SYNTHESIS OF NON-HALOGENATED FLAME RETARDANTS FOR POLYURETHANE FOAMS

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SYNTHESIS OF NON-HALOGENATED FLAME RETARDANTS FOR POLYURETHANE FOAMS

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ABSTRACT

SYNTHESIS OF NON-HALOGENATED FLAME RETARDANTS FOR POLYURETHANE FOAMS

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Polyurethanes are known to be the largest fuel loads which can easily ignite and once it ignites, lead to flashover, burning at fast rates. In the presence of fire these foams have a tendency to drip and flow as they burn. Commercially available fire retardants for polyurethane foams are in need of replacement due to negative environmental impact, especially chlorinated and brominated compounds. The purpose of this project was to study the existing commercially available flame retardants, as well as to synthesize new non-halogenated flame retardants for polyurethane foams which utilize char formation as the primary mechanism of flame retardancy.

The new phosphorous and boron based flame retardants were tested for heat release with a micro combustion calorimeter (ASTM D7309). The results showed that the addition of boronic acids greatly lowered the heat release, due to condensed (char formation) phase mechanism. The new FR's were also solvent blended in Texin 990R (mimic for polyurethane foam) and tested for heat release and the results indicated that the boronic acids showed significant reduction in flammability.

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Lastly, I offer my regards to all those who supported me in any respect during the completion of the project.

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LIST OF ABBREVIATIONS

1. AcOH: Acetic Acid
2. BFRs: Brominated flame retardants
3. BH_3.THF: Borane Tetrahydrofuran
4. $Bi(OTf)_3$: Bismuth Triflate
5. CD_3OD: Methanol-*d*
6. CH_2Cl_2: Methylene dichloride
7. CO: Carbon Monoxide
8. CO_2: Carbon dioxide
9. D_2O: Deuterium Oxide
10. DMSO: Dimethyl sulfoxide
11. DMSO-d_6: Methyl Sulfoxide-d_6
12. $(dppp)_2NiCl_2$:
13. Et_3N: Triethyl Amine
14. EtOAc: Ethylcacetate
15. EtOH: Ethanol
16. H_2O: Water

17. HCL: Hydrochloric Acid

18. H_2SO_4: Sulfuric Acid

19. KI: Potassium Iodide

20. $KMnO_4$: Potassium permanganate

21. KOAc: Potassium acetate

22. KOH: Potassium hydroxide

23. $LiAlH_4$: Lithium Aluminum hydride

24. MeOH: Methanol

25. mp: Melting point

26. $NaBH_4$: Sodium Borohydride

27. n-BuLi: n-Butyllithium

28. NaCl: Sodium chloride

29. NaH: Sodium Hydride

30. $NaNO_2$: Sodium nitrite

31. NaOH: Sodium hydroxide

32. NH_4Cl: Ammonium Chloride

33. NMR: Nuclear magnetic resonance

34. *p*-TsOH: para-Toulenesulfonic acid

35. $PdCl_2$: Palladium Chloride

36. Ph_3P, $Pd(OAc)_2$: Triphenyl Phosphine, Palladium Acetate

37. PU: Polyurethane

38. TGA: Thermogravimetic Analysis

39. THF: Tetrahydrofuran

40. THP: Tetrahydropyranyl

41. TLC: Thin layer chromatography

42. TPU: Thermoplastic polyurethane

43. wt: Weight

CHAPTER 1

INTRODUCTION

Polyurethanes (PU) belong to a versatile class of polymeric materials, which come in a variety of forms including coatings, sheets, extruded & injection molded parts, and foams.[1] The chemistry of polyurethane materials can also be quite diverse and that chemistry dictates its properties. Polyurethanes offer good elasticity with reasonably high mechanical strength and abrasion resistance. They also have an outstanding resistance to solvents and chemicals with good weather stability, good pigment wetting properties.[2] With the right chemistry, they can be converted into flexible foams which have excellent cushioning and physical properties. PU materials additionally can offer advantageous performance properties such as good resistance to water, to atmospheric conditions, to oils, greases, organic solvents, diluted acids and alkalis and in case of non-aromatic PU's also resistance to photo-oxidative ageing. Again, polymer chemistry and formulation can yield a variety of different properties and this flexibility in chemistry and formulation is part of the reason why polyurethanes continue to be a widely used class of modern materials.

Among the various kinds of polyurethane products flexible polyurethane foams are used worldwide and they account for about 5% of the total world consumption of plastics.[3] They are widely used in a variety of applications like mattresses, upholstered furniture, automotive, carpet padding and also as insulating panels for buildings.[2] Flexible cellular PU's became inherent in comfort providing elements, especially in furniture making and automotive industry.

The major drawback of polyurethane foam is that it can easily ignite and once it ignites, lead to flashover, burning at fast rates. Therefore polyurethanes are known to be the largest fuel load in the household.[4] The reason for this fire risk is in two parts. The first is the tendency of the flexible polyurethane foam to drip and flow as it burns. The dripping and flowing of PU foams (especially the ones used in home furniture and bedding) creates a pool of burning liquid fuel. The second is that the high heat release of PU provides significant heat, which causes polyurethane foam fires to lead to flashover conditions. The fire resistance of polyurethane foams can be improved by incorporating flame retardants like organic and inorganic phosphorous-based compounds, nitrogen-based compounds and halogenated compounds. Due to environmental concerns researchers are focusing mainly on non-halogenated flame retardants as halogenated flame retardant solutions for foams are phased out of use. [5]

Flammability

Due to the high level of flammability of PU foams, as described above, fire involving ignition of residential upholstered furniture constitutes a leading cause for fire deaths and injuries. In 1998, 11,600 residential fires started in the USA because of ignition of upholstered furniture and 543 people died in the course of fire.[6] According to NFPA (National Fire Protection Association) in 2009, U.S. fire department responded to about 362,500 home fires causing 12,650 civilian injuries and 2656 civilian deaths. Therefore, flame retardancy of materials is needed to help prevent these fire losses from increasing. Obviously the cause of the fires is from sources of ignition which includes cigarettes, small open flames like matches or small lighters, large open flames such as torches, heat or flame from malfunctioning equipment and electrical short circuits. As long as there are ignition sources, there is the potential for fire.

Being organic (carbon containing), by their nature these foams ignite when subjected to a heat source.[7] Polyurethanes when exposed to heat decompose generating combustible gases which react with the oxygen in the atmosphere to form an ignitable blend. For the development of sustained fire the essential elements are fuel (combustible volatiles evolved from thermally degrading carbon rich substance), heat (external source or exothermal oxidative decomposition of the fuel) and oxygen (atmosphere).[8, 9]

The flammability of polyurethane foam depends strongly on the structure of the polyol and isocyanurate matrix.[4] The density is another important factor for the flame spread.[1, 7] The higher the porosity, the higher the tendency of the foam to have fast flame propagation and a higher thermal emission.

The principal process during thermal damage which results in first degradation and then decomposition of the foam is depolymerization i.e., decomposition of PU to yield its parent substance diisocyanate and polyols. The initial decomposition temperature is important for the thermal stability of PU plastics. The decomposition temperature is dependent on thermal stability of the weakest points within the polyurethane macromolecule: urethane bonds and ester bonds. Decomposition of urethane bonds in PU’s obtained from MDI, polyester of adipic acid and ethylene glycol begins at 240 °C, it reaches its maximum rate at 337 °C - 356 °C, ester bonds which involve an aliphatic acid undergo destruction at 344 °C, while those which involve aromatic acid groups occur at 386 °C - 400 °C.

If the polyurethane does not contain any flame retardant, further degradation of polyols occurs to yield small organic species. But in the presence of reactive organo-phosphorous flame retardants such as phosphine oxide, phosphonate, phosphazene and phosphate, the PU does not decompose into its monomers but rather forms a char via cross linking of reactive sites on the polymer chains which forms a carbon char-rich barrier on the surface of the foam.[10] In theory, this effect of cross-linking and char formation could address the dripping and fuel pool fire of polyurethane foams. If one can get the char formation to occur fast enough, then the pool fire may not form and less fuel will be released, which will reduce heat release and therefore reduce the chance of flash over and major fire losses. The present research in this thesis is mainly about synthesis of phosphorous and boron containing reactive flame retardants that have low heat release, char forming tendency, and may be able to react directly into the polyurethane backbone for superior fire protection.

Mechanism of flame retardants

Depending upon the polymer, flame retardants act in one or more of the stages of the combustion process: heating, decomposition, ignition, flame spread, smoke process. FR materials interfere with the combustion process during heating, pyrolysis, ignition or flame spread.[9]

Flame retardants can act via physical or chemical mechanisms, and within those two general mechanisms, there are various potential ways in which flame retardants can react.

Physical

- By cooling

The FR additives can degrade endothermally which cools the substrate to a temperature which is below the temperature that is required for sustaining the combustion, pyrolysis, and thermal decomposition processes.

Example: Metal hydroxides such as aluminum hydroxide and magnesium hydroxide.

- By forming protective layer

The additives can form a shield with low thermal conductivity, reducing the heat transfer from source to polymer. Further reduces the degradation rate of the polymer and decreases the fuel flow that feed the polymer.

Example: Intumescent systems, expandable graphite.

- By dilution

The incorporation of inert substances like (fillers, such as talc and chalk) and additives dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas phase is not reached.

Chemical

- Gas phase

The radical mechanism of gas phase during combustion is inhibited by use of FR materials, further stopping the exothermic processes occurring in the flame, cooling down the system. The supply of flammable gases is reduced and eventually stopped. The high-reactive radicals HO· and H· can react in gas phase with other radicals formed in the degradation of FR materials [Fig. 1] [11].

Example: - Phosphorous based flame retardants, Halogenated flame retardants

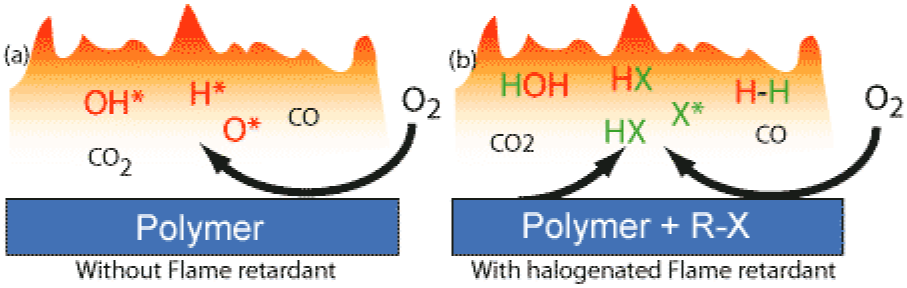


Figure 1. Gas Phase mechanism of Flame Retardant.

- Condensed phase

Flame retardants can form a layer of carbon (charring) on the polymer surface. This is formed by dehydrating action of flame retardant. These processes form a carbonaceous layer through cross linking processes. The char barrier acts as an insulating layer to reduce the heat transfer from the flame to the combusting product. The proposed mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phases.[2, 12]

Example: - Boron based flame retardants, Phosphorous based flame retardants.

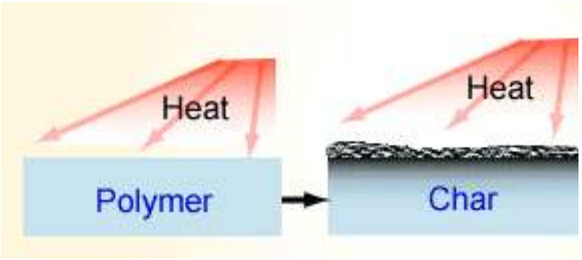


Figure 2. Char Formation in the presence of Flame Retardant.

The flame retardants synthesized in this project mostly act by the mechanism of either gas phase or condensed phase.

Purpose

A significant quantity of low-density polyurethane foam is used in residential upholstered furniture. Without any flame retardant the foam is highly flammable. To improve the fire safety performances of polyurethane foams flame retardant additives are incorporated into polymeric matrix.[1,8,13] Halogen-containing flame retardants, particularly bromine based compounds, play a very important role in flame retardancy. Brominated flame retardants (BFRs), such as pentabromo diphenyl ether, act by chemical interaction to prevent the spread of a fire. Combustion is typically propagated by a series of chemical reactions, where oxygen combines with chemicals in the burning product. BFRs interrupt some of these reactions by volatilizing halogen radicals to react with the product in place of oxygen, slowing combustion.

Inclusion of fire retardant chemical will change some aspect of polyurethane's mechanical and thermal properties as well as its appearance. Depending upon the application these differences may be important or insignificant. The other major factors to be considered when developing FR products are the material's cost, its properties and processing capabilities, worker health and safety during manufacturing and environmental concerns. In the real world when the FR polymer catches fire, smoke and combustion products may be different from those of non-FR polymer and those combustion products may be of some concern depending upon the building environment the foam is placed in.

The thermal degradation or burning of flame retardant polyurethane with halogen-containing compounds releases toxic gases.[5] Some halogen compounds like tris (dibromopropyl) phosphate has been banned in the early 1970's because of its toxicity and pentabromodiphenyl ether has been banned recently in Europe (August 2004) and some states of USA because of certain environmental contamination problem, namely persistence in the environment as well as some biotoxicity and accumulation. The use of brominated diphenyl oxide flame retardants was also restricted by the European community (EU) because highly toxic and potentially carcinogenic brominated furans and dioxins may form during combustion in waste incinerators when those incinerators are not properly operated or not equipped with exhaust afterburners and scrubbers.[14, 13]

While benefits achieved through enhanced fire safety are critical, they should be achieved in a manner that minimizes risk to human health and the environment. The development of flame retardant materials in household applications is mainly driven by the increasing safety awareness of consumers and by environmental issues.[14] Mainly, because of environmental concerns there has been growing interest in halogen free compounds.

The majority of literature on non-halogen flame retardants focuses on phosphorous and boron based products. In this present report non-halogenated flame retardants like boronic and phosphonic acids and esters were synthesized, which were further solvent blended into thermoplastic polyurethane (TPU's). TPU was used as a small-scale mimic for PU foam flammability testing since TPU can be worked with easily while foam manufacture is quite difficult and resource consuming. The flame retardants synthesized are not only non-halogenated but also can be used as reactive flame retardant (incorporated into the polymer backbone). They can be environmentally safer, economically feasible and satisfy fire safety requirements while meeting industry performance needs. The present research not only focuses on reducing the flammability of polyurethane foams, produce compounds which are environmentally friendly, but have potential for industrial application.

Reactive Versus Non-reactive (additive) flame retardants

Additive (Non-reactive flame retardants)

Additive flame retardants are incorporated into the polymer by dissolving/melt compounding/blending into the polymer after the manufacture of the polymer.[15] This method provides most economical and expeditious way of promoting flame retardancy for polymers. In general, additive flame retardants react when heated and either (a) emit substances that displace the oxygen needed for a fire to burn, (b) form a protective coating on the surface of a flammable substrate, thereby limiting access of the fire to fuel sources, or (c) do a combination of both. Halogenated flame retardants act in the gas phase by releasing chlorine or bromine free radicals in the gas phase.

Since they are not chemically bonded into the polymer matrix, non-reactive FR additives may be volatile and can leech out of the polymer and enter the environment under some conditions.[15] They can also have poor compatibility, and may also reduce the mechanical properties.

Some of the commercially available additive flame retardants for polyurethane foams are Tris(1-chloro -2 propyl) (TCPP) and Tris (1,3- dichloro -2 propyl) phosphate

(TDCP). The most frequently used among the two of them is TDCP (ICL-IP Fyrol® FR-2, Albermarle Antiblaze 195).[16]

Reactive flame retardants

Reactive flame retardants are chemically bound to the polymer by incorporating their chemical structure into polymer backbone during polymerization or by grafting into them. As they are chemically bonded, reactive flame retardants have greater effect on the properties of the polymer than additive flame retardants. Leaching of the flame retardant into the environment is less for reactive flame retardants when compared to additive (non-reactive) flame retardants.[15]

Reactive phosphorus - containing and boron - containing compounds are known to be highly effective flame retardants in many polymeric applications (mainly thermosetting polymers). The flame retarding effect of reactive compounds reduces the formation of toxic smoke and the heat release rate, preventing the outbreak of large fires even from small ignition sources.[17]

Reactive flame retardants can be introduced by either the design of new flame retarding polymer or modification of existing polymers through copolymerization with a flame retarding unit in the chain. Covalently incorporating the flame-retarding unit in the polymer backbone imparts the flame retardancy permanently, and the original physical and mechanical properties can be maintained, or are not as greatly reduced compared to additive flame retardants.

The majority of the research efforts reported in this thesis are centered on this approach. Flame retardants like boronic acids, cyclic phosphates etc., can be attached to one of the monomer molecules (polyol or isocynate), which are further used for the synthesis of polyurethane foams.

Phosphorous-based flame retardants

Phosphorous exists in different oxidation states like phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphates. Therefore the range of phosphorous containing flame retardants is very wide and versatile.[14] But for this project reactive flame retardant organophosphonates are used.

Triphenyl phosphate and tricresyl phosphate were two of the earliest commercialized phosphorous flame retardants.[4,18] Some of the commercially available phosphate based flame retardants for polyurethane foams are oligomeric ethyl phosphate marketed by ICL-IP as Fyrol® PNX, triaryl phosphates such as isopropylphenyl diphenyl phosphate.[16]

Phosphorous acts in the vapor phase by a radical mechanism to interrupt the exothermic process and suppress combustion.[14] Phosphorous also act as a catalyst in the condensed phase in three steps. [16]

1. By thermal decomposition phosphorous may form anhydrides of phosphoric or related acids, which in turn act as dehydrating agents, extracting water from pyrolysing PU, promoting char formation.
2. Phosphoric and related acids retard the formation of CO_2 via oxidation (which is exothermic), decreasing the heating process.

3. The acids form a glassy protective layer on the surface, decreasing the diffusion of fuel to the flame front of the burning polymer, which reduces heat and mass transfer between the polymer and atmosphere. Thus the barrier disturbs the oxidation process of carbon at the CO stage, decreasing the exothermic heat of combustion.[14]

The mechanism involves char formation on the surface forming a protective barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air (oxygen).[14, 19, 20] Phosphorous containing compounds can provide flame retardation of the polymer with non-toxicity and good compatibility between polyurethane and flame retardants.[5]

Boron-based flame retardants

The incorporation of boron into the backbone of polymer matrices has gained importance in recent years as it improves thermal stability, electrical resistance, oxidative resistance flexibility and especially flame retardancy than its virgin polymer.[20]

Boron based flame retardants act mainly in the condensed phase by redirecting the decomposition process in favor of carbon formation rather than CO or CO_2 formation. Boron compounds promote char formation which forms a protective barrier to prevent oxidation of carbon in the burning process. The char formation relates to the thermal action of boronic acid with alcohol moieties. They reported a significant improvement of flame retardancy through a mechanism involving the formation of a protective barrier of boron oxide, which prevents the degradation of the polymer.[21,9]

Among the boron based flame retardants boronic acids are of particular interest because during heating these boronic acids form boroxine network [Fig. 3] which contribute to the formation of char and prevent the fuel molecules being transported to the combustion surface.[14]

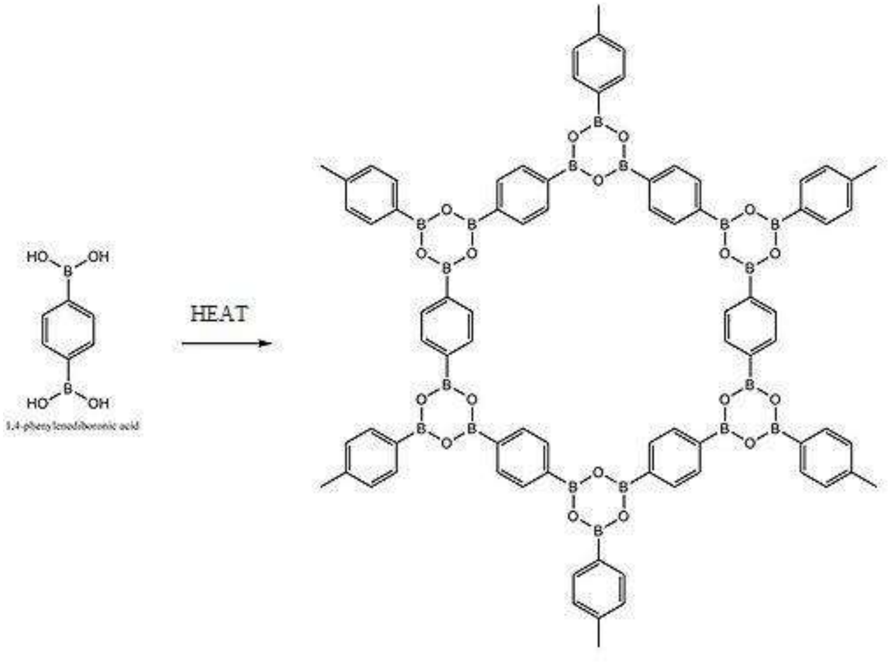


Figure 3. Aromatic boric acid and boroxine network.

In summary, the synthesized flame retardants can be used as reactive non-halogenated flame retardants. They can be incorporated into the polyurethane matrix and in theory should not interfere with the physical properties of PU foam. The main objective of this research is not only to improve the flame retardancy of PU foam but also scale up the synthesis methods for industrial applications.

CHAPTER 2

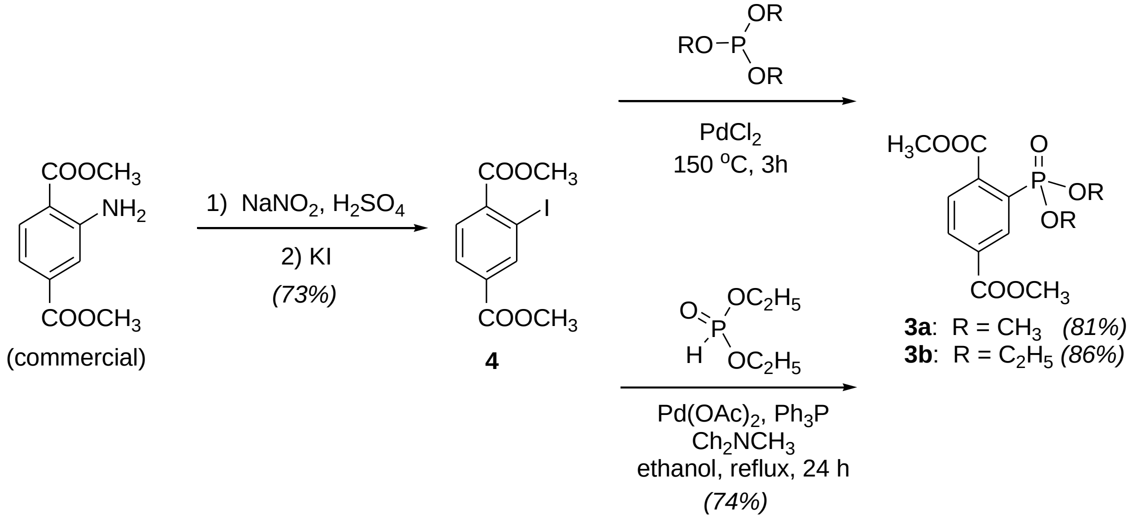
RESULTS AND DISCUSSION

Part I: Derivatives of dimethyl 2-iodoterephthalate and dimethyl 2,5-diiodoterephthalate

Preparation of dimethyl 2-iodoterephthalate **(1):**

Dimethyl 2-iodoterephthalate was synthesized successfully by a single step procedure (diazotization) using dimethyl 2-aminoterephthalate as the starting material (Scheme 1). Dimethyl amino terephthalate was diazotized in H_2O/H_2SO_4 mixture followed by reaction with KI solution.[22] Compound **4** was further subjected to palladium or nickel catalyzed coupling reactions to prepare phosphonic and boronic esters.

Scheme 1

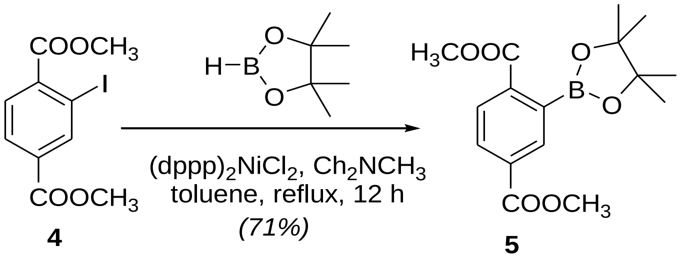


Preparation of phosphonic esters **(3a,b) :**

Iodo-terephthalate **4** was used as the starting material to successfully synthesize phosphonic esters **3a,b** by one of two strategies. (*Route 1* and *Route 2* in Scheme 1). Thus triethylphosphite and trimethylphosphite were successfully employed in the synthesis of compounds **3a, b** (*Route 1*). The protocol was adapted from a patented work of Hashiba *et al.* and **4** was subjected to reaction with large excess of trialkylphosphite (also used as a solvent for the reaction) in the presence of $PdCl_2$ as a catalyst at elevated temperatures.[23]

The generation of phosphonate esters *via* route 2 utilized dialkylphosphites and compound **4** as starting materials and was accomplished following the procedure of Dezfuli and Goosen.[24] The reaction was conducted in ethanol as a solvent, dicyclohexylmethylamine (or triethylamine) as a base and catalytic amount of $Pd(OAc)_2/Ph_3P$.

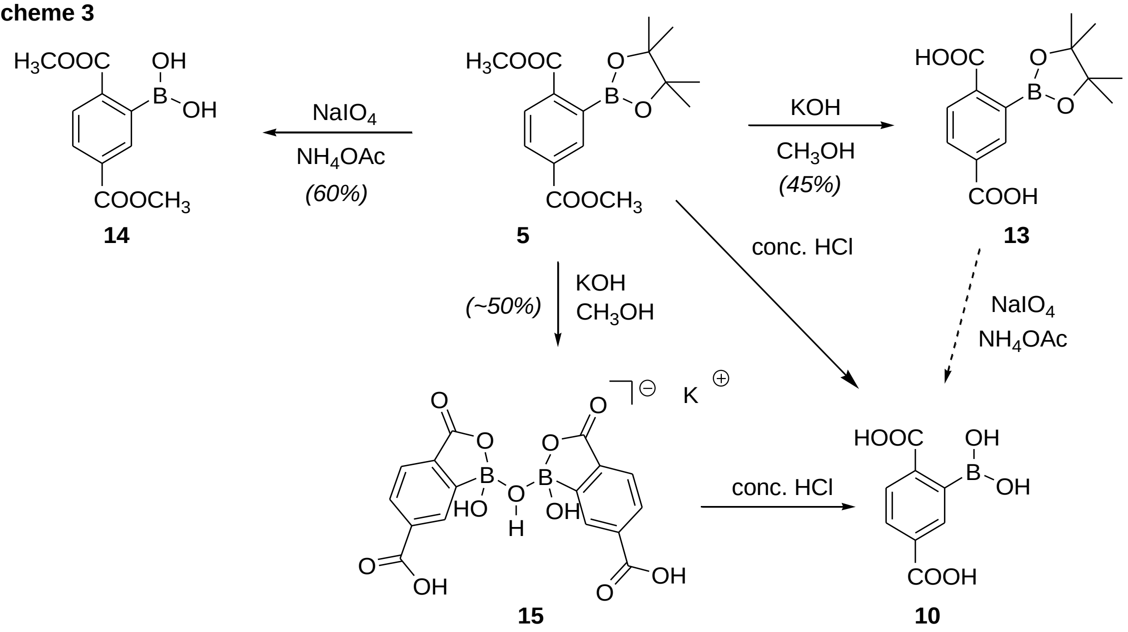
Scheme 2



Preparation of boronic ester **(5):**

Iodoterephthalate **4** proved to be an excellent starting material for the generation of boronic esters. Cyclic boronic ester **5** was synthesized in good yield, by using compound **4** and pinacolborane as the starting materials. The reaction was conducted in toluene as a solvent, triethylamine (or dicyclohexylmethylamine) as a base, $(dppp)_2NiCl_2$ as a catalyst.[25] Dimethyl terephthalate is formed as a byproduct, which required purification by column chromatography. According to the literature, in the presence of a base deborylation of **4** occurs. The boronate ester moiety is replaced by hydrogen, forming dimethyl terephthalate. This may be preventable by reducing the reaction time.

Scheme 3



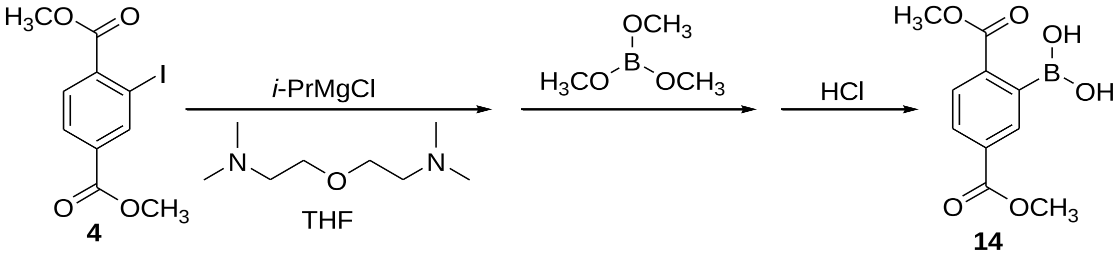
Preparation of boronoterephthalic acid **(10):**

Preparation of boronoterephthalic acid **10** is shown in Scheme 3. Initially Compound **5** was subjected to HCl catalyzed-hydrolysis in a THF/HCl mixture. But the reaction yielded a very complex mixture which was difficult to purify and analyze.

Then suitable conditions for selective hydrolysis either of the carboxylic or the boronic ester were found (Scheme 3). The boronic ester can be hydrolyzed using $NaIO_4$

and ammonium acetate in water/acetone mixture, in mild conditions, leading to the generation of boronic acid **14**.[26] The selective hydrolysis of the carboxylic ester **5** was successfully done in the presence of KOH using methanol as a solvent.[27] The reaction was incomplete when done for a limited amount of time (1 hour). But when exposed to longer periods of time, the reaction resulted in the formation of a stable salt, compound **15**. It proved very difficult to protonate the salt, even in concentrated HCl. The salt forms in basic conditions so acidic conditions were further applied for hydrolysis of the boronic ester. Therefore compound **5** was successfully hydrolyzed by using 3M HCl.

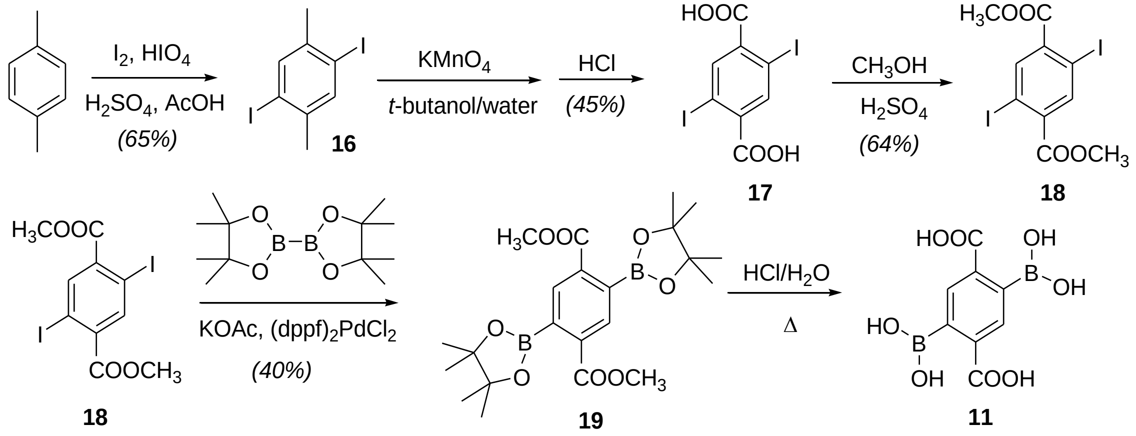
Scheme 4



Attempted preparation of boronoterephthalic acid **(10):**

An alternate procedure for the synthesis of the boronic acid, based on the available literature was attempted.[28] A Grignard reagent was reacted with trimethyl borate to couple compound **4** with the boronic ester. Then the resulting ester was acidified by using HCl. The reaction was unsuccessful and resulted in the recovery of the starting material (Scheme 4).

Scheme 5



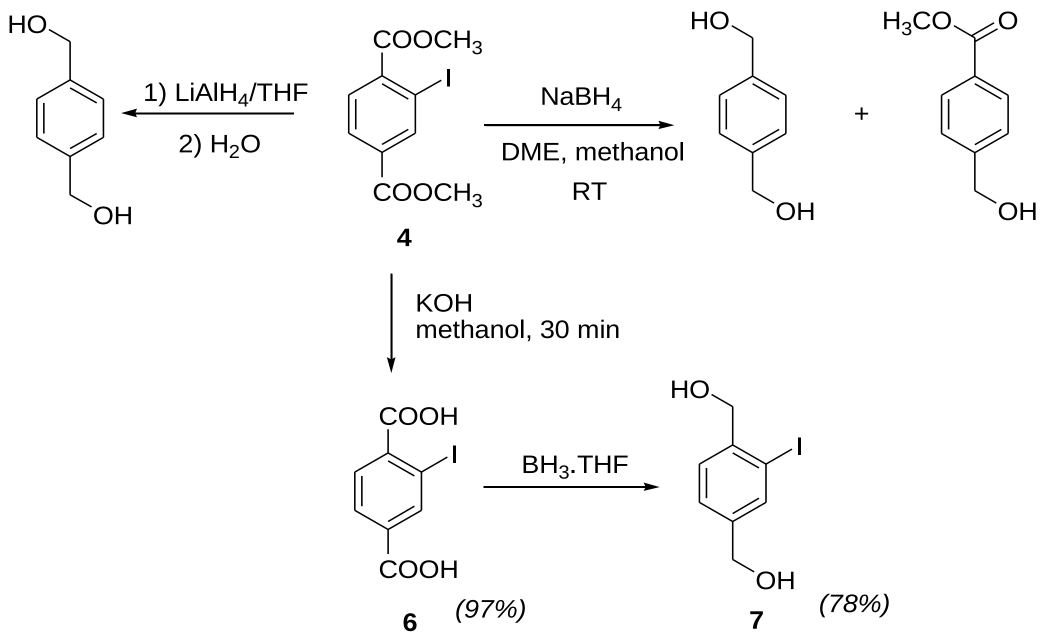
Preparation of 2,5-diboronoterephthalic acid **(11):**

p-Xylene was diiodinated by using periodic acid/iodine, in a mixture of acetic acid, sulfuric acid and water, to yield 2,5-diiodo-xylene **16.**[29] 2,5-Diiodoterephthalic acid **17** was successfully synthesized by subjecting **16** to oxidation, using $KMnO_4$ in a *t*-butanol/water solvent mixture. Compound **17** was esterified in excess methanol, using sulfuric acid as a catalyst. Compound 1**8** was then subjected to transition metal catalyzed coupling, to generate diboronic ester **19**.

Initial attempts were unsuccessful and in most of them the starting material was recovered. Conditions employed in preparation of **5** resulted in synthesis of a mixture of products. Along with the required product compound **19**, the mixture consists of compound **5** and dimethyl terephthalate as byproducts. The reason for this could be the deborylation. Therefore we tried to employ other coupling reaction methods. Compound **19** was tried to synthesize by using bis(pinacolato)diboron, with $(dpph_3)_2PdCl_2$ as a catalyst and KOAc as a base in dioxane. There was no reaction and the starting material was recovered in this procedure too.

The diboronic ester **19** was synthesized by using bis(pinacolato)diboron, with $(dppf)_2PdCl_2$ as a catalyst and KOAc as a base in DMF (Scheme 5).[25] The conditions for hydrolysis of **19** were similar to that of monoboronic ester **5**.

Scheme 6

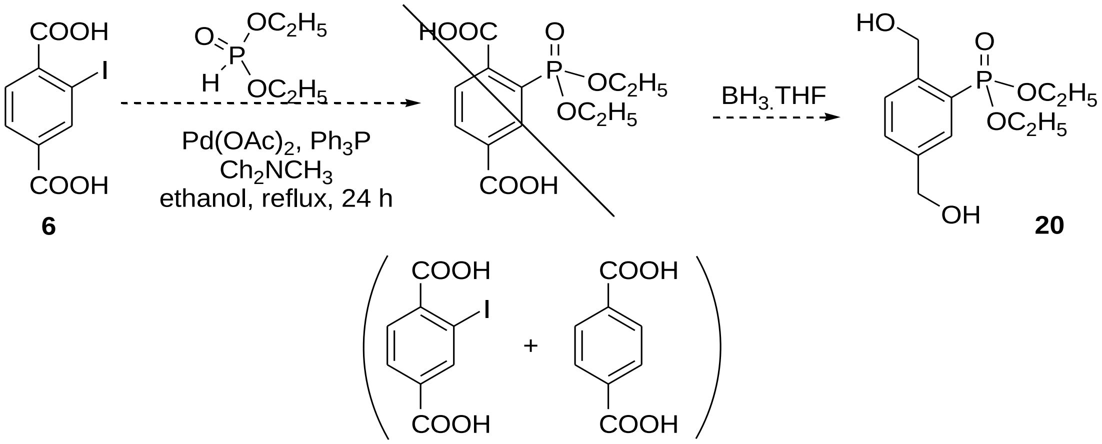


Preparation of 2-iodo-1,4-bis(hydroxymethyl)benzene **(7):**

2-Iodo-1,4-bis(hydroxymethyl)benzene was prepared in good yield *via* the iodoterephthalic acid **6**, which was generated by an efficient base-promoted hydrolysis of **4,** with KOH in methanol.[27] The acid was then reduced with BH_3.THF, to deliver 2-iodo-1,4-bis(hydroxymethyl)benzene **7** in 85–90% yield (Scheme 6).[30]

Attempts to reduce **4** directly with complex hydrides were not successful. Reduction of iodoterephthalate **4** in the presence of $LiAlH_4$, even at ambient temperature led to the removal of iodine and generation of 1,4-bis(hydroxymethyl)benzene, in high yield. Likewise, $NaBH_4$ reduction, in dimethoxymethane-methanol solvent[31], at ambient temperature, led to products without the iodine, 1,4-bis(hydroxymethyl)benzene and methyl 4(hydroxymethyl)benzoate. The presence of the latter clearly demonstrates the preference for iodine removal over ester reduction.

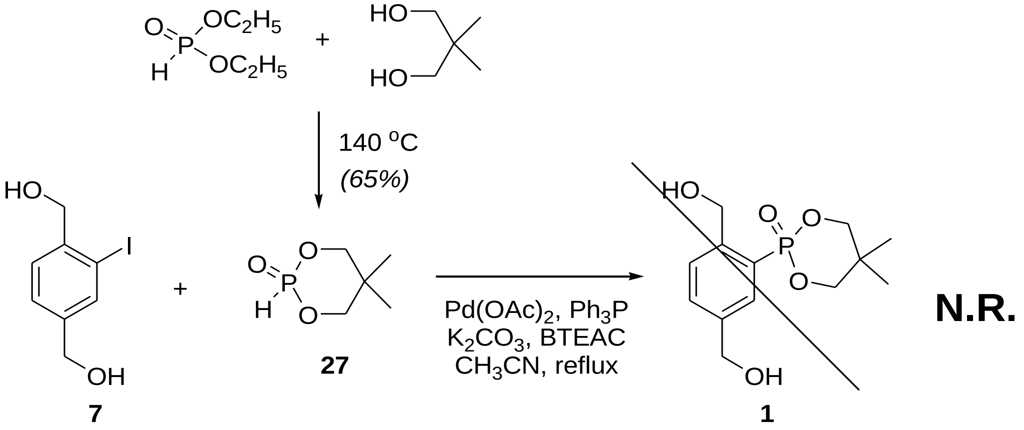
Scheme 7



Attempted preparation of diethyl 2,5-bis(hydroxymethyl)phenyl phosphonate **(20):**

To obtain the desired diol **20**, terephthalic acid is coupled with phosphonic ester moiety first and then treated with BH_3.THF, because the iododiol **7** is less reactive towards esters and the coupling after reduction of terephthalic acid is not possible. In theory, much greater selectivity is possible using a terephthalic acid and treating it with BH_3.THF. However, coupling of 2-iodoterephthalic acid **6** with phosphonic ester moiety was not successful (Scheme 10).[24] The isolated product mixture consisted of unreacted acid **6**, and some quantity of terephthalic acid.

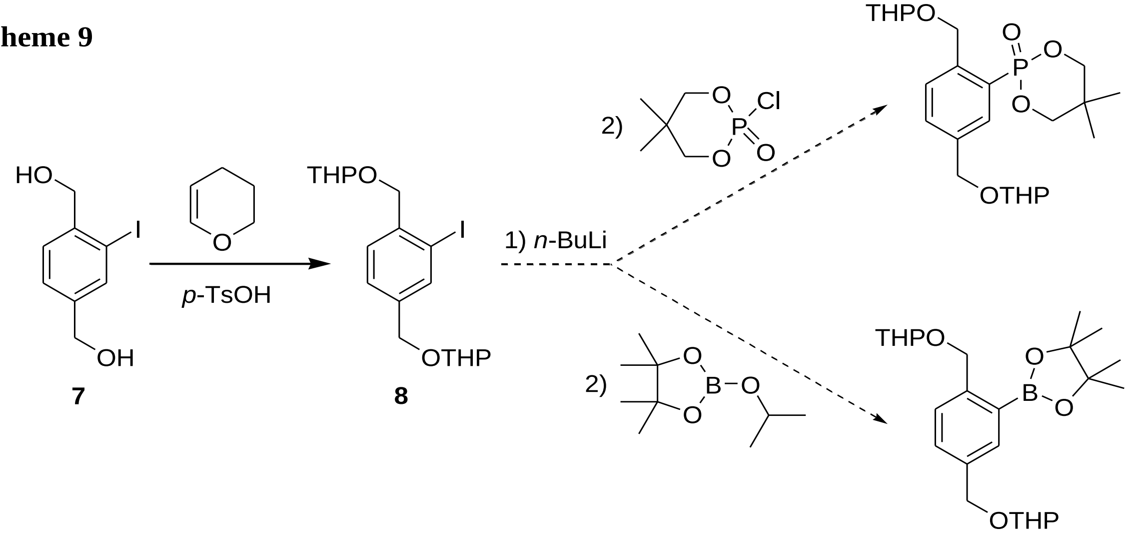
Scheme 8



Attempted preparation of 1,4-bis(hydroxymethyl)-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yl)benzene **(1):**

Cyclic phosphite **27** was synthesized using diethyl phosphite and neopentyl glycol at higher temperatures.[32] The cyclic phosphite **27** was used for direct replacement of iodine by a phosphonic ester moiety, but was not successful (Scheme 8). The reaction in the presence of $Pd(OAc)_2$ as a catalyst and a base, led to the complete recovery of the starting material. Use of diethyl phosphite led to the same result.

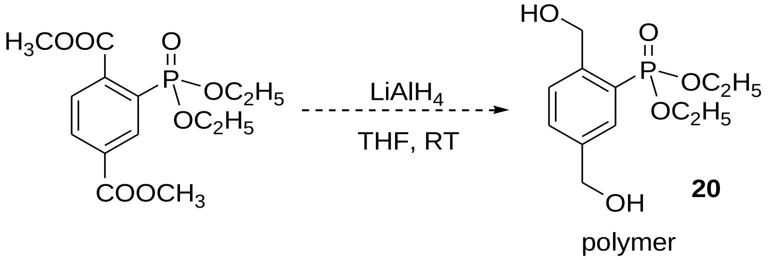
Scheme 9



Attempted preparation of 2,2'-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4,phenylene)bis(methylene)bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(2-methyl-tetrahydro-2H-pyran **:**

The hydroxyl groups are likely interfering with the reaction, so the next step was to use protecting groups, in particular the conversion of the hydroxyl groups into tetrahydropyranyl ethers (Scheme 9). Compound **8** was synthesized successfully by reaction of **7** with dihydropyran, in CH_2Cl_2, in the presence of catalytic *p*-TsOH.[33] Then compound **8** was subjected to transition metal catalyzed coupling in toluene as a solvent, dicyclohexylmethylamine as a base, $(dppp)_2NiCl_2$ as a catalyst. The reaction formed a complex mixture which was very difficult to purify.

Scheme 10



Attempted synthesis of diethyl 2,5-bis(hydroxymethyl)phenylphosphonate **(20):**

Lithium aluminium hydride was used to reduce compound **3b** in THF as a solvent (Scheme 10). The product seemed to be highly insoluble, some kind of polymer. It seems that reduction of carboxilic esters, without simultaneously affecting the phosphonic or boronic ester moieties, cannot be achieved by using complex hydrides like $LiAlH_4$ and $NaBH_4$.

MICRO COMBUSTION CALORIMETRY [Pyrolysis-Combustion Flow Calorimetry (PCFC)]:

Micro Combustion Calorimeter is an instrument used for determining the flammability characteristics of combustible materials at milligram scale. PCFC data correlates with fire test data (Cone Calorimeter), flammability results (LOI, UL-94) and heat of combustion tests (Bomb Calorimeter). The method is a standard technique under ASTM D7309. In this project the inherent heat release rate of the synthesized molecules to serve as flame retardants is tested by using this technique.[53-59] The following (figure 4) are some of the boron and phosphorous based molecules subjected to PCFC test.

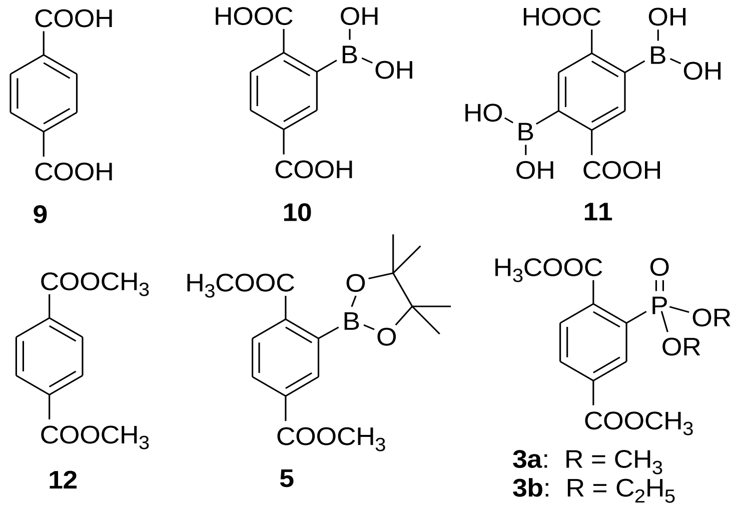


Figure 4. Structures of flame retardants, studied by PCFC (**10, 11, 5 & 3a,b**).

Table 1 describes the following measurements obtained from the PCFC:

Char Yield: The difference in the weights of samples before and after pyrolysis accounts to char yield. It can also be called as pyrolysis residue. The more is the amount of char formed, more carbon/ inorganics is left behind. If the char yield is more the total heat release should decrease.

HRR Peak Value: The peak maximum Heat Release Rate (HRR) during the experiment is the HRR peak value. The higher the HRR value, the more heat is released during the pyrolysis of the compound.

HRR Peak Temperature: The temperature at which the peak HRR value is obtained. The higher the HRR peak temperature, higher the HRR peak value.

Total HR: Total Heat Release for the sample is the area under the curve(s) for each sample analysis. Percent heat reduction is also calculated.

Char Description: The physical description of the char formed during pyrolysis.

Table 1. PCFC summary data for compounds **3a-b**, **5**, and **9 - 12**.

Compound	Char Yield (wt%)	HRR Peak Value (W/g)	HRR Peak Temps (^oC)	Total HR (kJ/g)	% HR Reduction	Char Description
9	0	450	378	19.3	0	none visible
	0	441	382	19.4	0	
	0	501	380	19.4	0	
10	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	
11	66.1	5, 21	365, 407	0.7	96.4	dark brown powder
	66	5, 20	365, 406	0.7	96.4	
	65.9	5, 21	365, 407	0.7	96.4	
12	0	613	247	16.8	0	none visible
	0	611	249	22.7	0	
	0	619	248	19.5	0	
5	2	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	
3a	0	402	326	17.9	8.7	very thin gray film on bottom
	0	390	323	17.5	10.7	
	0	399	324	17.6	10.2	
3b	0	44, 345	175, 312	18.1	7.7	none visible
	0	44, 333	183, 315	18.4	6.1	
	0	41, 341	184, 314	18.3	6.6	

In the table above, samples **9** and **12** are the control samples as they represent the molecules without the flame retardant functionalities (phosphorous or boron containing). From the data we can clearly see that addition of phosphorous and boron based compounds lowers the HR rate of the molecule except for structure **5**.

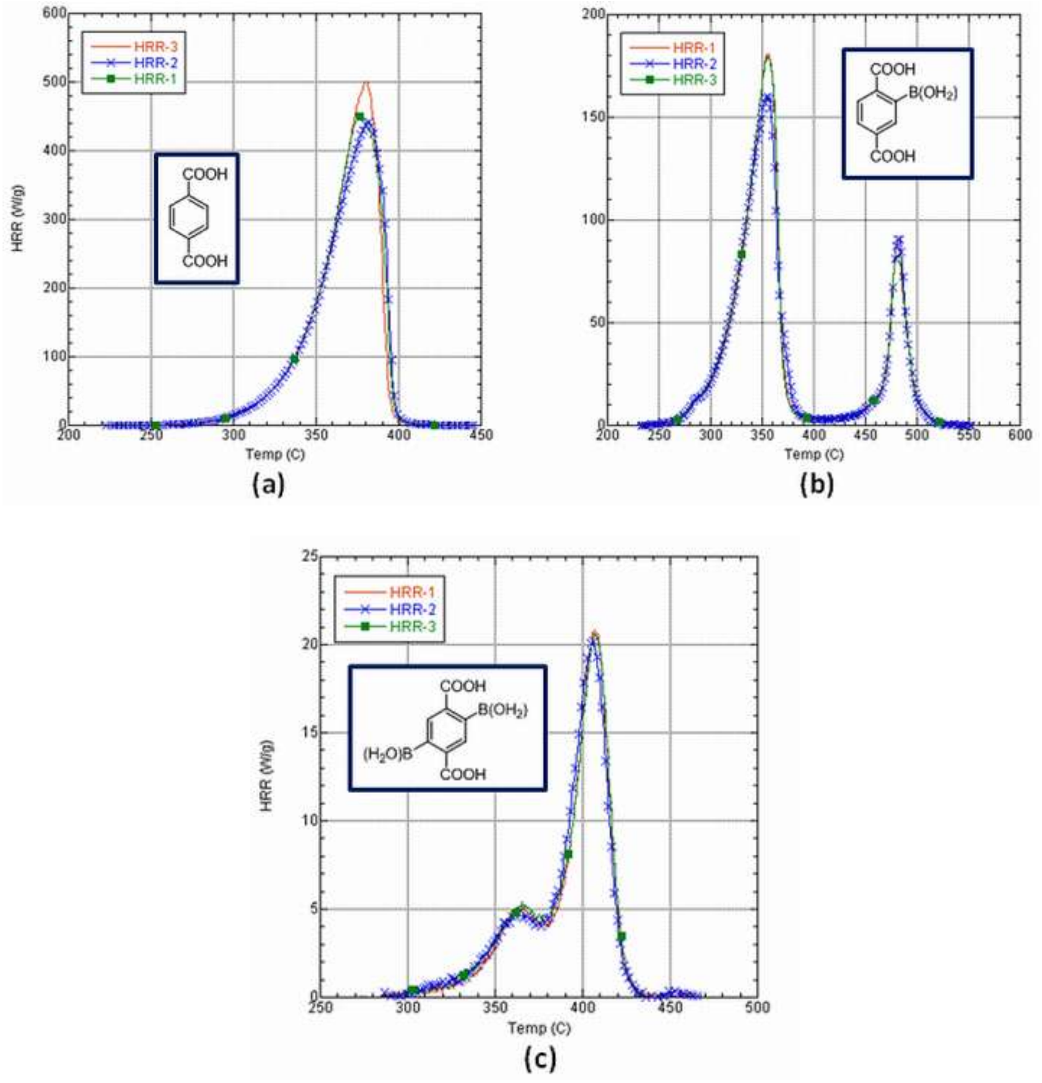


Figure 5. HRR curves for (**a**) terephthalic acid, (**b**) monoboronic acid and (**c**) diboronic acid

If we consider the addition of boronic acid moiety to the terephthalic acid structure, we can see boronic acid greatly increases the char yield and the percent reduction in heat release is almost 50% for mono-boronic acid and 96% for diboronic acid. However we see two peak heat release behavior when compared to the control molecule (figure 5). The reason for this different heat release behavior could be due to the formation of boroxines, when boronic acids are heated.

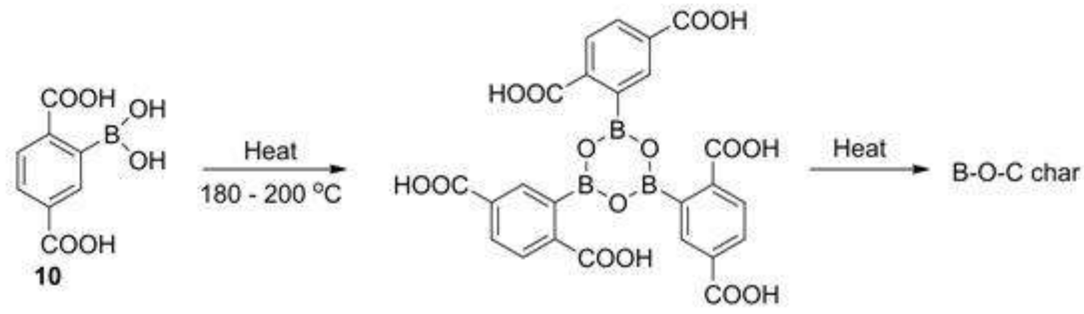


Figure 6. Proposed mechanism for the thermal decomposition of mono boronic acid **10**

Boroxine structures are formed when boronic acids are heated at about 180 °C - 200 °C, and once the network is formed, it has tendency to char rather than burn. The monoboronic acid forms a single boroxine, and when this is heated further, the carboxylic groups become involved, creating a complex boron oxycarbide structure (figure 6). The first peak of HRR is probably from some initial combustion of the monomeric boroxine, and the second peak of HRR is probably from thermal decomposition of the boron oxycarbide as it forms.[21,34]

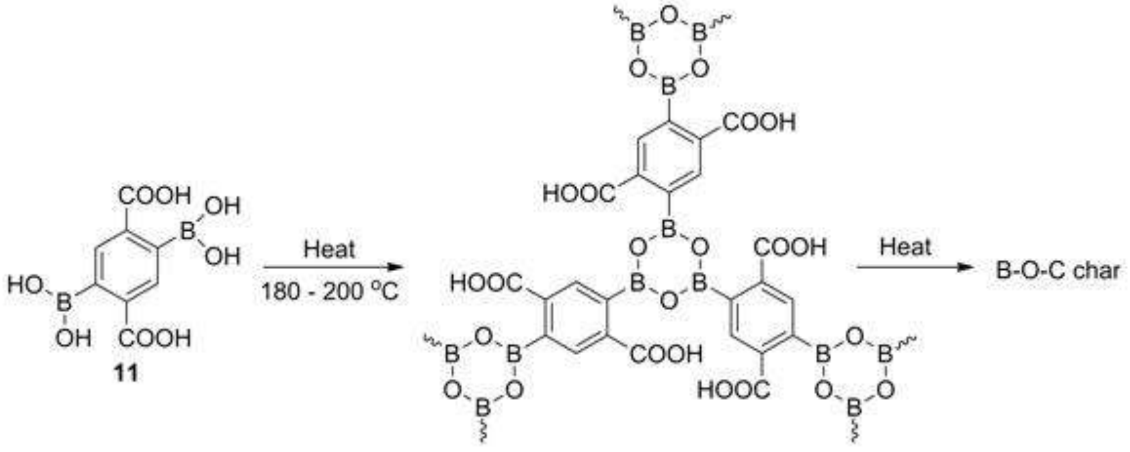


Figure 7. Proposed mechanism for the thermal decomposition 2,5-diboronoterephthalic acid **11**

In the case of diboronic acid a boroxine network is formed right away, which is then formed into thermally stable boron oxycarbide char (figure 7), thus resulting in much lower peak HRR and a smaller secondary peak at lower temperature. The formation of boroxine is clear, but the mechanism of condensation between the boroxine and carboxylic acids (thermal decomposition of the carboxylic acids into additional cross-linked structures) is not clear, and is a likely complex thermal condensation reaction.

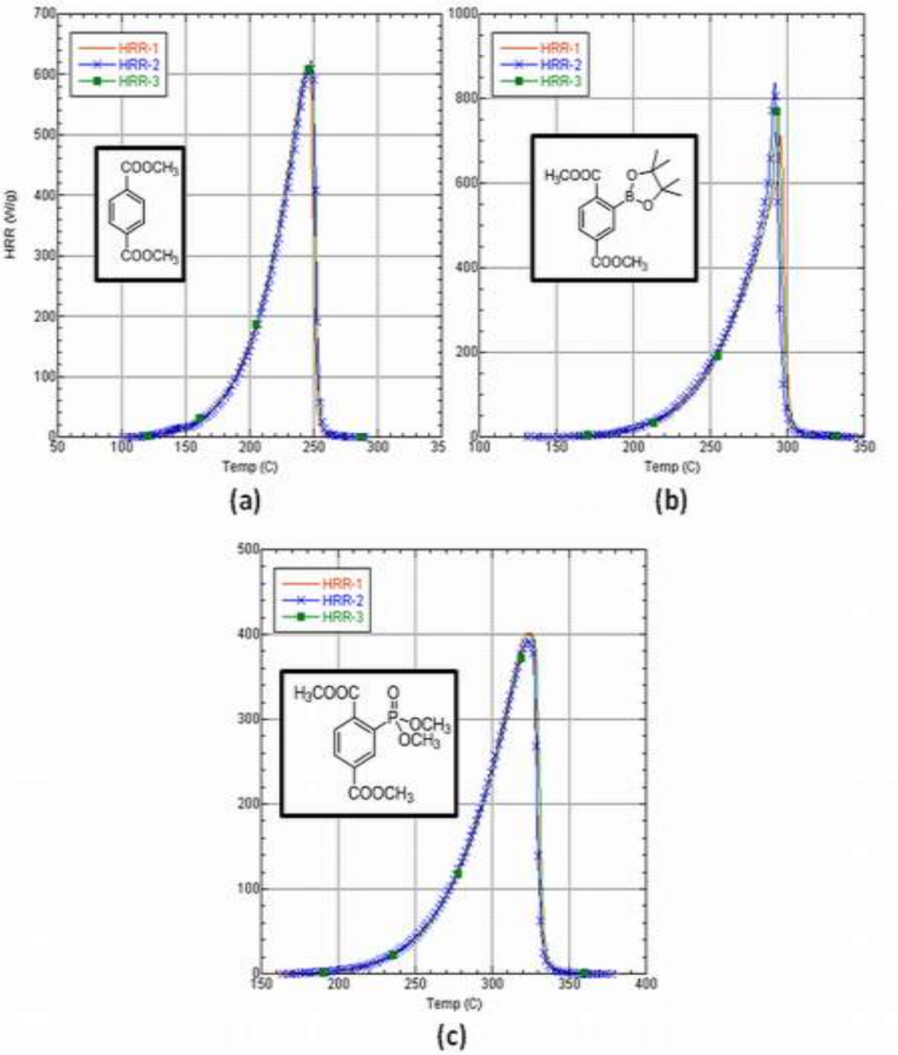


Figure 8. HRR curves for (**a**) dimethyl terephthalate, and its (**b**) pinacolboronate and (**c**) dimethylphosphonate derivatives.

When studying the inherent flame retardancy of pinacolboronate (**b**. in Figure 8) the heat release rate is higher than the control sample, dimethyl terephthalate. By capping the boronic acid with pinacol functionality, no boroxine network can form and so heat release actually increases for this molecule relative to the control. In pinacolboronate compound there is more carbon to be combusted and there is no formation of boroxine network the molecule is free to pyrolyze completely and burn to completion. The HRR curve for this sample is sharper indicating a rapid pyrolysis and combustion.

When tested the inherent flame retardancy of dimethyl phosphonate shows no formation of char indicating the molecule was fully pyrolyzed but there was reduction in heat release. Therefore the molecule could be a vapor phase flame retardant such that the phosphonate breaks off from the terephthalate after the molecule is pyrolyzed and reacts with the OH* and H* free radicals, reducing the heat release rate. As mentioned earlier in the introduction, phosphorous sometimes also acts as vapor phase flame retardant which inhibits combustion.[35] 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 pinacolboronate has no vapor phase activity.

Solvent Blending Experiments:

Thermoplastic polyurethane (TPU) is used as a screen matrix for mixing the flame retardant via solvent blending for additional PCFC testing. Solvent blending enables very small scale experiments (1gm of TPU with flame retardant in total) with homogeneous mixing. TPU is dissolved in solvent with flame retardant and then the solvent is removed.

TPU is good for small scale testing. Although TPU is not an ideal mimic for polyurethane foams it seems to be a reasonable choice if we compare HR data.

Texin 990R (TPU) was used for solvent blending experiments as polyurethane foam is difficult to make. TPU was used as a mimic for polyurethane foams as they both of have similar heat release characteristics. In this approach we do not react the flame retardant molecules into polyurethane backbone but we can at least have an idea as to what extent they reduce the heat release in the polyurethane matrix by looking at how the FR molecules reduce heat release in TPU.

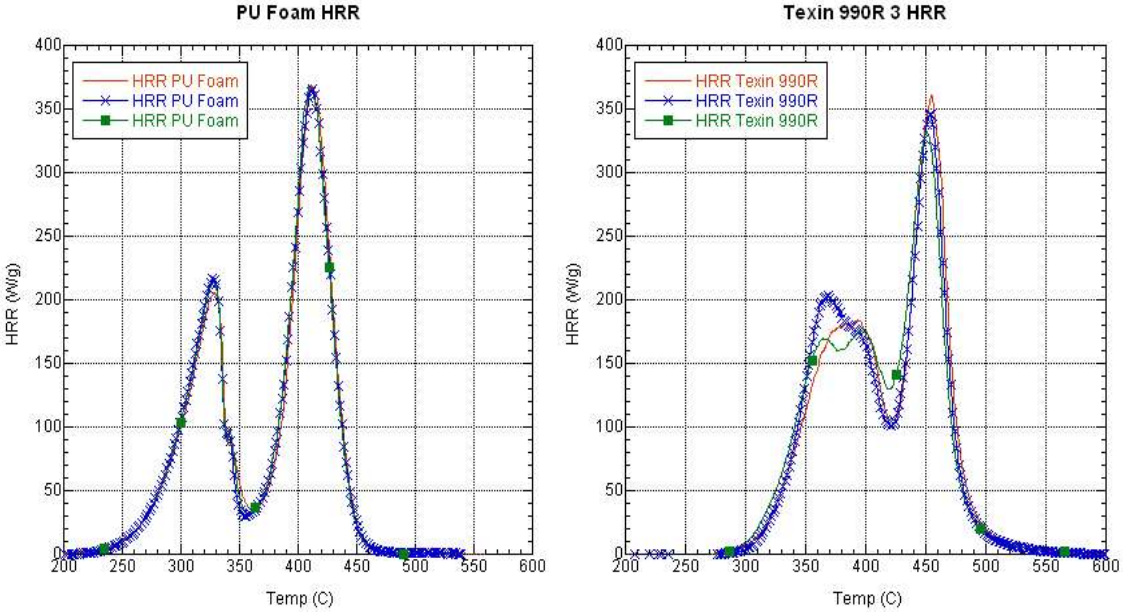


Figure 9. HRR curves for PU foam (left) and Texin-990R (right)

Table 2. PCFC summary data for TPU , compound **10**.

Sample	**Char Yield (wt%)**	**HRR Peak Value (W/g)**	**Total HR (kJ/g)**	**% HR Reduction**	**Char Description**
Texin 990R-1	6.20	243,198	26.2	0	Shiny black, cover entire bottom of pan
Texin 990R-2	6.11	213,367	25.6	0	
Texin 990R-3	7.08	215,415	25.8	0	
TPU 990 + FR#10	15.09	244,67,48	21.9	16.7	Black shiny clump in the middle of the pan
TPU 990 + FR#10	15.11	195,72,47	21.9	16.7	
TPU 990 + FR#10	14.98	251,63,49	22.2	15.6	

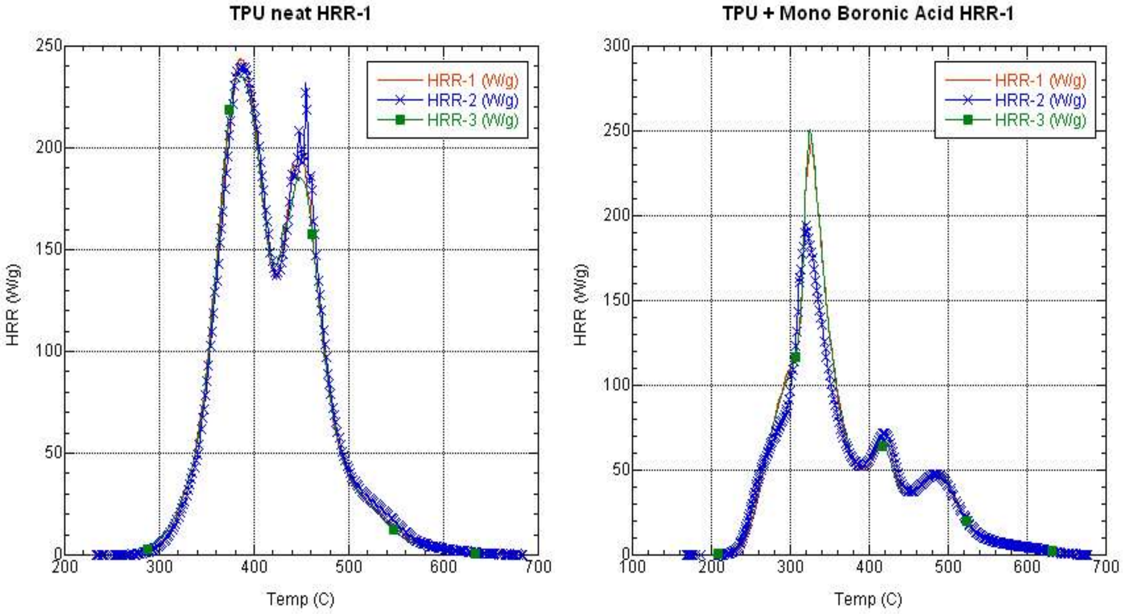
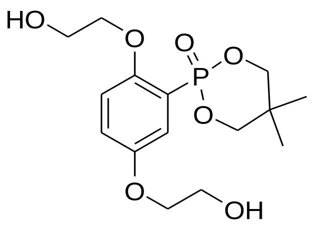


Figure 10. HRR curves for TPU (left) and TPU+mono boronicacid **10** (right)

The mono boronic acid **10** was solvent blended with TPU and PCFC results were collected. When compared to the TPU without FR compound the TPU with mono boronic acid showed a significant improvement in flame retardancy of TPU. It showed an increase in char yield and reduction in total HR. The HRR profile (figure 10) is changed when compared to the profile of TPU because the mono boronic acid could be reacting with the TPU to assist in char formation early in the thermal decomposition process. When examined at the final char, the TPU film has shrunk and there was no flow on the pan. Therefore the mono boronic acid when solvent blended not only promotes char formation, it may also prevent dripping by shrinking of the TPU.

Part II: Preparation of 1,4-bis(2-hydroxyethyl)benzene derivatives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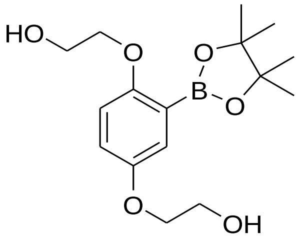
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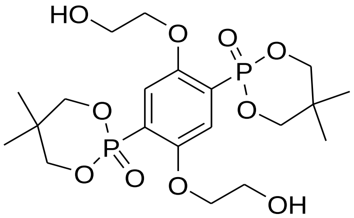
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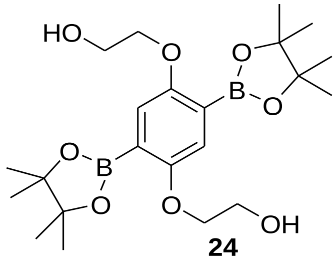
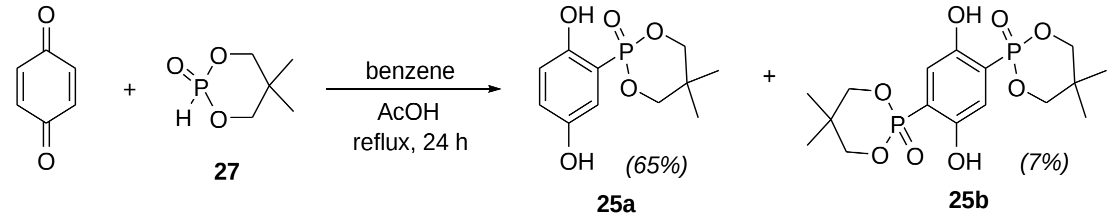

24

Structures like phosphonate and boronate moieties are chemically attached to 1,4-bis-(hydroxymethyl)benzene. Compounds **21 - 24** can be further used as monomers (diols) for synthesis of polyurethane foams. Due to the presence of phosphonate and boronate in the polyurethane backbone, effective flame retardancy could be achieved.

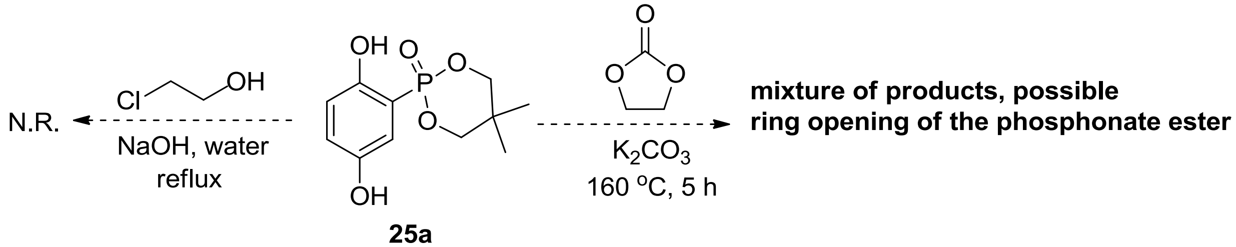
Scheme 11



Preparation of 1,4-bis(hydroxyl)-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene **(25a,b)**:

1,4- Benzoquinone was reacted with cyclic hydrogen phosphate **27** in benzene to form monophosphonated hydroquinone **25a** as a major product (Scheme 11) and small amount of diphosphonated hydroquinone **25b**, in the presence of acid as a catalyst.[36,37] The reaction was tried in toluene instead of benzene, and the same results were seen as before. The product was a mixture of **25a** and **25b** which was further purified by silica gel column chromatography. Synthesis of only diphosphonated hydroquinone was tried in dioxane but the product was a mixture of **25a** and **25b**.

Scheme 12

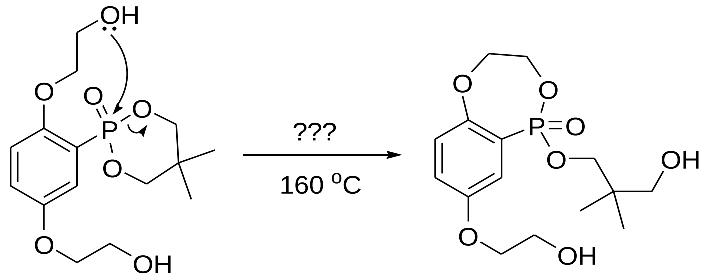


25a

Attempted preparation of 1,4-Bis(hydroxyl)-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene **(21):**

The conversion of hydroquinone to 1,4-bis(2-hydroxyethyl)benzene is well documented in literature.[38-41] The reaction of compound **25a** was attempted by a variety of reagents, such as 2-chloroethanol, 2-bromoethanol, or ethylene carbonate (Scheme 12). The reaction with 2-chloroethanol, 2-bromoethanol and some of the reactions with ethylene carbonate resulted in the recovery of starting material. Reaction with ethylene carbonates at elevated temperatures lead to a complex mixture.

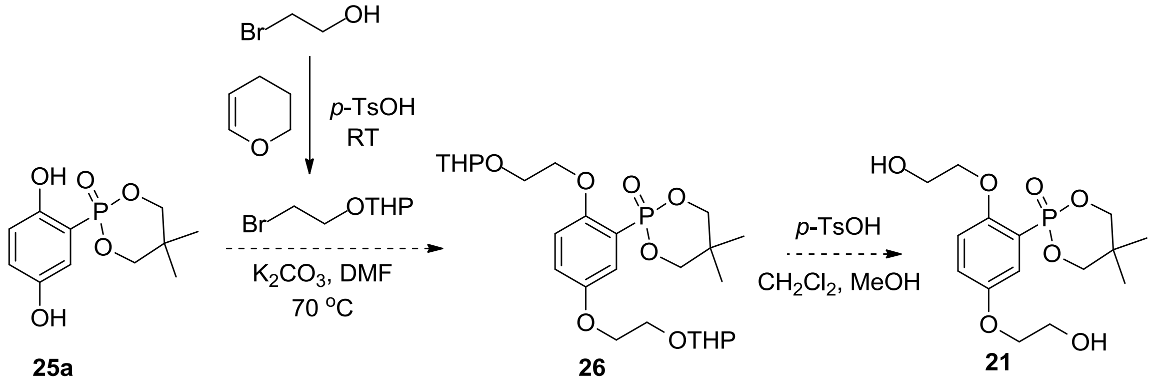
Scheme 13



*Complex reaction of **25a** with ethylene carbonate at higher temperature***:**

The reactions with ethylene carbonate were conducted at 150 °C - 160 °C, as recommended by literature. At elevated temperatures a reaction of the 2-hydroxyethyl chain with the cyclic phosphonate is possible, leading to cleavage of the ring (Scheme 13).

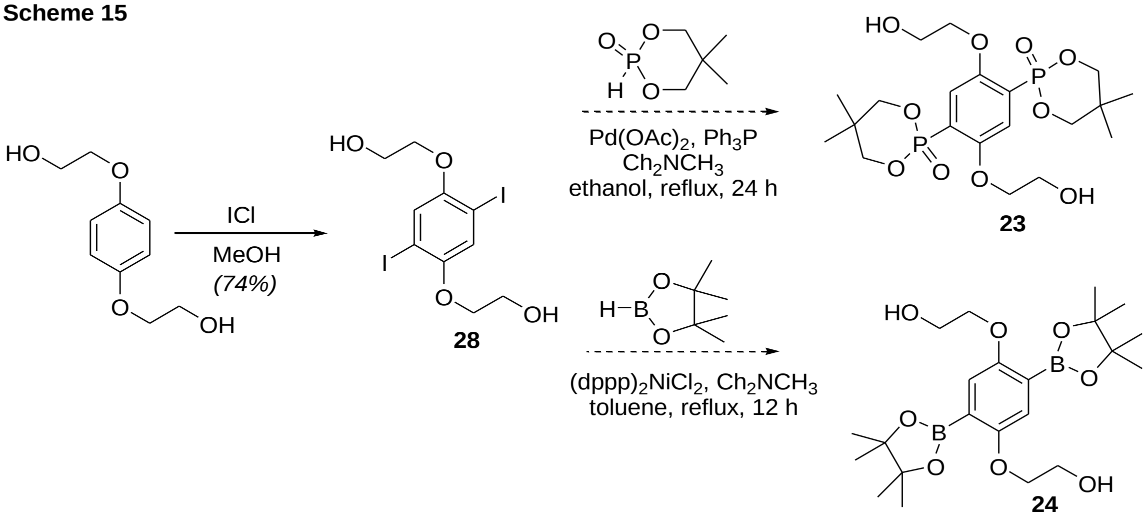
Scheme 14



Attempted preparation of 2-oxo-1,3-dioxolan-4-yl bis(2-(tetrahydro-2H-pyran-2-yloxy)ethyl)phosphate **(21):**

Since the hydroxyl groups could be interfering with the reaction, they were protected. 2-Bromoethanol was converted to the corresponding THP ether (Scheme 10).[42] Then it was reacted with **25a** followed by removal of the THP groups. The reaction resulted in a mixture.

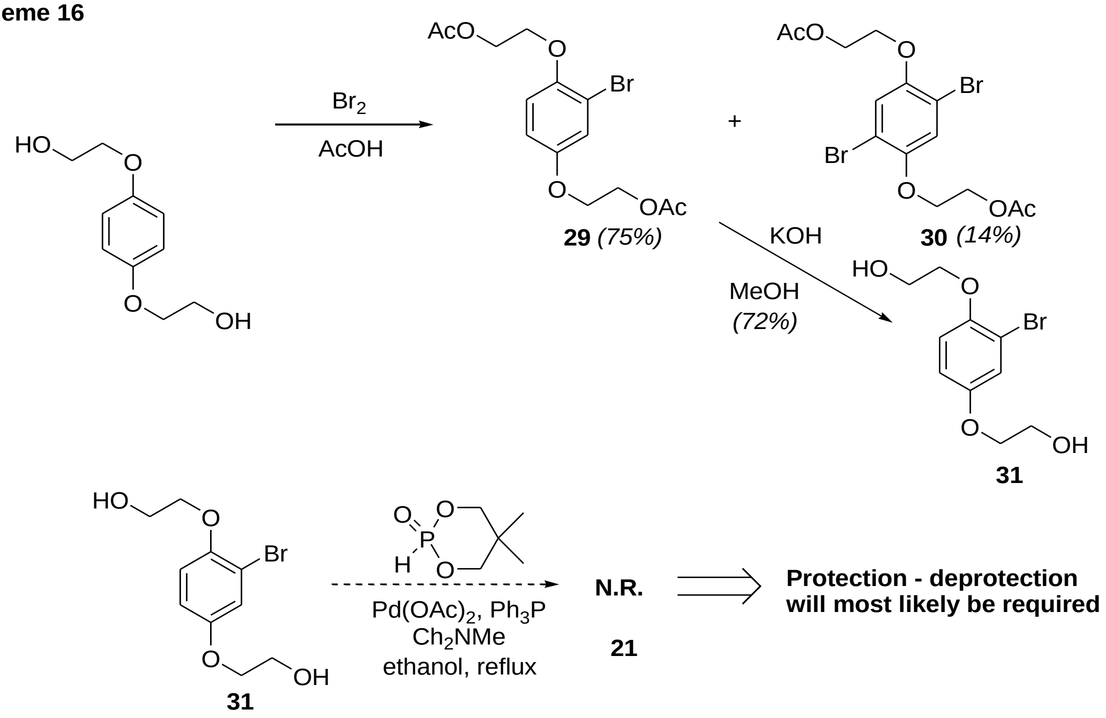
Scheme 15



Preparation of 1,4-Bis(hydroxyethoxy)-2,5-diiodo benzene (**28):**

According to Scheme 15, 1,4-bis(2-hydroxyethoxy)benzene was successfully diiodinated using the protocol of Inagaki *et al.*[43] Iodine can be replaced easily when compared to bromine so Scheme 15 was adapted. Then compound **28** was subjected to coupling reactions with the cyclic phosphite **27**, resulting in recovery of the starting material.[24] Similar results were obtained in the attempted coupling of pinacolboronate. The hydroxyl groups are likely interfering with the reaction, so the next step was to protect the hydroxyl groups by converting them into tetrahydropyranyl ethers.

Scheme 16

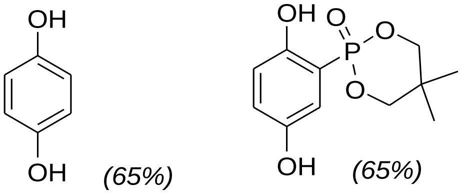


Preparation of 1,4-bis(2-hydroxythoxy)-2-bromobenzene **(31):**

Commercially available 1,4-bis(2-hydroxyethoxy)benzene was mono and dibrominated, with the intent to subsequently replace the halogens with the phosphonate/boronate esters. 1,4-Bis(2-hydroxyethoxy)benzene was brominated in the presence of acetic acid, yielding monobrominated diacetyl derivative **29** as the major product and some quantity of dibrominated derivative **30** (Scheme 16).[44,45] Hydrolysis of compound **29** in the presence of KOH and methanol led to the clean conversion of **29** into bromodiol **31.**[25] Palladium catalyzed coupling of **31** was attempted but led to the recovery of the starting material.[24] The success of this reaction might also require protection-deprotection of the alcohol groups.

MICRO COMBUSTION CALORIMETRY

The inherent heat release of the synthesized molecule **17a** to serve as flame retardants is tested by the PCFC technique.



32 **25a**

Figure 11. Structure of flame retardant, studied by PCFC (**25a**).

Table 3. PCFC summary data for compounds **25a, 32**.

Compound	**Char Yield (wt%)**	**HRR Peak Value (W/g)**	**HRR Peak Temps (^{o}C)**	**Total HR (kJ/g)**	**% HR Reduction**	**Char Description**
32	0.1	652	261	24.4	0	none visible
	0.1	712	259	24.5	0	
	0	684	259	24.6	0	
25a	42.19	817	321	9	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	

Unlike the structure **3a,** compound **25a** shows high char yields and low heat release. Though it is phosphonate ester it shows opposite effect to compound **3a** due to the presence of free hydroxyl groups. This particular compound acts in the condensed phase char forming flame retardant despite the alkyl phosphonate. Therefore, in the case of compound **25a**, the phosphorus and oxygen react first, before volatilizing, while compound **3a** volatilizes first and then reacts.

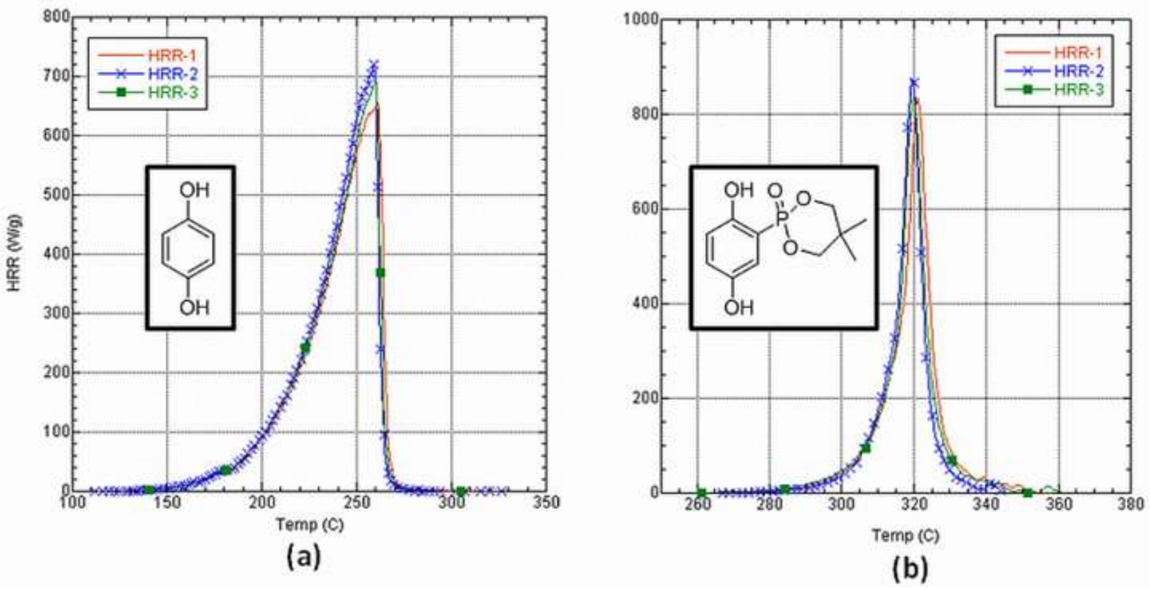
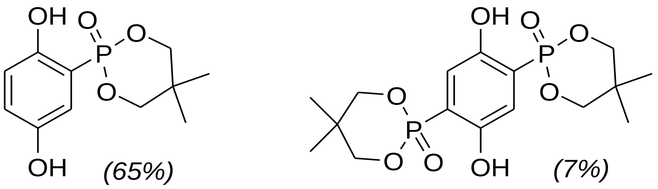


Figure 12. HRR curves for (**a**) hydroquinone, and (**b**) its cyclic phosphonate ester.

The phosphonate ester (3a,b) showed reduction in heat release when tested by itself. But when solvent blended in TPU matrix and tested it did not show very good flame retardancy, rather made the flame retardancy worse.



25a **25b**

Figure 13. Structures of FR blended into TPU (**25a** & **25b**).

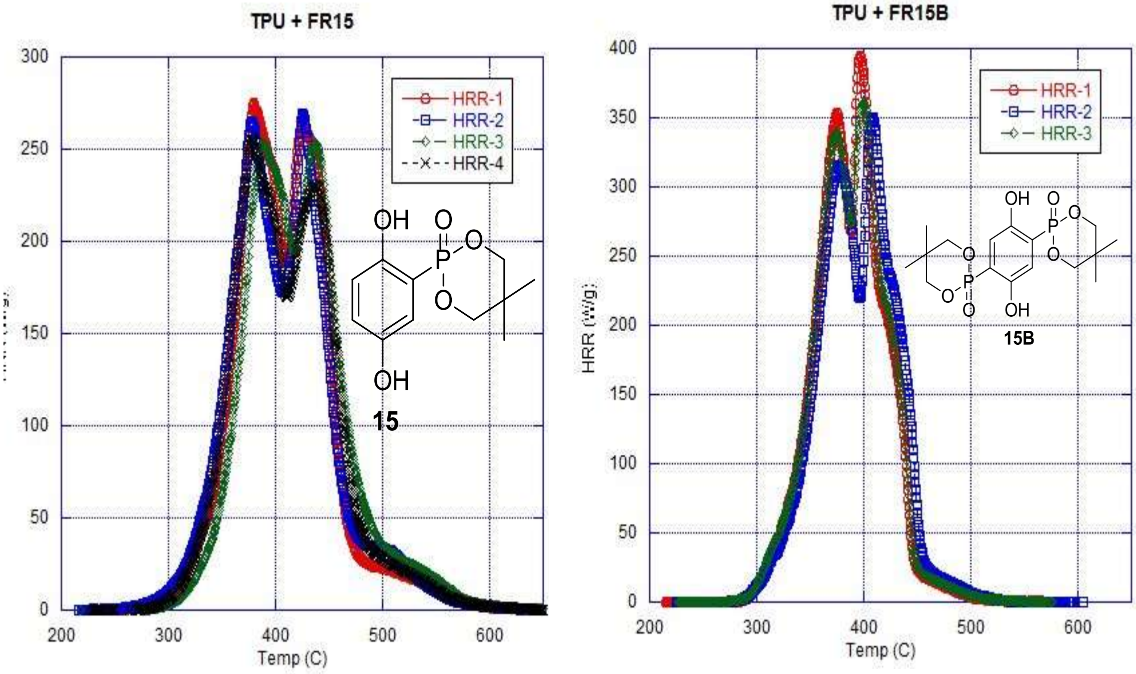


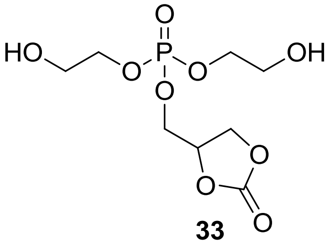
Figure 14. HRR curves for TPU +**25a** (left) and TPU+**25b** (right).

The phosphonate esters (**25a, 25b**) showed reduction in heat release when tested by themselves. But when solvent blended in TPU matrix and tested, it did not show very good flame retardancy, rather made the flame retardancy worse. Instead of reducing the heat release of TPU it increases the heat release. The reason for this could be that the phosphonate group pyrolyzes out of the polymer even before it gets a chance to form char or cross link.

Table 4. HRR data for TPU and TPU + FR blends (**25a,25b**)

Sample	**Char Yield (wt%)**	**HRR Peak Value (W/g)**	**Total HR (kJ/g)**	**% HR Reduction**	**Char Description**
Polyurethane foam-5	0.91	217,399	25.5	0	light black residue all over pan, one small dot on bottom
Polyurethane foam-6	0.82	213,367	25.6	0	
Polyurethane foam-7	0.93	215,415	25.8	0	
Texin 990R-1	1.14	169,176,332	27.5	0	Black thin fine film all over inside of pan and top part of outside
Texin 990R-2	0.53	203,346	27.2	0	
Texin 990R-3	0.95	184,361	27.5	0	
TPU 990 + 10% FR#25a-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#25a-2	4.91	265,269,32	27.5	-0.36	
TPU 990 + 10% FR#25a-3	5.51	253,253,19	27.3	-0.36	
TPU 990 + 10% FR#25-4	5.61	256,230	27.4	0	Black all over inside of pan, no flakes, small residue around edge
TPU 990 + 10% FR#25b-2	2.49	353,395	28.6	-4.38	
TPU 990 + 10% FR#25b-4	2.32	315,350	28.4	-3.65	
TPU 990 + 10% FR#25b-5	2.58	339,361	28.7	-4.74	

Part III: Preparation of (2-oxo-1,3-dioxolan-4-yl) phosphorodichloridate derivatives



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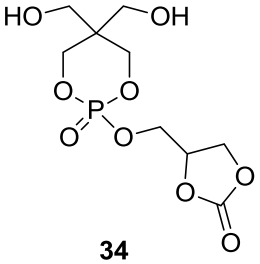

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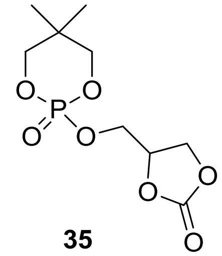
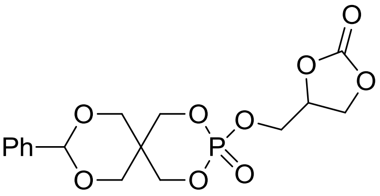


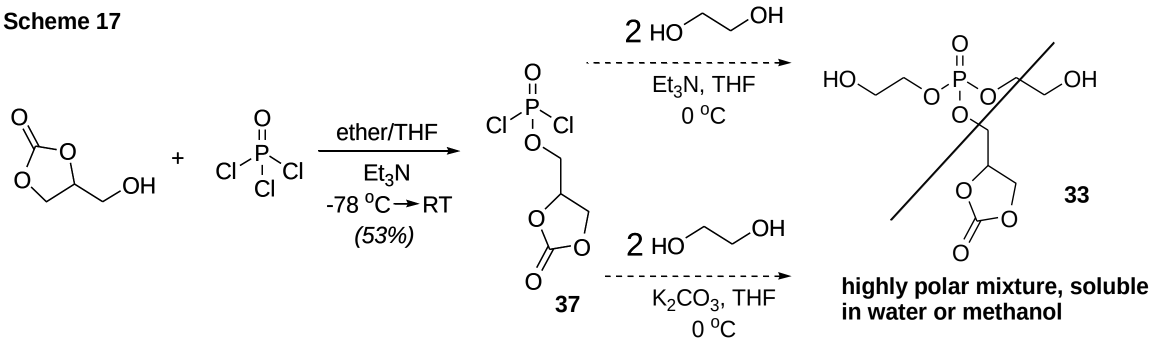
35



36

Glycerol carbonate, easily derived from glycerol, could be beneficial, if incorporated in fire retardant (FR) polymers. At higher temperatures the cyclic carbonate ring is likely to yield CO_2. Also at these temperatures carbonate ring might facilitate cross-linking. Structures **33** and **34** have a phosphorous moiety and hydroxyl groups. Due to the presence of hydroxyl groups these compounds can further be used as monomers (polyols) for synthesis of polyurethane foams. Because the phosphorous moiety is chemically bonded to the backbone of the foam, effective flame retardancy can be achieved.

Scheme 17



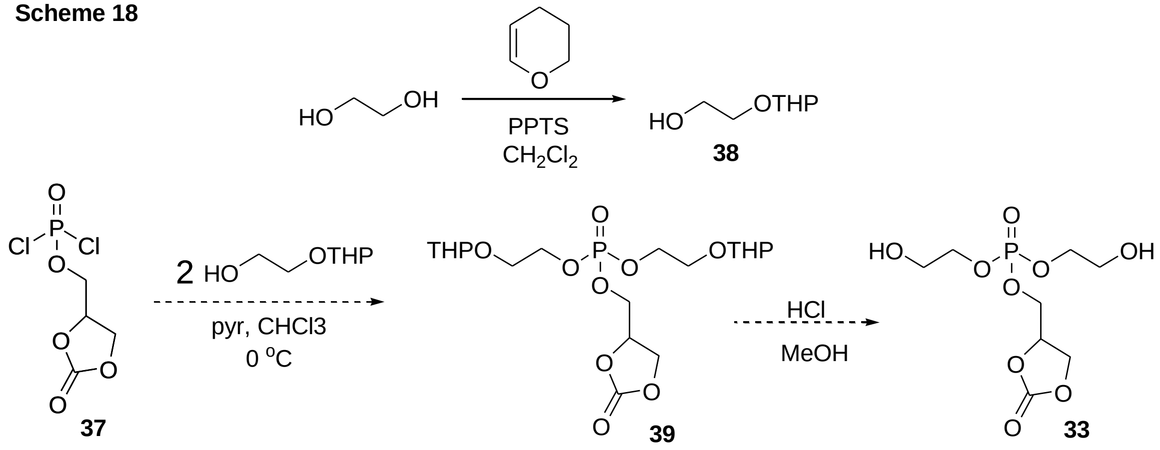
Preparation of (2-oxo-1,3-dioxolan-4-yl) phosphorodichloridate **(37):**

Commercially available phosphorous oxychloride is reacted with glycerol carbonate at -78 °C using triethyl amine as a base using ether/THF as solvents to form crude compound **37** (Scheme 17).[46] Earlier reactions were successfully conducted in THF, but the yield was lower. The isolated crude product was successfully purified *via* recrystallization from toluene.

Attempted preparation of bis(2-hydroxyethyl) 2-oxo-1,3-dioxolan-4-yl phosphate **(33):**

Compound **37** was reacted with ethylene glycol in order to generate target structure **33** (Scheme 17). However the recovered material was highly polar, and soluble in water or methanol. NMR did not indicate the presence of expected product.[47]

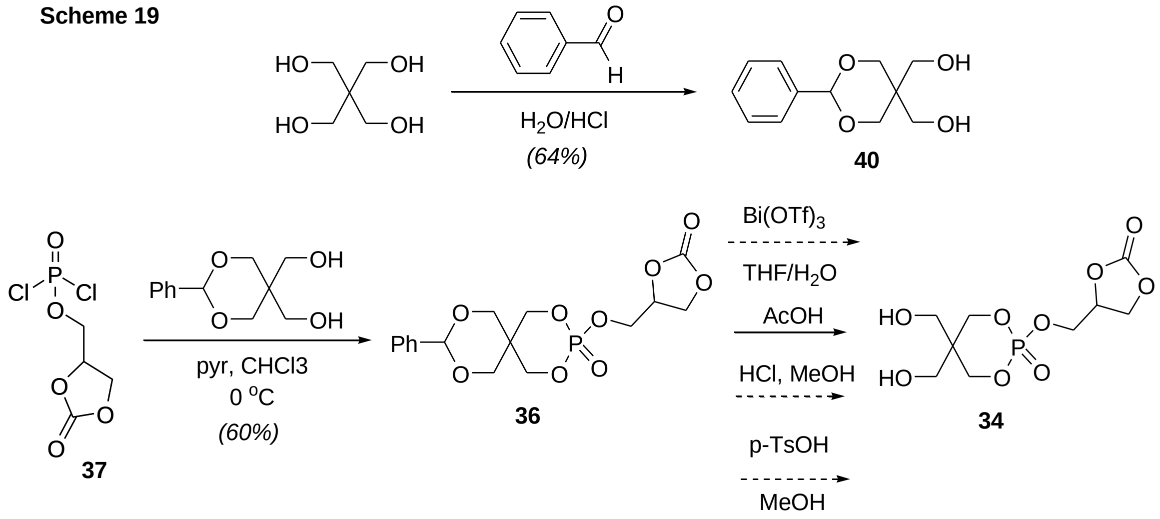
Scheme 18



Attempted preparation of 2-oxo-1,3-dioxolan-4-yl bis(2-(tetrahydro-2H-pyran-2-yloxy)ethyl)phosphate **(39):**

The hydroxyl groups in the ethylene glycol might lead to formation of polymers, so ethylene glycol was mono-protected (compound **38**, Scheme 18) to the corresponding THP ether[30,48]. The latter was reacted with **37** in the presence of triethylamine (or pyridine) as base in THF at lower temperature to form **39**. NMR showed that the starting material compound **38** was recovered. There was no reaction.

Scheme 19

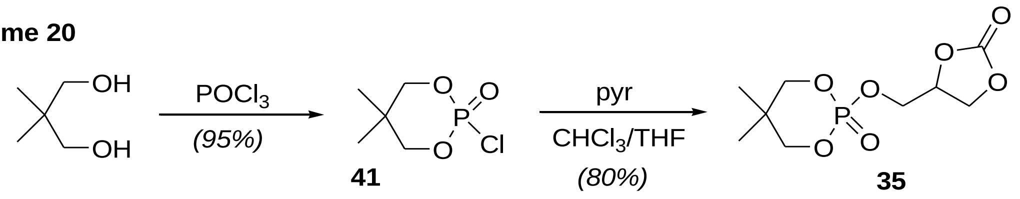


Preparation of 4-[(5,5-bis(hydroxymethyl)-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl]-1,3dioxolan-2-one **(34):**

The preparation of target structures **34** and **36** is presented in Scheme 19. Pentaerythritol was reacted with benzaldehyde in water, using HCl as acid catalyst, leading to the formation of monobenzalpentaerythritol compound **40.**[49,50] Several attempts, at different conditions, were carried out, in order to optimize the yield of **36**, that was initially very low. The reaction was carried out in benzene, resulting in an impure product and very low yields.[9] Finally **36** was successfully synthesized by reacting the dichloride **37** with diol **40** using pyridine as a base and chloroform as solvent. The product was further purified *via* recrystallization from ethanol.

Several attempts were made to synthesize target structure **34**. Deprotection of **36** was done using Bi(OTf)$_3$ or *p*-TsOH as a catalyst and THF/H$_2$0 as solvents. However the starting material was isolated intact. When HCl was used as catalyst, NMR showed loss of the carbonate ring. Finally deprotection was successfully achieved in the presence of Acetic acid using water as a solvent.

Scheme 20



Preparation of (5,5-dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl-1,3-dioxolan-2-one **(35):**

Glycerol carbonate-containing compounds, like structures **35** and **36** could be useful in layer-by-layer (LBL) protective coating applications for PU foams,[51] since the cyclic carbonate would likely be reactive towards polymer amino groups, enhancing flame retarding properties. Structure **41** was synthesized by drop wise addition of phosphorous oxychloride to the stirred solution of neopentyl glycol in chloroform at about 0°C and slow warm-up to ambient temperature (Scheme 20). Structure **41** was further reacted with glycerol carbonate using pyridine as a base and chloroform and THF as solvents, to synthesize structure **35**.

MICRO COMBUSTION CALORIMETRY

The inherent heat release of the synthesized molecules **35** and **36** to serve as flame retardants is tested by the PCFC technique.

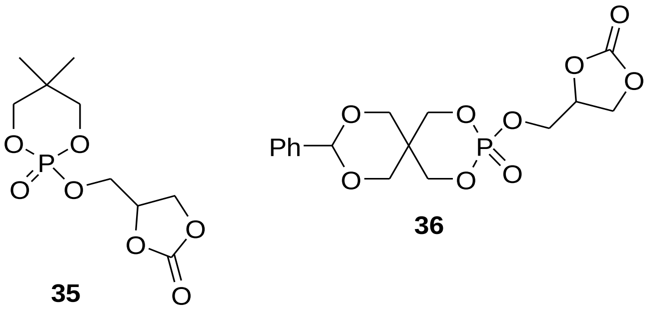
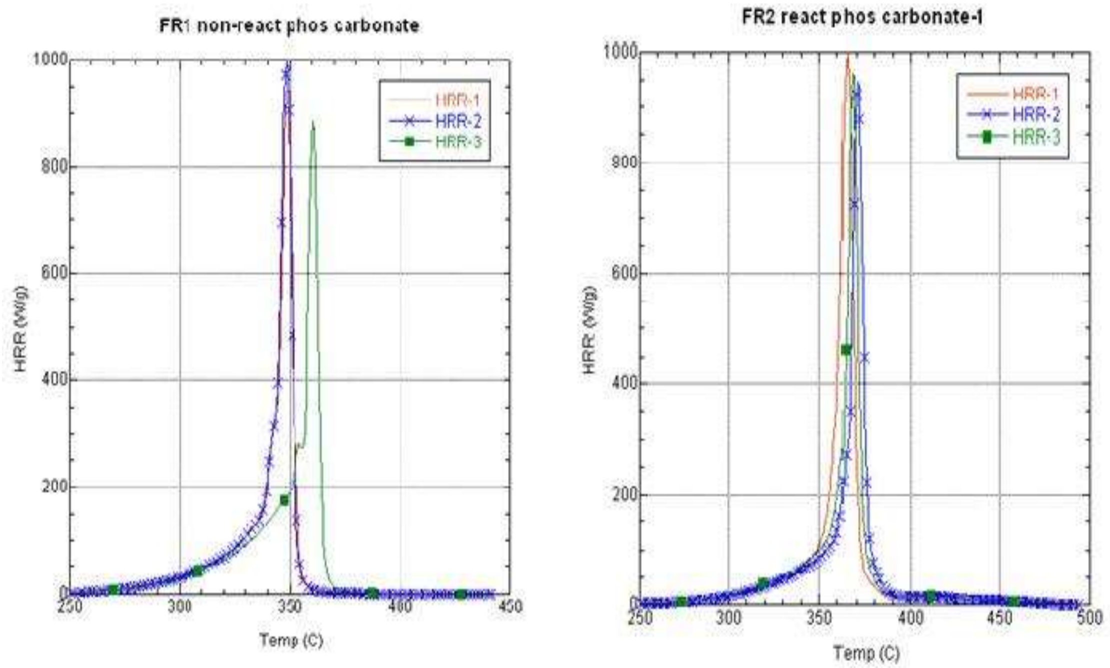


Figure 15. Structure of flame retardant, studied by PCFC (**35** & **36**).

The PCFC data of compound **35** and compound **36** shows char formation. The heat release rate is very high indicating that there is possibility that part of the compounds pyrolyze leaving behind the phosphates which char.

Table 5. PCFC summary data for compounds **35** and **36**.

Compound	Char Yield (wt%)	HRR Peak Value (W/g)	HRR Peak Temps (^oC)	Total HR (kJ/g)	Char Description
35	14.83	952	349	24.4	Black dull ash over half pan.
	13.56	997	348	24.5	
	15.17	885	361	24.6	
36	31.51	999	365	9	Black dull ash over half pan.
	29.32	948	371	8.2	
	30.05	957	368	8.8	



(a) (b)

Figure 16. HRR curves for (**a**) compound **35** (FR1), (**b**) compound **36** (FR2)

Table 6. HRR data for TPU and TPU + FR blends (**35, 36**)

Sample	**Char % Yield**	**HRR Peak(s) Value (W/g)**	**HRR Peak Temps (°C)**	**Total HR (kJ/g)**	**Char Notes**
Texin 990R-1	6.20	248,198	386,451	26.2	Black thin fine film all over inside of pan and top part of outside
Texin 990R-2	6.11	240,232	389,455	26.6	
Texin 990R-3	7.08	235,185	382,448	26.1	
TPU + FR#35-1	5.38	226, 303	374, 436	26.8	black film all over pan, little ash around edges
TPU + FR#35-2	5.25	236, 301	380, 435	26.7	
TPU + FR#35-3	5.44	233, 309	375, 436	26.5	
TPU + FR#36-1	6.57	313, 335	382, 397	26.8	shiny black crusty residue over 3/4 pan
TPU + FR#36-2	6.86	304, 337	379, 394	27.0	
TPU + FR#36-3	6.98	303, 333	381, 396	27.2	

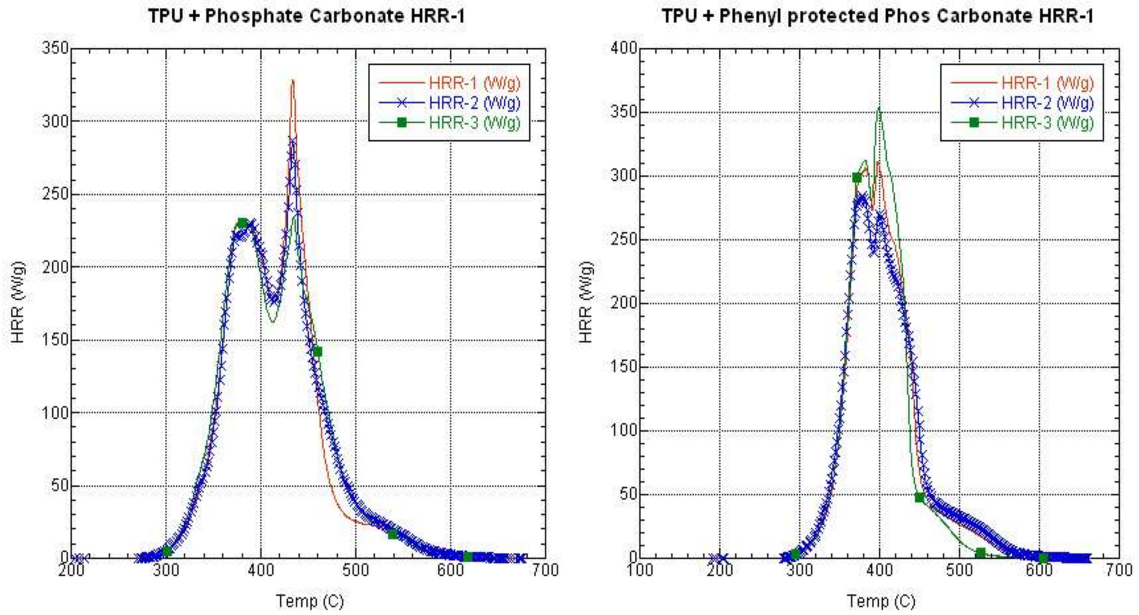


Figure 17. HRR curves for TPU+**35** (left) and TPU+**36** (right)

The table 6 above gives the HRR data for compounds **35** and **36**. When compared, the HRR data of compound **35** is not much different than the HRR data of TPU. The carbonate group did not have much effect on the HRR of compound **35**. Table 6 gives the HRR data for TPU, TPU + compounds **35** and **36**. When compared, the HRR data of compound **36** with that of TPU, there is slight reduction in the heat release but the difference is insignificant and likely within the % error for the PCFC technique. The reason for this could be that the carbonate group pyrolyzes even before it gets a chance to crosslink/char. But compound **36** does not volatilize as quickly as **35**, and therefore might have a potential for condensed phase char formation. Therefore these compounds are not much of use as flame retardants when solvent blended with TPU but when reacted with polyurethane foams the results might be different.

CHAPTER 3

EXPERIMENTAL

Pyrolysis combustion flow calorimetry (PCFC) was accomplished with the MCC 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 TA Instruments Q1000 DSC, under nitrogen from 25 to 300 ^{o}C at 5 ^{o}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). X-ray structures were obtained using an *Oxford Diffraction Xcalibur3* diffractometer with graphite monochromatic Cu K_{α} radiation. Structure solution and refinement was performed using the SHELXTL 6.10 software package. 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 2-iodoterephthalate (4).[22] Dimethyl aminoterephthalate (10.50 g, 50.0 mmol) was taken in a 100 mL conical flask. To this 10 mL of water, 40 g of ice and 15 mL of H_2SO_4 were added and stirred for about 5 min. Solution of $NaNO_2$ (3.65 g, 50.00 mmol) and 10 mL of water was added drop wise for a period of 30 min at 0 ^{o}C. The reaction was continued for another 30 min at 0 ^{o}C. Then the reaction mixture was added slowly to the stirring solution of KI (9.96 g, 50.00 mmol) and water (10 mL). The reaction was continued for 20 min at 60 °C. Iodine formed in the reaction was removed by adding it to a solution of $NaHSO_3$ and water. The solids were filtered and recrystallized with methanol. Yield: 73% (11.17 g, 34.89 mmol). ^1H NMR (DMSO) δ 3.87 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 8.00 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.43 (d, J = 1.6 Hz, 1H).

Phosphonate esters 3 (Route 1).[23] A mixture of dimethyl iodoterephthalate (100.00 mmol), trialkyl phosphite (400.00 mmol) and $PdCl_2$ (10.00 mmol) 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 over $MgSO_4$ and the solvent 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.

Dimethyl (dimethylphosphono)terephthalate (3a). Yield: 81%. Colorless oil. ^1H 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 (3b). Yield: 86%. Colorless oil. ^1H 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).

Ethyl 2-ethyl-5-(hydroxymethyl)phenyl(methyl)phosphonate (20). To the stirring solution of $LiAlH_4$ (1.108 g, 29.00 mmol) and THF (50mL), **3b** (3.96 g, 11.90 mol) and THF (35 mL) were added dropwise by means of addition funnel under nitrogen at 0 $^{\circ}$C. After complete addition, the reaction mixture was brought to ambient temperature and stirred for 12 h in inert conditions. The reaction mixture was extracted with ethyl acetate, organic layer dried over $MgSO_4$, and solvent removed under reduced pressure. The product appeared to be some kind of polymer. Modifying carboxilic esters without effecting phosphonic and boronic esters cannot be achieved by using complex hydrides like $LiAlH_4$ and $NaBH_4$.

Dimethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate (5).[25] 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 $(dppp)_2NiCl_2$ (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_2Cl_2) indicated the presence of two main components: the target material (slower running) and dimethyl terephthalate. 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_2Cl_2 = 1: 1), the solvent removed under reduced pressure and the product was isolated as a white solid. Yield 71% (2.51 g, 7.84 mmol). The product was further purified by using pentane. Mp 69 ^{o}C - 71 ^{o}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_3CN) 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.

2-Boronoterephthalic acid (10): To compound **5,** HCl (3M) was added and stirred for 4 h at 60 °C then cooled to room temperature, was solvent evaporated and recrystallized with H_2O. The product was confirmed by NMR. The product decomposes at higher temperatures starting from 305 °C (white solid turns brown). Yield 55%. ^{1}H NMR (D_2O) 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_2O) δ 127.2, 132.3, 135.9, 141.4, 173.1, 177.5; Anal. Calcd. for $C_8H_7BO_6$: C, 45.77; H, 3.36. Found: C, 45.34; H, 3.26.

2-Iodoterephthalic acid (6).[27] Dimethyl iodoterephthalate **4** (3.00 g, 9.37 mmol) was dissolved in 15 mL of methanol and KOH (2.1 g, 13.75 mmol) was added to the solution. The reaction was continued for 30 min at 35 °C. Then 30 mL of water was added. The aqueous layer was extracted with ether (2*25). The aqueous layer was acidified to pH 2 with conc. HCl, cooled for about 2 h and solids filtered. Yield 98% (2.68 g, 9.18 mmol).^{1}H NMR (DMSO) δ 7.74 (d, J = 8.0 Hz, 1H), 7.96 (dd, J_1 = 7.98 Hz, J_2 = 1.6 Hz, 1H), 8.39 (d, J = 1.5 Hz, 1H).

2-Iodo-1,4-bis(hydroxymethyl)benzene (7).[30] Dry THF (16.2 mL) was added to dimethyl iodoterephthalic acid **6** (1.84 g, 6.60 mmol) purged with nitrogen. Solution of borane/THF (24.2 mL) was added drop wise by means of addition funnel for a period of 20 min at 0 °C in inert conditions. The reaction was continued for 4 h at ambient temperature. Then 1:1 THF/ water mixture was added and extracted with ethyl acetate, dried over $NaSO_4$ and solvent removed under reduced pressure. The residue was purified on a silica gel column, using ethyl acetate. Yield: 78% (1.28 g, 5.19 mmol). Mp 96 °C -

98 °C. ^{1}H NMR (DMSO) δ 4.39 (d, J = 5.5, 2H), 4.44 (d, J = 5.8, 2H), 5.24 (t, J = 5.8 Hz, 1H), 5.39 (t, J_1 = 5.5 Hz, 1H), 7.328 (dd, J_1 = 7.87 Hz, J_2 = 1.5 Hz, 1H) 7.41 (d, J = 7.8 Hz 1H) 7.74 (d, J = 1.4 Hz, 1H). ^{13}C NMR (DMSO) δ 61.8, 67.1, 96.7, 126.2, 127.3, 136.3, 141.9, 143.3; Anal. Calcd. for $C_8H_9IO_2$: C, 36.39; H, 3.44. Found: C, 36.61; H, 3.35.

Attempted preparation of 2-iodo-1,4-bis(hydroxymethyl)benzene (7).[31] To the stirring mixture of iodoterephthalate **4** (3.00 g, 9.37 mmol), $NaBH_4$ (3.545 g, 9.370 mmol) and DME (16.6 mL, 9.3 mmol), methanol (9 mL) was added by means of additional funnel for a period of 1 h. After complete addition of methanol, reaction was continued for another 1 h. The reaction mixture was added to water in an ice bath and extracted with toluene, dried over Na_2SO_4, and solvent removed under reduced pressure. The recovered product was without iodine, 1,4-bis(hydroxymethyl)benzene and methyl 4(hydroxymethyl)benzoate. The reaction did not work.

5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yl (27).[32] Mixture of diethyl phosphite (58.00 g, 420.00mol) and neopentyl glycol (41.66 g, 400.00 mmol) was taken in round bottomed flask and stirred at 150 °C. Ethanol is formed as a byproduct in this reaction and was collected in a dry ice cooled flask. Reaction was continued for 6 h and allowed to cool to ambient temperature overnight. A mixture of 1:1 THF and hexane was added and heated with heat gun and then kept in the freezer for 1 h and the product was filtered. Yield: 65% (40.98 g, 0.27 mmol). ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 6H), 1.15 (s, 3H), 1.23 (s, 3H), 4.00 (m, 4H), 5.74 (s, 0.5H), 7.99 (s, 0.5H).

Attempted preparation of 1,4-bis(hydroxymethyl)-2-(5,5,-dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yl)benzene (1).[52] To the stirring mixture of Ch_2NMe (1.107 g, 5.67mmol), triphenylphosphine (0.062 g, 0.22 mmol) and Pd(OAc)$_2$ (0.0165 g, 0.0738 mmol), compound **7** (1.00 g, 3.78 mmol), compound **27** (0.679 g, 4.50 mol) and ethanol (16mL) was purged with nitrogen and refluxed for 12 h in inert atmosphere. EtOH was evaporated, extracted with ethyl acetate, organic layer separated, dried over Na$_2$SO$_4$ and solvent removed under reduced pressure. There was no reaction. The starting material was recovered. The hydroxyl groups were interfering with the course of reaction. The hydroxyl groups were protected for further reactions.

2,2’-(2,2’-(2-iodo-1,4,phenylene)bis(methylene)bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(2-methyl-tetrahydro-2H-pyran) (8).[33] 2-Iodo-1,4-bis(hydroxymethyl)benzene **7** (2.00 g, 8.00 mmol), 3,4-dihydro pyran (1.39 g, 16.00 mmol), DMF (2 mL), methylene chloride (20 mL) and *p*-toulene sulfonic acid (0.32 g, 1.66 mmol) were taken in a round bottomed flask and stirred for 24 h at ambient temperature. The reaction mixture was washed with water (3*30ml), dried over NaSO$_4$, and solvent removed under reduced pressure. The product was formed with some impurities.

2,2’-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4,phenylene)bis(methylene)bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(2-methyl-tetrahydro-2H-pyran) [25] Protected diol **8** (0.96 g, 2.30 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaboralane (0.365 g, 2.86 mmol), Ch$_2$NMe (0.575 g, 2.94 mmol), (dppp)$_2$NiCl$_2$ (0.0246 g, 0.04545 mmol), and toluene (3 mL) were added together under nitrogen and refluxed for 12 h in inert atmosphere. Washed with dil. HCl, organic layer separated, dried over MgSO$_4$ and solvent removed under reduced pressure. NMR showed there was partial deprotection of the starting material but there was no coupling reaction. The product was a mixture.

1,4-Diiodo-2,5-dimethyl benzene (16). A mixture of *p*-xylene (17.70 g, 167.00 mmol), periodic acid (15.20 g, 66.50 mmol), iodine (34.00 g, 134.00 mmol), acetic acid (80 mL), water (16 mL) and conc. H_2SO_4 (2.5 mL) were stirred at 70 ºC. An exothermic reaction occurred and the temperature increased to 80 ºC. The reaction mixture was cooled to 70 ºC and allowed to continue at that temperature for about 5 h. The reaction mixture was then cooled and poured into aq. $NaHSO_3$ to remove excess iodine. The solids were filtered and slurried in methanol (100 mL). The product was filtered and confirmed by NMR. Yield: 65% (36.43 g, 101.77mmol). ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 6H), 7.58 (s, 2H).

2,5-Diiodoterephthalic acid (17). $KMnO_4$ (6.618 g, 41.87 mmol) was added to the refluxing mixture of **16** (5.00 g, 13.96 mmol), water (180 mL) and *t*-butanol (100 mL) in 4 portions, once every 2 h. Then the reaction was continued at reflux for about 24 h. Hot filtered the reaction mixture and solvent was evaporated from the filtrate. Then the filtrate was extracted with ether, acidified with conc. HCL and refrigerated for 5 h. The product was filtered and washed with ether. Yield: 45% (2.62 g, 6.28 mmol). ^{1}H NMR (DMSO) δ 8.14 (s, 2H).

Dimethyl 2,5-diiodoterephthalate (18). Conc. H_2SO_4 (4 mL) was added to the solution of **17** (1.21 g, 28.95 mmol) in methanol (30 mL) and refluxed for 5 h. Then the reaction mixture was cooled in the refrigerator overnight and the product was filtered. Yield: 64% (0.82 g, 1.85 mmol). ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 8.16 (s, 2H)

Dimethyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate (19). To **18** (0.50 g, 1.12 mmol), bis(pinacolato)diboron (0.62 g, 2.44 mmol), KOAc (0.33 g, 3.37 mmol), $PdCl_2(dppf)_2$ (0.046 g, 0.0561 mmol), and DMF (10 mL) were added and the mixture purged with nitrogen. The reaction mixture was stirred for about 21 h at 80 ºC, in inert conditions. The mixture was cooled and DMF evaporated. Benzene (40 mL) was added to the product and the slurry filtered. The filtrate was washed with aq. NaCl and water, organic layer separated, dried over $MgSO_4$ and solvent removed under reduced pressure. The solids were washed with cold pentane to remove excess bis(pinacolato)diboron. Yield: 40% (0.20 g, 0.45 mmol). The product decomposed at higher temperatures due to the presence of impurities. NMR (CDCl3) δ 1.44 (s, 24H), 3.93 (s, 6H), 8.04 (s, 2H); Anal. Calcd. for $C_{22}H_{32}B_2O_8$: C, 59.23; H, 7.23. Found: C, 56.17; H, 6.21.

2,5-Diboroterephthalic acid (11). Conc. HCl (2 mL) was added to **19** (0.5 g, 1.12 mmol) and stirred for about 4 h at 40 ºC. Then solvent was removed under reduced pressure and the product was confirmed by NMR. Yield: 77% (0.22 g, 0.86 mmol). The product requires further purification. ^{1}H NMR (D_2O) δ 7.76 (s, 2H).

1,4-Bis(hydroxyl)-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (25).[36,37] To the stirring solution of cyclic phosphite **27** (2.84 g, 18.90 mmol) and toluene (30 mL), mixture of *p*-quinone (2.00 g, 18.50 mmol), toluene (20 mL), and acetic acid (0.1128 g, 1.90 mmol) was added drop wise for a period of 20 min. The reaction was continued at reflux overnight (110 $^{\circ}$C). Solvent was removed under reduced pressure and washed with acetone. Solids filtered and solvent removed under reduced pressure from filtrate. The product was washed with ether and purified by using silica gel column using methylene chloride. Yield: 65% (3.40 g, 11.88 mmol). ^{1}H NMR (DMSO) δ 0.59 (s, 6H), 1.15 (s, 6H), 3.33 (d, 4H), 3.65 (m, 4H), 7.06 (m, 2H), 9.1 (s, 1H), 9.85 (s, 2H).

1,4-Bis(hydroxyethoxy)-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphoaphan-2-yl)benzene (21).[38-41]

Route 1:-Prolonged heating of ethylene carbonate led to complex reactions.

Route 2:- 2-Bromoethanol has been converted to the corresponding THP ether. [42]

1,4-Bis(hydroxyethoxy)-2,5-diiodo benzene (28).[43] Iodine monochloride (28.50 g, 350.00 mmol) was added drop wise to methanol (40 mL) at 10 °C - 15 °C. Then 1,4-bis(2-hydroxyethoxy)benzene (7.00 g, 70.00 mmol) was added to the above mixture. Then the reaction was refluxed for 4 h and cooled to 5 °C and product filtered. Yield: 74% (11.81 g, 26.12 mmol). ^{1}H NMR (DMSO) δ 3.70 (t, 4H), 3.98 (t, 4H), 7.38 (s, 2H).

1,4-Bis(2-hydroxythoxy)-2-bromo)benzene (31). [44, 45] To the stirring solution of 1,4-bis(2-hydroxyethoxy)benzene (5.00 g, 25.200 mmol) and acetic acid (35.12 mL), bromine (4.33 g, 27.10 mmol) and acetic acid (18.6 mL) were added drop wise for a period of 1 h. Then water (21 mL) was added and reaction was continued for another 1 h. The product was extracted with chloroform. Acetic acid was removed by adding Na_2CO_3 solution. But the product formed was 1,4-bis(2-acetoxyethoxy)-2-bromobenzene and was further hydrolyzed by MeOH and KOH. Yield: 72% (6.07 g, 18.17 mmol). ^{1}H NMR (DMSO) δ 3.68 (m, 4H), 3.95 (m, 4H), 4.83 (td, J_1 = 5.61 Hz, J_2 = 1.43 Hz, 2H), 6.89 (dd, J_1 = 8.99 Hz, J_2 = 2.91 Hz, 1H) 7.05 (d, J = 9.03 Hz, 1H) 7.14 (d, J = 2.91 Hz, 1H).

Attempted preparation of 1,4-bis(2-hydroxyethoxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ylbenzene (22).[25] In a round bottomed flask 1,4-Bis(2-

hydroxythoxy)-2-bromo)benzene (1.00 g, 3.62 mmol), pinacol borolane (0.656 mL, 4.52 mmol), Ch2NMe (1.32 mL, 6.75 mmol), $(dppp)_2NiCl_2$ (0.0566 g, 0.010440 mmol), toluene (7 mL) were mixed together and refluxed for 12 h. Then dil. HCl was added to reaction mixture, organic layer separated, dried over Na_2SO_4 and solvent removed under reduced pressure. There was no reaction.

2-Oxo-1,3-dioxolan-4-yl phosphorodichloridate (37).[46] To the stirring solution of phosphorous oxychloride (10 mL, 107.20 mmol), THF (30 mL), ether (120 mL), mixture of glycerol carbonate (4.52 mL, 107.20 mmol), triethyamine (7.48 mL, 107.20 mmol), ether (120 mL) and THF (30 mL) was added drop wise for a period of 2 h at -78 °C. The reaction was continued for 24 h slowly bringing to ambient temperature. Filtered the solids and solvent was removed under reduced pressure from the filtrate. But the yield was less, so the solids were redissolved in 250 mL THF, stirred for 5 min and filtered to remove the solids. Solvent was removed under reduced pressure from the filtrate. The product was recrystallized from toluene. Yield: 53% (13.35 g, 56.82 mmol). Mp 65 °C - 67 °C. ^{1}H NMR ($CDCl_3$) δ 4.46 (m, 2H), 4.62 (m, 2H), 5.02 (m, 1H). ^{13}C NMR (DMSO) δ 64.8, 65.6, 75.1, 154.8. Anal; Calcd. for $C_4H_5Cl_2O_5P$: C, 20.45; H, 2.14. Found: C, 23.13; H, 2.48.

Bis(2-hydroxyethyl)2-oxo-1,3-dioxolan-4-yl phosphate (33).[47]

Route 1: To the stirring mixture of ethylene glycol (1.58 g, 0.02550 mol), triethyl amine (1.72 g, 17.00 mmol) and THF (5 mL), **37** (2.00 g, 8.51 mmol) and THF (20 mL) was added drop wise at 0 °C for a period of 2 h. Precipitate formed which was filtered and solvent removed under reduced pressure from the filtrate. The obtained product was ethylene glycol. There was no reaction.

Route 2: The reaction was done with similar procedure except K_2CO_3 was used as a base instead of triethylamine. The product was highly polar mixture which was soluble in both water and methanol. Therefore further reactions were done with mono protected ethylene glycol.

2-(2-Methyl-tetrahydro-2H-pyran-2-yloxy)ethanol (38).[48] To the stirring mixture of ethylene glycol (10.00 mL, 179.00 mmol), PPTS (0.45 g, 17.85 mmol) and methylene chloride (250 mL), 3,4-dihyropyran (10.8 mL, 119.00 mmol) in methylene chloride (50 mL) were added drop wise for a period of 1.5 h. The reaction was continued for 12 h and solvent removed under reduced pressure. The product was purified by column chromatography by using 4:1 Hexane: Ethyl Acetate. Yield: 87% (20.51 g, 140.29 mmol).

Attempted preparation of (2-Oxo-1,3-dioxolan-4-yl)bis(2-tetrahydro-2H-pyran-2-yloxy)ethyl phosphate (39).[47] To the stirring mixture of mono protected ethylene glycol **38** (1.24 g, 8.51 mmol), triethyl amine (0.861 g, 8.51 mmol) and THF (3mL), **37** (1.00 g, 4.25 mmol) in THF (10 mL) were added drop wise for a period of 2 h. Added 10 mL of ether and filtered the solids. Solvent was removed under reduced pressure from the filtrate. There was no reaction.

(2-Phenyl-1,3-dioxane-5,5-diyl)dimethanol (40).[49,50] A mixture of pentaerythritol (18.00 g, 132.00 mmol) and water (130 mL) was taken in round bottomed flask and heated with a heat gun while stirring until dissolved completely. The mixture was then cooled to ambient temperature and conc. HCl (0.66 mL) was added. Then 3 mL of benzaldehyde was added and stirred. When precipitate started to form, benzaldehyde (14.70 g, 138.00 mmol) was added drop wise for a period of 1 h. The reaction was continued for another 3 h. The precipitate was filtered and washed with ice cold mixture of Na_2CO_3 and water (10 mL). A mixture of cold Na_2CO_3 and water (100 mL) was added to the precipitate and heated and hot filtration was done. Cooled for 18 h at -30 ºC and recrystallized with toluene. Yield: 64% (18.85 g, 84.14 mmol). ^{1}H NMR (DMSO) δ 3.22 (d, 2H), 3.7 (d, 2H), 3.80 (d, 2H), 3.90 (d, 2H), 4.55 (t, 2H), 5.40 (s, 1H), 7.55 (m, 5H).

3-Oxo-3-(2-oxo-1,3-dioxolan-4-yl)methoxy-8-phenyl-2,4,7,9-tetraoxa-3-phosphaspiro [5,5]undecane (36). Pyridine (0.67 g, 8.50 mmol) was added to solution of monobenzalpentaerytritol **40** (0.95 g, 4.25 mmol) and chloroform (10 mL), and the resultant solution purged with nitrogen. Then mixture of **37** (1.00 g, 4.25 mmol) and chloroform (10 mL) was added drop wise for a period of 30 min at 0 °C in inert atmosphere. The reaction was continued for 24 h slowly bringing it to ambient temperature. The solvent removed under reduced pressure and water (30 mL) was added, extracted with ether (3*35 mL), dried over $MgSO_4$ and recrystallized with ethanol. Yield: 60% (1.03 g, 2.68 mmol). Mp 200 °C - 204 °C. ^{1}H NMR ($CDCl_3$) δ 3.68 (d, 1H), 3.91 (m, 2H), 4.13 (m, 1H), 4.30 (m, 1H), 4.41 (m, 2H), 4.51 (m, 1H), 4.64 (m, 2H), 4.98 (m, 2H) 7.40 (m, 6H). ^{13}C NMR (DMSO) δ 33.9, 65.7, 66.2, 66.3, 67.4, 68.0, 71.1, 71.2, 71.3, 71.4, 74.7, 74.8, 101.3, 126.2, 128.1, 129.0, 137.8, 154.8; Anal. Calcd. for $C_{16}H_{19}O_9P$: C, 49.75; H, 4.96. Found: C, 49.8; H, 4.84.

5,5-Dimethyl-2-chloro-2oxo-1,3,2-dioxaphosphane (41). **[53]** Neopentyl glycol (52.08 g, 500.00 mmol), and $CHCl_3$ (300 mL) were charged into a 500 mL flask with an addition funnel and rubber pipe to transport the HCl into the KOH solution. Phosphorous oxychloride (76.67 g, 500.00 mmol) was added drop wise at 0 °C. After the complete addition of $POCl_3$, the temperature was increased to 20 °C - 30 °C and the reaction was continued for 2 h. Solvent was removed under reduced pressure and the product confirmed by NMR. Yield: 97% (89.24 g, 483.68 mmol). ^1H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.31 (s, 3H), 3.95 (dt, J_1 = 10.5 Hz, J_2 = 1.6 Hz, 1H), 4.05 (dt, J_1 = 11.4 Hz, J_2 = 1.7 Hz, 1H), 4.21 (m, 1H), 4.25 (m, 1H).

(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl-1,3-dioxolan-2-one (35). Cyclic phosphate **41** (2.00 g, 10.80 mmol), pyridine (0.87 g, 10.80 mmol), glycerol carbonate (0.92 mL, 10.80 mmol), THF (5 mL) and chloroform (15 mL) were purged under nitrogen and refluxed for 18 h in inert atmosphere. Evaporated the solvent and the oily product was extracted with methylene chloride, organic layer separated, dried over $MgSO_4$ and solvent removed under reduced pressure. The resulting product was a solid, which was further purified by recrystalizing with toluene. Yield: 80% (2.308 g, 8.67 mmol). Mp 122 °C - 125 °C. ^1H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.29 (s, 3H), 4.00 (m, 2H), 4.13 (dt, J_1 = 8.9 Hz, J_2 = 2.3 Hz, 2H), 4.26 (m, 1H), 4.34 (m, 1H), 4.50 (m, 1H), 4.59 (t, J_1 = 17.2 Hz, J_2 = 8.6 Hz, 1H) 4.95 (m, 1H). Anal. Calcd. for $C_9H_{15}O_7P$: C, 40.61; H, 5.6800. Found: C, 40.82; H, 5.68.

Attempted preparation of (5,5-dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl-1,3-dioxolan-2-one (35).

Route 2: To the stirring mixture of glycerol carbonate (1.28 g, 10.80 mmol), THF (10 mL) and triethyl amine (1.092 g, 10.80 mmol), cyclic phosphate **41** (2.00 g, 10.80 mmol) and THF (10 mL) was added drop wise for a period of 30 min at -78 °C and gradually brought to ambient temperature stirring for 18 h. Filtered the solids formed and solvent was removed under reduced pressure from the filtrate. Added diethyl ether to the filtrate and filtered the solids. The NMR showed that the product formed was neopentyl glycol, the reactant used for synthesis of cyclic phosphate.

Route 3: The same procedure was followed as route 2 but used NaH as a base instead of triethyl amine. NMR shows the crude product as a mixture.

Route 4: To the stirring mixture of neopentyl glycol (0.89 g, 8.50 mmol), THF (10 mL) and triethyl amine (1.72 g, 17.00 mmol), solution of **37** (2.00 g, 8.50 mmol) in THF (10 mL) was added drop wise for a period of 30 min at 0 °C and gradually increased to ambient temperature while stirring for about 18 h. The solids formed were filtered and solvent removed under reduced pressure from filtrate, extracted with ethyl acetate, dried over Na_2SO_4. Solvent was removed under reduced pressure. The extracted product was neopentyl glycol. There was no reaction.

CHAPTER 4

CONCLUSIONS AND FUTURE WORK

The objective of this research project was to synthesize non-halogenated flame retardants for polyurethane foams. Efforts were made to synthesize phosphorous and boronated flame retardants.

In part I an approach of transition metal catalyzed coupling reactions was adapted to synthesize mono and disubstituted boronic esters. The PCFC tests were conducted to determine inherent flame retardant (FR) properties of boronate esters prove to that the flame retardant properties of boronate esters are worse when compared to that of the molecule without boronate moiety. When the boronate and phosphonate esters were blended into the TPU matrix they worsen the FR property by increasing the heat release rate. Instead of reducing the flammability they increase it.

The boronate esters were further hydrolyzed to make boronic acids. The PCFC data of mono and di boronic acids by themselves showed promising results when compared to that of the molecule without the boronic acid moiety. At higher temperature the boronic acids form boroxine networks which contribute to the formation of char which acts as a protective layer on the surface of polyurethane foams thereby reducing the heat release. When mono boronic acid was solvent blended with TPU it showed a significant improvement in flame retardancy. The HRR profile is changed when compared to the profile of TPU because the mono boronic acid could be reacting with the TPU to assist in char formation early in the thermal decomposition process. When examined at the final char, the TPU film has shrunk and there was no flow on the pan. Therefore the mono boronic acid when solvent blended not only promotes char formation, it may also prevent dripping by shrinking of the TPU.

In part II 1,4-benzoquinone was reacted with cyclic phosphite in acid conditions to yield mono and di phosphonated hydroquinone. The PCFC testing of these molecules when tested by themselves showed reduction in heat release when compared to hydroquinone. We concluded that the phosphorous acts in the vapor phase by a radical mechanism because there was reduction in heat release but no char formation.

The mono and di phosphonated hydroquinone were further solvent blended with TPU. The PCFC data showed no reduction in the heat release when compared to the virgin TPU. The reason might be that the cyclic phosphite pyrolyzes out. The conversion of hydroquinone skeleton to 1,4-bis(2-hydroxyethyl)benzene has been well documented in the literature. But the reactions attempted based on the literature were unsuccessful. The presence of the cyclic phosphonate ester could be leading to a reaction of 2-hydroxy ethyl chain with the cyclic phosphonate at elevated temperatures.

In part III attempts were made to synthesize reactive phosphorous flame retardant (polyol) for polyurethane with glycerol carbonate attached to it. Glycerol carbonate can be beneficial if incorporated into the polyurethane matrix because at elevated temperatures the cyclic ring is likely to yield CO_2 and might facilitate cross linking. The intermediate **37** was successfully prepared which was further used for synthesis of compound **36**. When solvent blended in TPU and tested the flame retardancy of **36** it showed significantly very less reduction in heat release when compared to virgin TPU.

These research efforts led to the conclusion that when solvent blended in TPU some of the synthesized flame retardants did not show much improvement in flame retardancy. But when these compounds are reacted into the polyurethane backbone, flame retardancy may be improved.

Future Research

Future research calls for preparation of target structures **33** and **34**. Later the synthesized phosphonic and boronic compounds will be used as monomers for making polyurethane foams. The foams will further be analyzed by using PCFC for small scale and cone calorimeter to full scale flame spread tests. Compounds performing well in these tests will be evaluated in vertical orientation, melt drip experimental setup.

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