methanol, to yield white crystalline solid (2.01 g, 64%). ^{1}H NMR (CDCl$_3$) δ 3.84 (s, 6H), 8.34 (s, 2H).

Dimethyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate (8).
Method 1. A mixture of dimethyl 2,5-diiodoterephthalate **7** (1.00 g, 2.24 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaboralane (1.35 g, 10.54 mmol, 1.53 mL), triethylamine (0.93 g, 9.18 mmol, 1.28 mL) and $(Ph_3P)_2PdCl_2$ (0.11 g, 0.156 mmol) in toluene (25 mL) was purged with nitrogen and refluxed for 12 h in inert atmosphere. Water was added and the layers separated. The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified on a silica gel column (CH_2Cl_2), yielding the product as a white solid (0.51 g, 49%). Additional purification was achieved *via* recrystallization from methanol. Mp 253 - 255 °C. ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 24H), 3.93 (s, 6H), 8.05 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 25.1, 52.8, 84.5, 132.7, 136.4, 168.1; Anal. Calcd. for $C_{22}H_{32}B_2O_8$: C, 59.23; H, 7.23. Found: C, 59.51; H, 7.34. *Method 2.* Dimethyl 2,5-diiodoterephthalate **7** (0.50 g, 1.12 mmol), bis(pinacolato)diboron (0.62 g, 2.44 mmol), KOAc (0.33 g, 3.37 mmol) and $(dppf)_2PdCl_2$ (46 mg, 0.056 mmol) were placed in a flask, which was evacuated and backfilled with dry nitrogen. Anhydrous DMF (10 mL) was added and the reaction mixture was stirred for 20 h at 80 °C. The mixture was cooled and DMF evaporated under reduced pressure. Benzene (40 mL) was added and the suspension was vacuum filtered. The filtrate was washed successively with aq. NaCl and water, the organic layer was separated, dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was washed with cold pentane to remove excess bis(pinacolato)diboron, followed by purification on a silica gel column (CH_2Cl_2), leading to isolation of the product as a white solid (0.19 g, 38%).

2,5-Diboronoterephthalic acid (9). Diboronic ester **8** (0.25 g, 0.56 mmol) was placed in a flask and 3M HCl (4 mL) was added. The resultant mixture was stirred for 12 h at 40 °C. Then solvent was removed under reduced pressure, the residue was suspended in ether, stirred

for 30 min, then filtered and dried to yield an off-white solid (0.11 g, 77%). Mp 330 °C (dec). ^{1}H NMR (D_2O) δ 7.79 (s, 2H). ^{13}C NMR (D_2O, indirectly referenced to acetone-d_6 in D_2O) δ 127.0, 141.3, 179.0; Anal. Calcd. for $C_8H_8B_2O_8$: C, 37.86; H, 3.18. Found: C, 38.12; H, 3.33.

Solvent Blending of TPU + Flame Retardant General Procedures: A 2 g batch of TPU (Texin 990R) + flame retardant was prepared in the following manner. To 1.8 g of TPU, 0.2 g of flame retardant was added. This pellet + powder blend was added into a 250 mL glass beaker equipped with a magnetic stir bar. To this beaker was added 200 g of DMF (Aldrich, anhydrous, 99.8% purity) and the beaker was placed on a heated stir plate. The mixture was heated to 150 °C, and stirred at 300 rpm. All of the TPU dissolved in 4 hours, and the material was mixed for one additional hour, after all of the TPU was noted to have dissolved. After mixing, the material was allowed to cool, the mixture was poured into a porous Teflon sheet-lined aluminum tray, and dried in a vacuum oven at 160 °C for 12 hours. The final dried TPU film was then removed from the Teflon sheet and tested for residual solvent content *via* TGA. If solvent was found, the material was dried again for another 12 hours at 160 °C.

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