

Synthesis and Testing of New Flame Retardant Monomers and Polymer Additives

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1.1 Introduction- Boronic Acid Flame Retarding Polymer Additives

The development of synthetic polymers/plastics in the twentieth century has created a giant and growing industry. Due to their low cost and ease of manufacturing, they have taken over where other materials such as wood and steel have become outdated. Furthermore new products have emerged that could not have been fabricated from any other material. Polymers are commonly made from highly flammable hydrocarbons that burn quite readily upon ignition. Hence, making polymers resistant to burning is of great importance to their use in today's society. One way to make polymers flame retardant is through the use of additives. The development of flame retarding additives has been a subject of serious investigation for many years now. A considerable amount of these flame-retardants have been developed by companies such as Great Lakes, Inc. and Albemarle, Inc. The job at hand is to synthesize and test new flame retarding additives that could be used by industry to make inflammable polymers flame resistant, and in some cases even "poison" a fire that is already burning.

Flame retardancy can be achieved using any of three different approaches: (1) causing "char" formation in the pyrolysis zone, (2) adding material that decompose either to produce nonflammable gases or endothermically to cool the pyrolysis zone, and (3) prohibiting the combustion process in the vapor phase.¹ Many flame retardants have been developed to combat the thermal break down of polymers. The combustion of polymers has been shown to take place by several different free radical steps. It is these free radicals that aid combustion in both the pyrolysis zone and vapor phase.² When used with antimony oxide, halogenated flame retarding additives have been shown to be good radical traps by stopping free radical production in the pyrolysis zone and thereby quenching the combustion of the "polymer fuel". The halogenated additives also help in making the free radicals less active in the vapor phase.² One of the

problems with halogenated and inorganic flame retarding additives are that the smoke given off during the burning is highly toxic. Any smoke given off in a flame is toxic but the free radical halogens and heavy metal pollutants can produce an even more toxic environment.

The goal of this project is to develop novel ways of producing non-toxic flame retardant polymer additives that are less hazardous when burned. The use of boron materials has been investigated by Morgan *et al.* Due to several different properties that boronates exhibit upon combustion, it is believed that these boronates undergo a type of crosslinking to form a boronate glass to produce a char that inhibits flame growth in the pyrolysis zone. (**figure 1**)^{3,4}

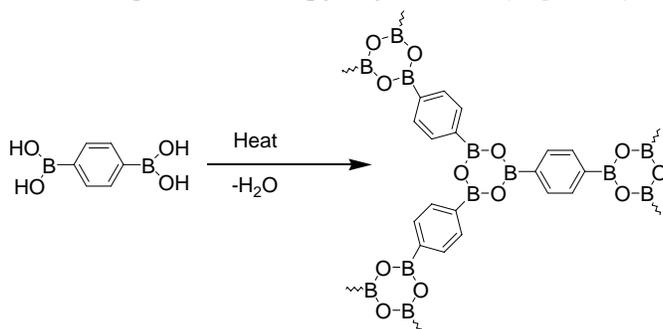


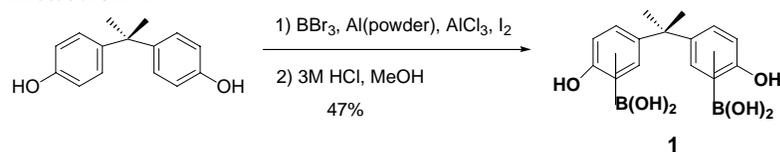
Figure 1. Morgan, A.B. Doctoral Dissertation, Univ. of South Carolina, 1998.

The formation of the boronate glass network will also act as a thermal insulator to protect the remaining unburned plastic from thermal degradation.^{3,4} The main goal in synthesizing these flame retardants, as shown by Morgan, is to use already available halogenated polymer starting materials to synthesize these boron flame retardants. The less that industry has to change in preexisting polymer manufacturing processes, the more viable use of these flame retardants will be.

1.2 Results and Discussion- Boronic Acid Flame Retarding Polymer Additives

The synthesis of the diboronic bisphenol A (**1**) was performed using a modified version of the traditional Friedel-Crafts alkylation.⁵ The purpose behind using this procedure was to run the reaction in a neat boron triboromide (BBr_3) solution and try a direct boronation of the aromatic rings. It was observed by Morgan that using BBr_3 in dichlorobenzene does not yield the desired product. After the boronation of bisphenol A, the reaction was hydrolyzed with 3M HCl that led to the formation of the boronic acid **1** (Reaction 1).

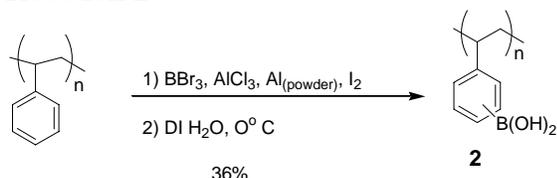
Reaction 1



The highly reactive nature of the BBr_3 gives rise to possible side reactions, such as bromination or possibly decomposition of the bisphenol A moiety. The product was blended into ABS (Acrylonitrile co-Butadiene, co-Styrene).

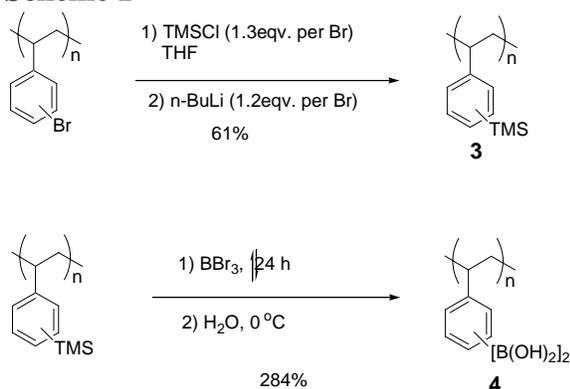
The boronation of low molecular weight polystyrene (Polyscience low M_w polystyrene (800-5000 M_w ; Lot # 461855) has proven to be a challenging endeavor. The first approach was a direct boronation of the polystyrene in neat boron tribromide to make a boronic acid polystyrene **2** (Reaction 2).

Reaction 2



The poor solubility of **2** in most common solvents limits the characterization of this product. With the incorporation of the boronic acid functional groups, the target molecule might be lost in the aqueous phase during the extraction procedure. A different method for synthesizing the similar product is as follows: dibromopolystyrene was subjected to lithium halogen exchange conditions and capped with trimethylsilane. The trimethylsilyl chloride was added first so that an excess of TMS would be present when *n*-butyllithium was added drop-wise. When the exchange took place, TMS would quench the reaction immediately to give the desired TMS capped polystyrene **3** (Scheme 1). The next step was to take **3** and convert the two TMS groups into boronic acid functional groups to make a diboronic acid polystyrene **4** (Scheme 1).⁶

Scheme 1



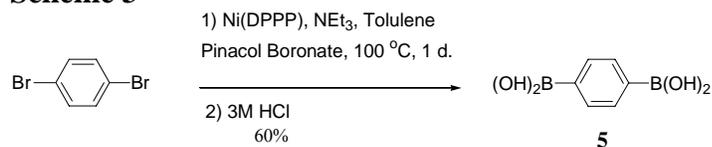
The reason for the high yield in the second reaction is due to the fact that quenching with water caused the excess boron tribromide to be converted into boric acid. The poor solubility of **4** in organic solvents makes the separation from the boric acid quite difficult. Likewise, characterization of **4** is also difficult to achieve. The burn results for these polymers are summarized in Table 1.

The next area of research this semester was two-fold. First, it was discovered by Morgan that the use of 1,4-benzene diboronic acid in polycarbonate gave a V-0 rating (0.1 wt % PTFE, 5 wt % 1,4-benzene diboronic acid). I have been studying the affects of **5** in ABS. It was discovered by Morgan that using the 1,4-benzene diboronic acid in ABS was plagued with long burn times, although char formations were very high. These high char yields are important because it shows that the 1,4-benzene diboronic does crosslink in ABS but does not act as an adequate flame retardant. Different Cloisite[®] Clays are being investigated as a synergist with **5** to help extinguish

the flame in ABS. The problem with these clays is that they have poor melt blendability. The burn result for these polymer and clay mixtures is summarized in Table 1.

The second part in focusing on the synthesis of **5** was getting important thermal analysis, elemental analysis, and X-ray powder diffraction data for a journal article, on a novel synthetic route in making 1,4-benzenediboronic acid using a Ni catalyzed cross coupling step (**Scheme 3**).

Scheme 3



The burn results for the boronic acid additives are summarized in Table 1.

Table 1

Additive	First Ignition ^a (sec)	Observed Dripping ^b	Second Ignition ^a (sec)	Observed Dripping ^b	UL-94 Rating
10 wt% 1 , ABS	385, 352	No, No	<1 ^d , <1 ^d	No, No	?, ?
10 wt% 2 , 1wt% PTFE, ABS	312, 350	Yes, Yes	<1 ^d , <1 ^d	No, No	?, ?
10wt% 4 ; 1wt% PTFE; ABS	292, 248	Yes, Yes ^c	<1 ^d , <1 ^d	No, No	?, ?
10 wt% 5 ; 10 wt% Cloisite 6A, ABS	351, 357	No, No	<1 ^d , <1 ^d	No, No	?, ?
10wt% 5 ; Cloisite 10A, 5wt%; 1wt% PTFE; ABS	372, 374	No, No	<1 ^d , <1 ^d	No, No	?, ?
10wt% 5 ; Cloisite 15A, 5wt%; 1wt% PTFE; ABS	302, 256	No, No	<1 ^d , <1 ^d	No, No	?, ?
10wt% 5 ; Cloisite 20A, 5wt%; 1wt% PTFE; ABS	314, 314	No, No	7, 8	No, No	?, ?

10wt% 5 ; Cloisite 25A, 5wt%; 1wt% PTFE; ABS	269, 307	No, No	9, 5	No, No	?, ?
10wt% 5 ; Melamine, 10wt%; 1wt% PTFE; ABS	384, 373	Yes, No	<1 ^d , <1 ^d	No, No	?, ?
10wt% 5 ; Polyvinyl Alcohol, 10wt%; PTFE, 10wt%; ABS	300	No	<1 ^d	No	?, ?
10wt% 5 ; Cloisite 30B, 5wt%; PTFE, 1wt%; ABS	361, 364	No, No	3, <1 ^d	No, No	?, ?
10wt% 5 ; 10wt% Polyacrylic Acid, 10wt% PTFE ; ABS	248	No	<1 ^d	No	?
10wt% 5 ; Sb2O3, 5wt%; PTFE, 1wt%; ABS	93, 236	Yes ^c , Yes ^c	<1 ^d , <1 ^d	No, No	?, ?
10wt% 5 ; ABS, 30wt%; PTFE, 0.1wt%; PC	100, 25	Yes ^c , Yes ^c	<1 ^d , 14	No, No	?, ?

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip onto cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition.

1.3 Experimental

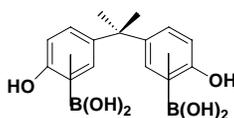
General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ¹H NMR spectra were observed at 400 MHz and ¹³C NMR spectra were observed at 100 MHz on a Bruker Avance 400 spectrometer. ¹H chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 °C scanning window at 10 °C/min. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5. An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade

tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

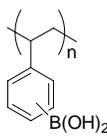
General Procedure for Blending Boron Containing Flame Retardant Additives and Plastic (ABS or PC) in Brabender 30 ml Type 6/2 Mixing bowl – Prep Center.⁷ The additive and plastic were weighed out in their respective amounts according to the wt % of additive: 25.41g batch (PC), 22.05 g batch (ABS). Heating temperatures for the blending bowl varied depending on the material involved. The processing temperatures used during the blending were: ABS 225 °C. PC: 270 °C. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additives was used, the plastic and additive were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE⁷ were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives was removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

General Procedure for Extruding Plastic in the UL-94 Test Bars.⁷ The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8" thick × 1/2" wide × 3" long rectangular bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved. The general processing temperature for the plastics used are as follows: mold temperature: 40-90 °C. PC: blending cup temperature: 270 °C, mold temperature 71-93 °C, ABS: blending cup temperature 225-230 °C.

General Procedure for the Modified HVUL-94 Burn Test.⁷ Two 1/8" thick × 1/2" wide × 3" long plastic (polymer + additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The setting on the methane tank pressure regulator was set to 23 psi. The pressure regulator HVUL-94 test station was set to 5 psi. The Bunsen Burner flame height was 125 mm, and the height from the top of the Bunsen Burner to the bottom of the test bar was 70 mm. All test bars underwent two trials, each trial consisting of ignition for 10 seconds, followed by flame removal and self extinguishing times were recorded.



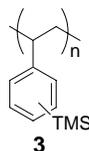
Diboronic Bisphenol A. (1, JLJ-I-3, 4, 5, 9).⁷ To a 500 mL round bottom flask equipped with a stir bar and flushed with nitrogen was added Bisphenol A (5.25 g, 23 mmol), aluminum powder (6.21 g, 230 mmol), aluminum trichloride (0.821 g, 5.75 mmol), and iodine (trace). The flask was equipped with a West reflux condenser and sealed under nitrogen atmosphere with a rubber septum. Boron tribromide (21.74 mL, 230 mmol) was added via syringe drop-wise to the sealed flask and condenser. Bubbling was observed and the solution turned to a dark brown color. The reaction was heated to reflux approximately 90 °C for 2 d. Upon completion of the reaction the dark brown solution was quenched with deionized water and ice at 0 °C. The resulting solution was extracted three times with diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and filtered through celite. The solution was then dried on the rotary evaporator and hydrolyzed with methanol and 3M HCl. A dark brown powder was achieved in 47% yield. ¹H NMR(300MHz, CD₃OD, DCl in D₂O) δ 7.56- 7.60(dd), δ 7.28(d), δ 7.27(m), δ 7.25 (d), δ 6.6-6.8 (m), δ 5.51(m), δ 1.17-1.21 (m). FTIR (KBr)(cm⁻¹) 3210.3, 1384.6, 1297.4, 1149.9, 1128.2, 825.5, 759.0, 646.2.



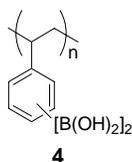
2

Styrene Boronic Acid (2, JLJ-I-13, 14, 15, 24, 33)⁷ To a 25 ml round bottom flask equipped with a stir bar and flushed with nitrogen was added polystyrene (219 mg, 2 mmol), aluminum powder (45 mg, 20mmol), aluminum trichloride (6.6 mg, 0.25 mmol), and iodine (trace). The flask was equipped with a West reflux condenser and sealed under nitrogen atmosphere, with a rubber septum. Boron tribromide (1.9 mL, 20 mmol) was added via syringe drop-wise to the sealed flask and condenser. Bubbling was observed and solution turned a dark reddish-brown color. The reaction was heated to reflux approximately 90 °C for 2 d. Upon completion of the reaction the dark brown solution was quenched with deionized water and ice at 0 °C. Several workup procedures were tried according to the procedure above (See JLJ-I-9) using methylene chloride and diethyl ether for extraction, but a new workup had been devised because of solubility problems. After the solution was quenched with deionized water and ice, the solution was stirred for 30 min. The solution was then filtered through celite and rinsed with copious amounts of water (1500-1600 mL). The filtrate was then rinsed with THF (5×), with acetone (5×), and with methylene chloride (5×). Solvent was then removed *via* a rotary evaporator to give a dark brown sticky residue. The product was then mixed with approximately 400 ml of methylene chloride and mixed overnight. The solution was then filtered through celite and rinsed with methylene chloride (3×). Solvent was removed using a rotary evaporator and then dried *in vacuo* for 24 h. The celite containing undissolved product was then mixed with acetone and stirred for 6 h. The resulting solution was then filtered again through celite to give a light brown solution. The solvent was then removed via the rotary evaporator and then 24 h *in vacuo*. The acetone portion of the product was redissolved in acetone and stirred for 2 h and then filtered through a fritted funnel to obtain a white powder. The fritted funnel was put in the vacuum oven for 2 days at 60 °C. ¹H NMR(300MHz, CD₂Cl₂) δ(ppm) δ 7.25(s), δ 6.97-7.20(bm), δ 3.80-3.88(bm), δ 3.43-3.47(bm), δ 3.74(s), δ 1.95(bs), δ 1.72(bs), δ 1.43(s), δ 1.38(s),

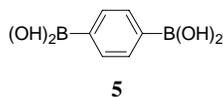
δ 1.25(s), δ .875-.967(bm). FTIR (KBr) (cm^{-1}) 3215.4, 1377.3, 1188.5, 1108.5, 752.6, 701.7, 643.6.



Poly(bistrimethylsilyl)styrene (2, JLJ-I-46). To a 1 L three neck round bottom flask, equipped with a mechanical stirrer and flushed with nitrogen was added dibromopolystyrene (5.28 g, 20 mmol). The reaction flask was sealed with a septum, evacuated, and backfilled with nitrogen (3 \times). Dry THF (500 mL) was added to the reaction flask via a cannula. Nitrogen purged, trimethylsilylchloride (6.59 mL, 52 mmol) was added via syringe and the reaction mixture was cooled to $-77\text{ }^\circ\text{C}$. n-butyllithium/hexane (30.3 mL/48 mmol) was added drop-wise, with a syringe pump. The solution was stirred overnight and allowed to warm to room temperature. The reaction was quenched with water and then diluted with methylene chloride. The organic layer was washed with brine (3 \times). The aqueous layers were combined and extracted with methylene chloride (3 \times). The organic layers were combined, dried with anhydrous magnesium sulfate, and filtered through celite. Solvent was then removed, *via* a rotary evaporation, and the sample was allowed to dry continuously *in vacuo* for 24 h. The solid was dissolved in methylene chloride and pipetted into a stirring solution of methanol (~800 mL) which caused the polymer to precipitate. The precipitate was then filtered and dried *in vacuo* for 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.8-6.6(m), 0.5-0(m). FTIR (KBr) 2954.7, 1571.7, 1452.1, 1250.9, 1122.34, 1040.4, 837.9, 757.0, 690.8, 455.1 (cm^{-1}).



Polystyrene diboronic acid (3, JLJ-I-50).⁷ To a 500 mL three neck round bottom flask equipped with a stir bar and flushed with nitrogen was added poly(bistrimethylsilyl)styrene (3.06 g, 12.24 mmol). The reaction flask was sealed with a septum, evacuated, and then backfilled with nitrogen (3 \times). Dry methylene chloride (37 mL) was added *via* syringe. The reaction was cooled to $-78\text{ }^\circ\text{C}$ and a solution of boron tribromide in methylene chloride (24.5 mL, 24.5 mmol, 1 M) was added drop-wise. The mixture was stirred and allowed to warm to room temperature overnight. The reaction was then heated to reflux for 24 h. and then was removed from the heat and allowed to cool to room temperature and quenched with ice water and stirred for 4 h. The solvent and water were removed by rotoevaporation then dried *in vacuo* for 24 h. ^1H NMR (400 MHz, DMSO) δ 8.13 (bs), 6.50 (bs), 3.32 (bs). FTIR (KBr) 3222.6, 2924.3, 2854.5, 1449.0, 1249.2, 1191.3, 1120.3, 1040.3, 837.3, 759.0, 647.4, 543.2, 476.3.



1,4-Benzene diboronic acid (5, JLJ-I-21, 31, 32, 38, 41, 53)⁷ To a 250 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was added 1,4-dibromobenzene and Ni(dppp)Cl₂ (6 mol%). The flask was sealed with a septa under nitrogen and toluene (35 mL), triethylamine (8 equivalents), and pinacol borane (2.6 equivalents) was added dropwise *via* syringe. The reaction was then heated to 100 °C for 24 h and then was allowed to cool to room temperature and a saturated solution of ammonium chloride (NH₄Cl) was added slowly to the flask to quench reaction. Ether was then added to dilute the reaction and the two layers were then separated. The organic layer was washed with ammonium chloride (3 ×) and dried with magnesium sulfate (Mg₂SO₄) and filtered through celite. The solvent was removed *via* rotary evaporation. The product was then hydrolyzed to the acid by heating in MeOH (150 mL) and HCl (3 M; 150 mL) until the product was dissolved. The solution was then allowed to cool slowly to room temperature and then refrigerated for 12 h to form crystals. The crystals were isolated by filtering through a buchner funnel and drying in the vacuum oven for 16 h at 50 °C. ¹H NMR(400MHz, CD₃OD, DCl in D₂O) δ 7.6 (s, 4 H), 5.5 (s, 4 H).

References

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2.1 Introduction-Halogenated Flame Retarding Additives

When halogenated flame retardant additives are used in conjunction with antimony oxide, it has shown to be good radical traps by stopping free radical production in the pyrolysis zone and thereby stopping the combustion of the “polymer fuel”. The halogenated additives also help in making the free radicals less active in the vapor phase. The problem with these halogenated and inorganic flame retarding additives is that the smoke given off during the burning is highly toxic. Any smoke given off in a flame is toxic but the free radical halogens and heavy metal pollutants can produce an even more toxic environment.

When used in conjunction with antimony oxide, halogenated flame retarding additives have been shown to be good radical traps by stopping free radical production in the pyrolysis zone and thereby quenching the combustion of the “polymer fuel”.¹ The halogen functionalities also help in making the free radicals less active in the vapor phase.² The problem with these halogenated and inorganic flame retarding polymers and additives is that the smoke given off during the burning is highly toxic.³ Any smoke given off in a flame is toxic but the free radical halogens and heavy metal pollutants can produce an even more toxic environment.

The area of my research that has been quite successful has been in adding different halogenated materials that have never before been used for flame-retarding purposes, to polymers and testing

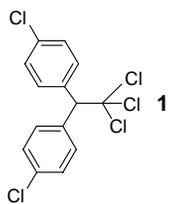
for flame retardancy. The common insecticide DDT [1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane] as well as various DDT analogs has been successful in giving V-0 results in both ABS and HIPS.

2.2 Results and Discussion- Halogenated Flame Retarding Additives

The focus has been the investigation of the flame retarding effects of DDT and its many analogs. 10 wt % (based on the weight percent of halogen) of DDT with 4 wt % antimony oxide and 1 wt % of an anti-drip additive (PTFE) gave a UL-94 V-0 result in both ABS and HIPS. It also gave promising results in polyethylene, but due to excessive dripping a V-0 result could not be obtained. Due to the public stigma of DDT's use as an insecticide, using it as a flame retardant in commercial plastics would likely be a problem. Thus, a major focus of the research here has been the synthesis of new analogs of DDT and DDE (Table1).

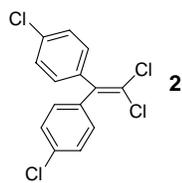
Table 1

DDT

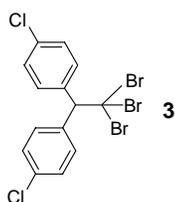


1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane

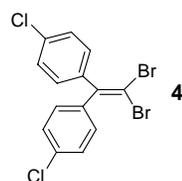
DDE



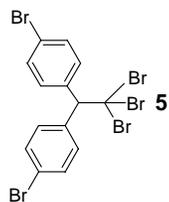
2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene



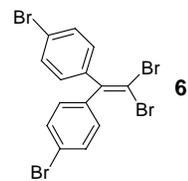
1,1-Bis(4-chlorophenyl)-2,2,2-tribromoethane



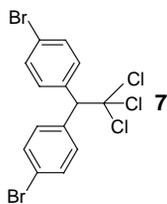
2,2-Bis(4-chlorophenyl)-1,1-dibromoethylene



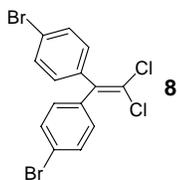
1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane



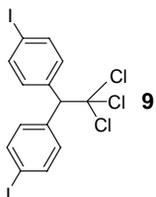
2,2-Bis(4-bromophenyl)-1,1-dibromoethylene



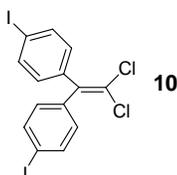
1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane



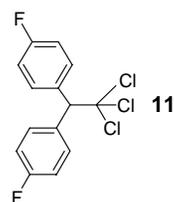
2,2-Bis(4-bromophenyl)-1,1-dichloroethylene



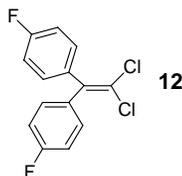
1,1-Bis(4-iodophenyl)-2,2,2-trichloroethane



2,2-Bis(4-iodophenyl)-1,1-dichloroethylene



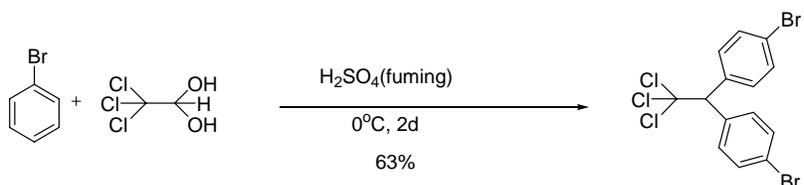
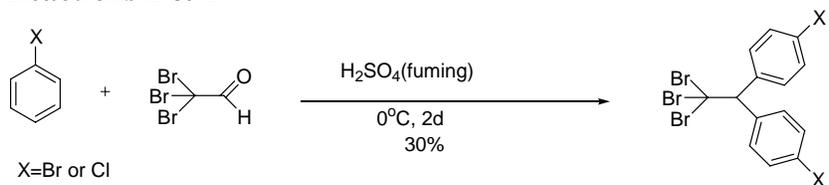
1,1-Bis(4-fluorophenyl)-2,2,2-trichloroethane



2,2-Bis(4-fluorophenyl)-1,1-dichloroethylene

The brominated and chlorinated version of DDT and DDE have been synthesized by a condensation reaction of tribromoacetylaldehyde (bromal) or trichloroethanediol (chloral hydrate) and a mono halogenated benzene with fuming sulfuric acid (Reactions 1 & 2).⁴

Reactions 1 & 2



Burn results from all of the DDT analogs in both ABS and HIPS gave a V-0 rating. The next step in the process was to convert the DDT analogs into their corresponding DDE analogs. This dehydrohalogenation was done by refluxing the appropriate DDT analog in 15 equivalents of a 3 M potassium hydroxide solution for 2 days. (Reaction 3).

Reaction 3

1 , 23.6wt%; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	3, 0	No, No	4, 8	No, No	V-0, V-0
1 , 23.6wt%; PTFE, 1wt%; ABS	274, 100	Yes ^c , Yes ^c	49, 98	No, No	?, ?
1 , 20wt%; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0, 1	No, No	<1 ^d , 2	No, No	V-0, V-0
1 , 20wt%; Sb2O3, 1wt%; PTFE, 1wt%; ABS	56, 9	No, No	83, 42	Yes ^d , Yes ^d	?, ?
1 , 20wt%, Sb2O3, 2wt%, PTFE, 1wt%; ABS	2, 2	No, No	1, 1	No, No	V-0, V-0
1 , 3wt%; Sb2O3, 1wt%; BDBA, 10wt%; PTFE, 1wt%; ABS	45, 75	Yes ^c , Yes ^c	123, 85	No, No	?, ?
1 , 20wt%; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	0, 0	No, No	8, 10	No, No	V-0, V-0
1 , 20wt%; Sb2O3, 4wt%; PTFE, 1wt%; PE	2, 2, 3	Yes ^c , No, Yes ^c	2, <1 ^d , 2	Yes, Yes ^d , Yes	?, ?, ?
1 , 10wt%*; Sb2O3, 2wt%; CaCO3, 14wt%; PE	3, 2	Yes ^c , Yes ^c	0, 18	Yes, Yes	V-2, V-2
2 , 22.2wt%; Sb2O3, 4wt%; ABS	1, 265	No, No	23, 23	Yes ^d , No	?, ?
3 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 0	No, No	V-0, V-0
3 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; HIPS	0, 1	No, No	0, 0	No, No	V-0, V-0
4 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 0	No, No	V-0, V-0

4 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	<1, <1	No, No	1,1	No, No	V-0, V-0
5 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; ABS	1, 0	No, No	0, 0	No, No	V-0, V-0
5 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; HIPS	0, 1	No, No	0, 0	No, No	V-0, V-0
6 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	1,1	No, No	V-0, V-0
6 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	1,0	No, No	2,1	No, No	V-0, V-0
7 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 1	No, No	V-0, V-0
7 , 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; HIPS	9, 1, 0	No, No, No	50, 0, 0	Yes, No, No	?, V-0, V-0
8 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0,1	No, No	0,1	No, No	V-0, V-0
8 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	38, 0, 10	No, No, No	0, 2, 1	No, No, No	V-1, V-0, V-0
13 , 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	189, 322	No, No	13, 0	No, No	?,?

Blending Sb₂O₃ and these halogen-containing monomers with thermoplastic polymers like ABS and HIPS, we have imparted flame retardancy to what are otherwise flammable plastics. While Sb₂O₃/halogen-compound additive systems are currently used to produce flame-resistant commercial plastics, most employ brominated compounds as the halogen source. In this study, we have opted for a chlorine-containing halogen source. The novelty in this lies in the types of chlorinated compounds used (chloral and its derivatives) and the fact that chlorine containing halogen sources are generally thought to be inferior, in flame retarding ability, to brominated sources. Despite this, we have created polymer blends that contain more than 75 wt % commercial polymers and still rate as V-0 in the industry-standard UL-94 flame test. This,

coupled with the low cost of chlorinated species, may yield a promising new class of flame-retarding materials.

2.3 Experimental

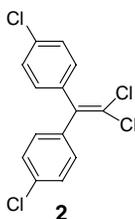
General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^1H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Bruker Avance 400 spectrometer. ^1H chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 $^\circ\text{C}$ scanning window at 10 $^\circ\text{C}/\text{min}$. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5 . An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory

General Procedure for Blending Flame Retardant Additives and Plastic (ABS or PC) in Brabender 30 ml Type 6/2 Mixing bowl – Prep Center.⁵ The additive and plastic were weighed out in their respective amounts according to the wt % of additive: 25.41g batch (PC), 22.05 g batch (ABS). Heating temperatures for the blending bowl varied depending on the material involved. The processing temperatures used during the blending were: ABS 225 $^\circ\text{C}$. PC: 270 $^\circ\text{C}$. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used, the plastic and additive were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE⁷ were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives was removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

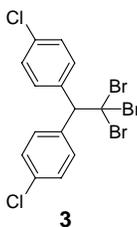
General Procedure for Extruding Plastic in the UL-94 Test Bars.⁵ The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8" thick \times 1/2" wide \times 3" long rectangular

bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved. The general processing temperature for the plastics used are as follows: mold temperature: 40-90 °C. PC: blending cup temperature: 270 °C, mold temperature 71-93 °C, ABS: blending cup temperature 225-230 °C.

General Procedure for the Modified HVUL-94 Burn Test.⁵ Two 1/8" thick × 1/2" wide × 3" long plastic (polymer + additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The setting on the methane tank pressure regulator was set to 23 psi. The pressure regulator HVUL-94 test station was set to 5 psi. The Bunsen Burner flame height was 125 mm, and the height from the top of the Bunsen Burner to the bottom of the test bar was 70 mm. All test bars underwent two trials, each trial consisting of ignition for 10 seconds, followed by flame removal and self extinguishing times were recorded.

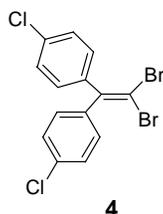


2,2-Bis(4-chlorophenyl)-1,1-dichloroethylene (2, JLJ-I-75, 78).⁶ To a 250 mL round bottom flask, equipped with a stir bar and purged with nitrogen, was added DDT, **6** (3.54 g/10 mmol); and after which, was sealed under nitrogen with a septum. THF (50 mL) was added via syringe. A nitrogen sparged KOH solution (10 mL, 30mmol, 3M) was added drop-wise via syringe. The reaction was then heated slightly (~50 °C) and stirred for 24 h. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with water (3×). Aqueous washes were then extracted with methylene chloride (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and dried *in vacuo* for 24 h. MP 87-88 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (dt, *J* = 8.7, 2 Hz, 4 H), 7.20 (dt, *J* = 8.7, 2 Hz, 4 H).

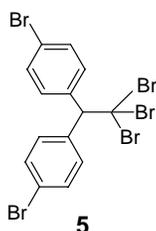


1,1-Bis(4-chlorophenyl)-2,2,2-tribromoethane (3, JLJ-I-97, 109)⁴. A 250 mL round bottom flask was equipped with a stir bar, an addition funnel, purged with nitrogen, and sealed with a septum. Tribromoacetylaldehyde [bromal] (1.89 mL, 18 mmol) and nitrogen sparged chlorobenzene (29 mL, 285 mmol) were added via syringe. The reaction was cooled to 2 °C and concentrated sulfuric acid was added, via the addition funnel, drop-wise over a period of 1h. Reaction mixture was stirred and kept below 6 °C for 24 h. The reaction mixture was then quenched with ice water. The reaction mixture was then extracted with ether (3×). The organic

layer was washed with a dilute solution of sodium bicarbonate (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed *via* rotary evaporation and dried for 24 h *in vacuo*, and with slight heating (50 °C), to remove any excess chlorobenzene. MP 106-108 °C. FTIR (KBr) 2919.3, 1484.3, 1402.3, 1091.4, 1007.94, 828.2, 734.9, 694.0, 637.0, 573.39, 511.3. ¹H NMR (400 MHz, CDCl₃) δ 7.6 (dt, *J* = 8.5, 2 Hz, 4 H), 7.3 (dt, *J* = 8.7, 2 Hz, 4 H), 5.2 (s, 1 H). HRMS calc'd for C₁₄H₁₀Br₃Cl₂: 487.7689. Found: 487.7591; 0.44 ppm error.

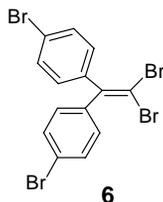


2,2-Bis(4-chlorophenyl)-1,1-dibromoethylene (4, JLJ-I-167, 187).⁴ To a 250 mL round bottom flask, equipped with a stir bar and a reflux condenser and purged with nitrogen, was added 1,1-Bis(4-chlorophenyl)-2,2,2-tribromoethane, **3**. The flask was then sealed under nitrogen with a septum. THF/H₂O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3 M) was added drop-wise via syringe. The reaction was heated to reflux and stirred for 2 d. After this period of time, the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed *via* rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 106-108 °C. FTIR (KBr) 3053.3, 2354.7, 1903.5, 1584.7, 1481.6, 1391.4, 1253.6, 1090.5, 1008.6, 831.3, 778.5, 640.3, 512.3. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dt, *J* = 8.56, 2.20 Hz, 4 H), 7.21 (dt, *J* = 8.66, 2.20, 4 H).

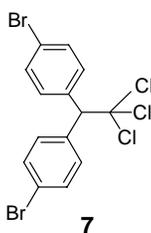


1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane (5, JLJ-I-141, 147, 175, 195).⁴ A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Tribromoacetylaldehyde [bromal] (3.8 mL, 36 mmol) and nitrogen sparged bromobenzene (60.02 mL, 570 mmol) were added *via* syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, *via* the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and diluted with CH₂Cl₂. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed *via* rotary evaporation and the

resulting solid was dried for 24 h *in vacuo* with slight heating ($\sim 50\text{ }^{\circ}\text{C}$) to remove any excess bromobenzene. MP 164-169 $^{\circ}\text{C}$. FTIR (KBr) 1897.7, 1587.2, 1482.6, 1398.2, 1071.3, 1006.8, 819.6, 715.7, 617.1, 571.5, 487.9. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dt, $J = 8.61, 2.18$ Hz, 4 H), 7.48 (dt, $J = 8.79, 2.22$ Hz, 4H), 5.17 (s, 1H).

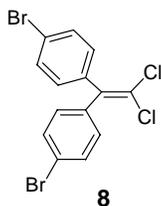


2,2-Bis(4-bromophenyl)-1,1-dibromoethylene (6, JLJ-I-183, 199)⁴ To a 250 mL round bottom flask, equipped with a stir bar, and reflux condensor, and purged with nitrogen, was added 1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane, **5**. The flask was then sealed under nitrogen with a septum. THF/ H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise *via* syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3 \times) and the aqueous layer was then extracted with ether (3 \times). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 119-121 $^{\circ}\text{C}$. FTIR (KBr) 2920.1, 1902.8, 1578.5, 1476.6, 1387.0, 1063.9, 1003.8, 824.8, 773.1, 715.8, 634.2, 481.0. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dt, $J = 8.58, 2.18$, 4 H), 7.52 (dt, $J = 8.60, 2.17$, 4 H).

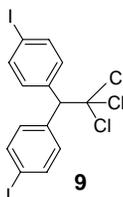


1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane (7, JLJ-I-151, 185, 207, 257)⁴ A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol [chloral hydrate] (5.95 g, 36 mmol) and nitrogen sparged bromobenzene (60.02 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 $^{\circ}\text{C}$ and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 $^{\circ}\text{C}$ for 2 d. The reaction mixture was then quenched with ice water and then diluted with CH_2Cl_2 . The organic layer was washed with a dilute solution of sodium bicarbonate (3 \times) and the aqueous layer was extracted with ether (3 \times). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating (50 $^{\circ}\text{C}$) to remove any

excess bromobenzene. MP 142-143 °C. FTIR (KBr) 1582.9, 1486.9, 1403.0, 1076.1, 1009.7, 848.6, 776.4, 761.0, 672.1, 611.6, 492.0. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dt, *J* = 8.82, 2.85 Hz, 4 H), 7.44 (dt, *J* = 8.75, 2.63 Hz, 4 H), 5.75 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 136.64, 131.61, 122.61, 100.52, 69.74. HRMS calc'd for C₁₄H₉Br₂Cl₃: 439.8137. Found: 439.8140; 0.67 ppm error.

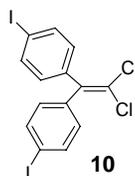


2,2-Bis(4-bromophenyl)-1,1-dichloroethylene (8, JLJ-I-193, 209, 258, 269).⁴ To a 250 mL round bottom flask, equipped with a stir bar, reflux condenser, and purged with nitrogen, was added 1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane, **7**. The flask was then sealed under nitrogen with a septum. THF/H₂O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 121-123 °C. FTIR (KBr) 2362.5, 1901.6, 1582.2, 1484.1, 1391.1, 1069.9, 1009.9, 970.1, 857.5, 821.6, 788.4, 715.7, 668.5, 489.5. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dt, *J* = 8.59, 2.25 Hz, 4 H), 7.14 (dt, *J* = 8.66, 2.23 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 138.32, 137.79, 131.63, 131.02, 122.51, 120.51. HRMS calc'd for C₁₄H₈Br₂Cl₂: 405.8348. Found: 405.8347; 0.32 ppm error.

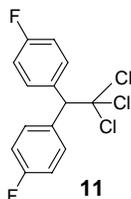


1,1-Bis(4-iodophenyl)-2,2,2-trichloroethane (9, JLJ-II-77, 111, 125). A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol [chloral hydrate] (5.95 g, 36 mmol) and nitrogen sparged iodobenzene (60.02 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and then diluted with CH₂Cl₂. The organic layer was washed with a dilute solution of sodium bicarbonate (3×) and the aqueous layer was extracted with ether (3×). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation

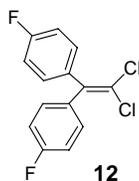
and the resulting solid was dried for 24 h *in vacuo* with slight heating (50 °C) to remove any excess iodobenzene. . ^1H NMR (400 MHz, CDCl_3) δ . FTIR (KBr)



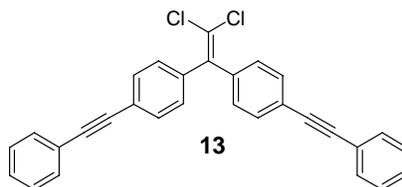
2,2-Bis(4-iodophenyl)-1,1-dichloroethylene (10, JLJ-II-78, 112). To a 250 mL round bottom flask, equipped with a stir bar, reflux condenser, and purged with nitrogen, was added 1,1-Bis(4-iodophenyl)-2,2,2-trichloroethane, **9**. The flask was then sealed under nitrogen with a septum. THF/ H_2O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3 \times) and the aqueous layer was then extracted with ether (3 \times). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 144 –145 °C. ^1H NMR (400 MHz, CDCl_3) δ . FTIR (KBr)



1,1-Bis(4-fluorophenyl)-2,2,2-trichloroethane (11, JLJ-III-43). A 500 mL three neck round bottom flask was equipped with a mechanical stirrer and an addition funnel, purged with nitrogen, and sealed with a septum. Trichloroethanediol [chloral hydrate] (5.95 g, 36 mmol) and nitrogen sparged iodobenzene (60.02 mL, 570 mmol) were added via syringe. The reaction was cooled to 0 °C and fuming sulfuric acid (81.8 mL, 570 mmol) was added, via the addition funnel, drop-wise over a period of 1h. The reaction mixture was stirred and kept at 0 °C for 2 d. The reaction mixture was then quenched with ice water and then diluted with CH_2Cl_2 . The organic layer was washed with a dilute solution of sodium bicarbonate (3 \times) and the aqueous layer was extracted with ether (3 \times). Organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried for 24 h *in vacuo* with slight heating (50 °C) to remove any excess fluorobenzene. ^1H NMR (400 MHz, CDCl_3) δ . FTIR (KBr).



2,2-Bis(4-fluorophenyl)-1,1-dichloroethylene (12, JLJ-III-44). To a 250 mL round bottom flask, equipped with a stir bar, reflux condenser, and purged with nitrogen, was added 1,1-Bis(4-fluorophenyl)-2,2,2-trichloroethane, **11**. The flask was then sealed under nitrogen with a septum. THF/H₂O (10:1 solution) was added via syringe. A nitrogen sparged KOH solution (15 equivalents, 3M) was added drop-wise via syringe. The reaction was then heated to reflux and stirred for 2 d. After this period of time the reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was then extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. ¹H NMR (400 MHz, CDCl₃) δ. FTIR (KBr).



2,2-Bis(p-phenyleneethynylene)-1,1-dichloroethylene (13, JLJ-I-229) To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser, was added 2,2-Bis(4-bromophenyl)-1,1-dichloroethylene **8**, (4.06 g/ 10 mmol), Copper Iodide (0.190 g/ 1mmol), bistriphenylphosphine palladium(II) dichloride (0.351 g/ 0.5 mmol), and triphenylphosphine (0.262 g/1 mmol). The flask was then sealed with a septum, evacuated, and backfilled with nitrogen (3×). Benzene (92 mL), Hunig's base (10.45 mL/60 mmol), and phenyl acetylene (3.3 mL/30 mmol) were added via syringe. The reaction was heated to reflux for 2 d. The reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. MP 128-131 °C. FTIR (KBr) 3414.1, 1599.6, 1504.9, 1439.6, 1399.8, 1104.9, 1019.6, 971.4, 862.8, 784.9, 754.7, 688.2, 575.9, 516.1. ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.48 (m), 7.36-7.32 (m), 7.27(dt, *J* =8.37, 1.81 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 139.31, 138.90, 131.66, 131.51, 129.55, 128.46, 128.39, 123.23, 123.04, 96.43, 88.90. HRMS calc'd for C₃₀H₁₈Cl₂: 448.0786. Found: 448.0787; 0.26 ppm error.

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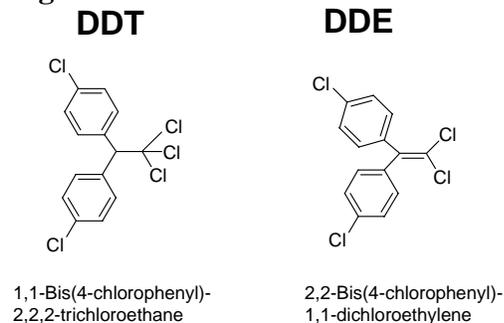
3.1 Flame Retardant Polymers using the Various DDT/DDE Derivatives

The increase of security and safety in our society has caused the regulations for fire safe material to become a top priority when it relates to FAA regulations. The field of flame retardant research has been around for many years, but the focus of developing heat resistant and fire retardant polymers was defined by federal law in the 1960's. Recently at an FAA conference it was put forth that the objective for designing flame retardant materials was to "eliminate burning cabin materials as a cause of death in aircraft accidents by 2010." The goal of my research is to develop a thermoplastic polymer that fulfills the promise made by the FAA. With that in mind polymers have been designed and synthesized that are inherently flame retardant, with no need for synergistic additives. It is important to note that not only are we looking for flame retardant materials we also need other desirable properties such as high heat deflection, high modulus, and desirable melting temperatures. These objectives have a few problems associated with them; one of the issues is that these high temperature polymers have sacrificed processibility for fire resistances. Several methods have been used to circumvent these problems.

The goal of this project is to save lives and to extinguish flames. While the idealized goal of this project is to produce a polymer which completely extinguishes a fire without the production of hazardous fumes, the recent focus has been to put out the fire regardless of the vapor toxicity. If the flames were put out quickly, toxic vapors would be less of a problem.

The goal of the research is to synthesize flame retardant polymers using the various DDT/DDE derivatives, as monomers (Figure 1). The excellent results obtained from using these molecules and their analogs as flame retardant additives has lead to the development of novel flame retardant polymers.

Figure 1

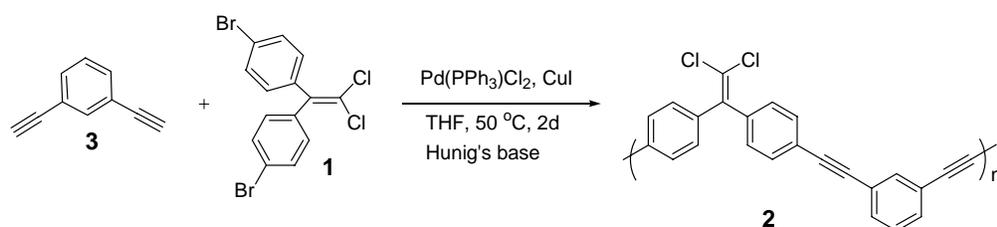


3.2 Results and Discussion for DDE based polymers

Flame propagation is a thermodynamically driven process. It has been the objective to design a polymer in its lowest energy state in order to diminish the spreading of fires. One of the approaches to creating these flame resistant materials is by using functional groups on the polymer (i.e. halogens) or incorporating certain non-flammable elements (i.e. boron or phosphorous) into the backbone of the polymer chain, thus creating a polymer that is inherently flame retardant. Incorporation of these functional groups can act as radical traps in the vapor phase and or moieties that will cross-link during the burn process to create char in the condensed phase. These processes will increase the polymer's flame resistant capabilities.

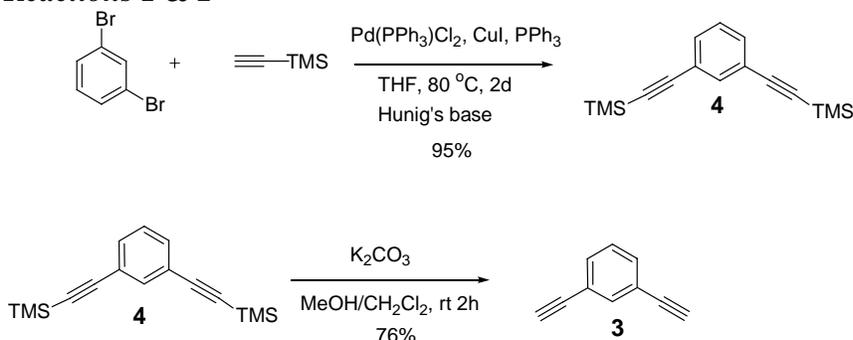
As was discussed earlier, it is known that alkynes can crosslink during the combustion process to increase char formation in the condensed phase. With this in mind the incorporation of an alkyne into a polymer was pursued using the bromo-DDE analog **1** to make a Poly[(2-phenylene-2'-phenylene-m-diethynylene)-1,1-dichloroethylene] **2**. This polymer was made by a Sonogashira coupling of 1,3-diethynylbenzene **3** with 2,2-bis(4-bromophenyl)-1,1-dichloroethylene **1** (Polymerization 1).

Polymerization 1



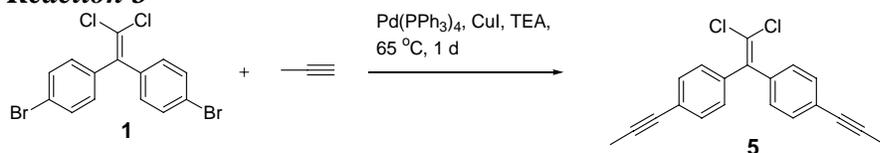
1,3-Diethynylbenzene **3** was synthesized by a Sonogashira coupling of 1,3-dibromobenzene with trimethylsilylacetylene to give the trimethylsilyl protected 1,3-diethynylbenzene **4** followed by deprotection with potassium carbonate to yield 1,3-diethynylbenzene **3** (Reactions 1 & 2)

Reactions 1 & 2

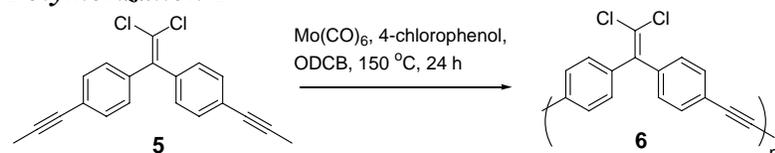


This polymer suffered extended burn times which hinders its use in ABS, but may work well in as a pristine polymer. The burn results are summarized in Table 1.

Another approach to making alkyne containing polymers is by utilizing the Acyclic Diyne Metathesis Polymerization (ADIMET) with the molybdenum catalyst. The monomer was synthesized from a DDE **1** analog. Starting with 2,2-bis(4-bromophenyl)-1,1-dichloroethylene **1** using Bunz's procedure for coupling with propyne, the diyne **5** was made. (Reaction 3)

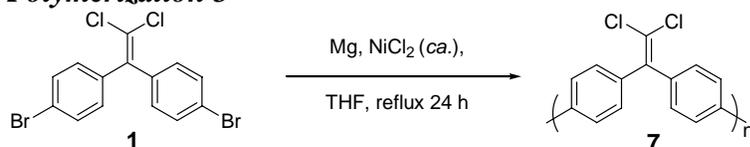
Reaction 3

The dipropyne monomer **5** was then polymerized using Bunz's ADIMET process, which uses $\text{Mo}(\text{CO})_6$ and 4-chlorophenol as a catalyst to produce polymer **6**. (Polymerization 2)

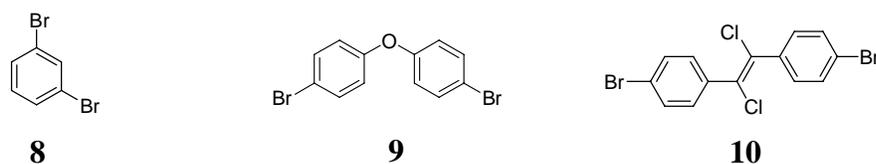
Polymerization 2

Thermal testing of this polymer was done as a blend with ABS and the burn results are summarized in Table 1.

One of the problems with the incorporation of the alkyne functional group is that the crosslinking process is exothermic. This exothermic event adds energy to the burn process, therefore increasing burn times with the HVUL-94 test. In order to circumvent this process the DDE core was polymerized by direct aromatic polymerizations using aryl-aryl coupling procedures. Several reaction conditions were tried, but the procedure that yielded high molecular weight polymer is the polymerization of the biphenyl ethylene analog **1** in the presence of magnesium and catalytic nickel chloride (Polymerization 3).

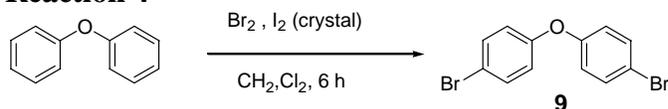
Polymerization 3

High molecular weight polymer **7** has been synthesized; but due to its rigid structure, it yields a polymer that does not melt. Several different linker groups have been synthesized and copolymerized with DDE analog **1** to help break up the stiffness in the polymer and lower the melting point (Table 2).

Table 2**Linker Groups**5 mol % **8** M_w : 16,000 M_n : 2,30010 mol % **8** M_w : 65,300 M_n : 54,3005 mol % **9** M_w : 8,500 M_n : 2,60010 mol % **9** M_w : 8,600 M_n : 2,50020 mol % **10** M_w : 102,100 M_n : 68,000100 mol% **10** M_w : XXX M_n : XXX

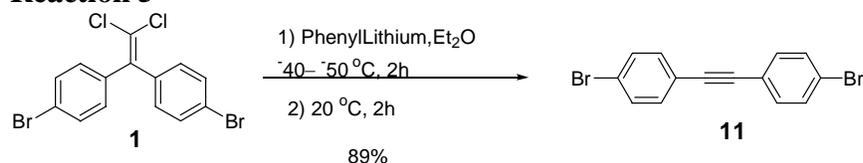
The 1,3-dibromobenzene **3** was bought commercially from Aldrich, the others were made in the laboratory. The synthesis of 4,4'-dibromodiphenylether **9** was achieved by brominating diphenylether in the presence of catalytic iodine (Reaction 4).

Reaction 4



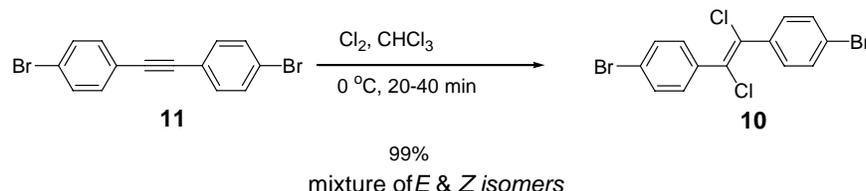
The synthesis of the E-1,2-Bis(4-bromophenyl)-1,2-dichloroethylene required two steps. The starting product **1** was transformed to the 4,4'-dibromotolane **11** using phenyl lithium at -40 to -50 °C for 2 hours followed by warming to room temperature and stirring for an additional 2 hours (Reaction 5).⁶

Reaction 5



The chlorination of the triple bond of **11** was achieved by bubbling chlorine gas through a solution of chloroform and the dibromotolane at 0 °C for 20 minutes to yield **10** (Reaction 6).

Reaction 6



Even with the various linker groups in the polymer backbone, this polymer is not melt blendable. In light of this fact, the polymer was pressed together using a Carver pellet press. A piece of it was held in and above the flame of a Bunsen burner. After removing the plastic from the ignition source the flame went out.

In our attempt at making flame resistant polymers the process of reacting chloral hydrate **12** directly into a polymer was investigated. It has been shown that chloral hydrate will condense with diphenylether in the presence of trifluoroacetic acid, trifluoroacetic anhydride, and boron trifluoride to yield polymer **13**. Polymer **13** gave the more stable dichlorovinylidene **14** after dehydrochlorination in refluxing pyridine (Polymerization 4).

Polymerization 4

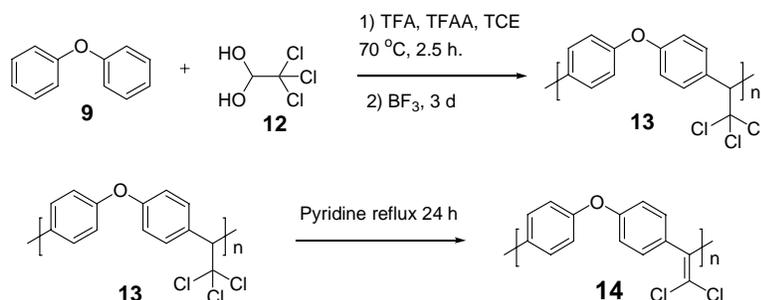


Table 1

Additive	First Ignition ^a (sec)	Observed Dripping ^b	Second Ignition ^a (sec)	Observed Dripping ^b	UL-94 Rating
2 , 10wt%*; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	175, 192	No, No	0,0	No, No	?, ?
6 , 8.5 wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	198, 195	No, No	0, 0	No, No	?, ?
7 , 10wt% ;Sb ₂ O ₃ , 4wt%; PTFE, 1 wt%; ABS	40, 275	Yes ^c , No	X, 7 ^d	No, No	?, ?
7 , 10wt% ;Sb ₂ O ₃ , 4wt%; PTFE, 1 wt%; HIPS	30, 29	Yes ^c , Yes ^c	19, X	Yes, No	?, ?
7 , 10wt%* ;Sb ₂ O ₃ , 4wt%; PTFE, 1 wt%; ABS	0, 33 ^d	No, No	143 ^d , 45 ^d	No, No	?, ?
7 , 10wt%* ;Sb ₂ O ₃ , 4wt%; PTFE, 1 wt%; ABS	51 ^d , 36 ^d	No, No	42 ^d , 81 ^d	No, No	?, ?
7 , 10wt%* ;Sb ₂ O ₃ , 4wt%; PTFE, 1 wt%; HIPS	134 ^d , 128 ^d	No, No	158 ^d , 110 ^d	No, No	?, ?

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that

only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content.

3.3 Experimental

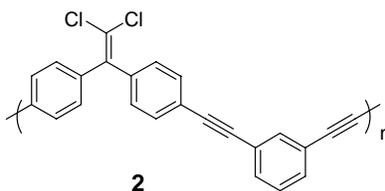
General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^1H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Bruker Avance 400 spectrometer. ^1H chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 $^\circ\text{C}$ scanning window at 10 $^\circ\text{C}/\text{min}$. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5 . An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. The molecular weights of the polymers have been analyzed on either a Waters GPC 150 C and/or a Polymer Laboratory GPC 220, using THF (40 $^\circ\text{C}$, 1 mL/min) as the eluent. The GPC samples were analyzed by both refractive index and UV absorption. The synthesized polymers were compared with polystyrene standards with known molecular weights of 1000000, 900000, 435500, 96000, 30300, 22000, 5050, 1250, and 580. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

General Procedure for Blending Flame Retardant Plastic and Additives in either the Brabender 30 ml Type 6/2 Mixing bowl – Prep Center or the Thermo Haake Mini lab Rheomex CTW5. The additive and plastic were weighed out in their respective amounts according to the wt % of additive. Heating temperatures for the blending bowl varied depending on the material involved. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used, the plastic and additives were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives were removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

General Procedure for Extruding Plastic in the UL-94 Test Bars. The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8" thick \times 1/2" wide \times 3" long rectangular bar mold. Heating temperatures for *the blend cup and the extrusion mold varied depending on the material involved.*

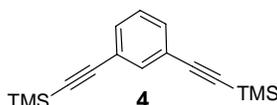
General Procedure for the HVUL-94 Burn Test. The flame resistance of the new polymers was tested using the horizontal and vertical Underwriters Laboratory test for flammability of plastic materials (HVUL-94). Two 1/8 inch thick \times 1/2 inch wide \times 3 inches long plastic (polymer + anti-drip additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The methane tank pressure regulator was set to 20 psi. The pressure regulator on the HVUL-94 test station was set to 4.5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. The flame is blue with an intense blue inner cone with a flow rate 90 cc/min. All test bars underwent two trials; each trial consisting of ignition for 10 seconds, followed by flame removal and a recording of the time for the bar to be considered self-extinguished.

General Procedure for the Pyrolysis Combustion Flow Calorimetry (PCFC, done at the FAA Labs) PCFC measurements were taken using 0.1-0.2 mg of the polymer sample with an interface temperature just below the onset of decomposition. The samples were pyrolyzed to a temperature of 930 °C at 4.3 °C/s in a nitrogen atmosphere. The polymer was then completely combusted at 900 °C. The sample results are an average of five measurements. The PCFC is a new method used to characterize the potential flame retardancy of a polymeric material. It gives three important data points that are used to evaluate the materials performance: 1. Heat Release Capacity, a calculated variable derived from the polymeric structure, this is a true material property which is dependent upon thermodynamic state variables, independent of sample size and heating rate. 2. Total Heat Release, is measured value that is derived from the controlled pyrolysis of the polymer in an inert gas (to avoid oxidizing the char), the fuel gas is then mixed with oxygen at elevated temperatures (900 °C) and the heat of combustion is measured. 3. Char yields, are important because char doesn't burn and helps to add an insulating layer between the flame front and the polymeric fuel. It has been shown that the data obtained from PCFC measurements and correlates well with other pyrolysis methods such as, Cone Calorimetry, UL-94 test for flammability of plastic materials, and oxygen bomb calorimetry.

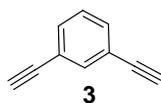


Poly[(2-phenylene-2'-phenylene-m-diethynylene)-1,1-dichloroethylene] (2, JLJ-I-243, 255). To a screw cap tube, equipped with a stir bar, was added 2,2-Bis(4-bromophenyl)-1,1-dichloroethylene **1**, (3.245 g/ 8 mmol), 1,3-diethynylbenze (0.835 g/ 8 mmol), Copper Iodide (0.076 g/ 0.4mmol), bistriphenylphosphine palladium (II) dichloride (0.280 g/ 0.4 mmol), and

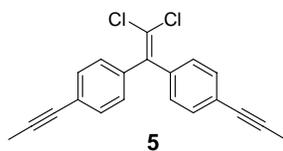
triphenylphosphine (0.210 g/0.8 mmol). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). THF (30 mL), and Hunig's base (5.6 mL/32 mmol) were added via syringe. The septum was replaced with a screw cap and placed in an oil bath at 50 °C for 2 d. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried in vacuo for 24 h. FTIR (KBr) 3417.4, 3033.6, 1588.3, 1503.5, 1399.7, 1014.4, 969.2, 855.0, 788.2, 733.4, 680.9.



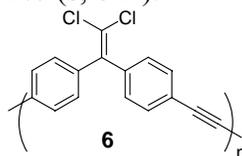
1,3-Bis[(trimethylsilyl)ethynyl]benzene (4, JLJ-I-215, 227, 245). To a screw cap tube, equipped with a stir bar, was added Copper Iodide (0.380 g/ 2mmol), bistrisphenylphosphine palladium(II) dichloride (0.702 g/ 1 mmol), and triphenylphosphine (0.525 g/2 mmol). The flask was sealed with a septum, evacuated, and backfilled with nitrogen (3×). THF (30 mL), Hunig's base (10.45 mL/60 mmol), and phenyl acetylene (3.3 mL/30 mmol) were added via syringe. To a 25 mL pear shaped flask was added 1,3-dibromobenze (2.42 mL/20 mmol). The flask was frozen with liquid nitrogen, evacuated and backfilled with nitrogen (3×). The degassed 1,3-benzene was added to the screw cap tube via cannula and rinsed with dry THF (2 × 10 mL). TMS acetylene (8.5 mL/60 mmol) was added to the screw cap tube via syringe. The septum was replaced with a screw cap and placed in an oil bath at 80 °C for 2 d. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with methylene chloride(3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried in vacuo for 24 h. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (td, J =1.63, 0.52 Hz, 1 H), 7.37 (dd, J =7.75, 1.55 Hz, 2 H), 7.21 (td, J =7.74, 0.53 Hz, 1 H), 0.2184 (s, 1 H)



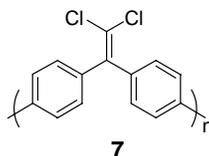
1,3-diethynylbenzene (3, JLJ-I-225, 239, 251). To a 250 mL round bottom flask, equipped with a stir bar, was added 1,3-Bis[(trimethylsilyl)ethynyl]benzene **4**, potassium carbonate (10 equivalents), and MeOH/CH₂Cl₂ (1:1). The reaction was sealed under nitrogen and allowed to stir at room temperature for 2 h. The reaction mixture was then diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried in vacuo for 1 h. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (t, J =1.50 Hz, 1 H), 7.44 (dd, J =7.77, 1.62 Hz, 2 H), 7.26 (td, J = 7.77, 0.55 Hz, 1 H), 2.08 (s, 1 H).



2,2-Bis(*p*-propynylphenyl)-1,1-dichloroethylene (5, JLJ-I-263, JLJ-II-17, 25). To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene **6** (4.06 g/10 mmol) copper iodide (0.190 g/ 1mmol), bistriphenylphosphine palladium(II) dichloride (0.351 g/ 0.5 mmol). The flask was then sealed with a septum, evacuated, and backfilled with nitrogen (3×). Triethylamine (40 mmol) was added via syringe. Propyne was bubbled in with a balloon and the reaction was heated to 65 °C for 24 h. The reaction mixture was diluted with methylene chloride. The organic layer was washed with ammonium chloride (3×) and the aqueous layer was extracted with ether (3×). The organic layers were combined and dried over magnesium sulfate and filtered through celite. Solvent was removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3419.8, 2916.2, 2252.6, 1588.0, 1504.3, 1400.0, 1020.9, 970.8, 855.0, 794.5, 686.2, 533.4. ¹H NMR (400 MHz, CDCl₃) δ 7.3 (dt, *J* = 8.4, 1.8 Hz, 4 H), 7.2 (dt, *J* = 8.5, 1.8 Hz, 4 H), 2.0 (s, 6 H).

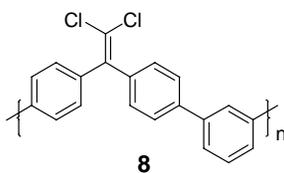


Poly[2,2-bis(*p*-ethynylphenyl)-1,1-dichloroethylene] (6, JLJ-I-287, JLJ-II-53) To a 250 mL round bottom flask equipped with a stir bar and reflux condenser and purged with nitrogen, was added 2,2-bis(*p*-propynylphenyl)-1,1-dichloroethylene **5** (3.24 g/10 mmol), molybdenum hexacarbonyl (.264 g/ 1 mmol), 4-chlorophenol (1.28 g/ 10 mmol), and *o*-dichlorobenzene (40 mL). The flask was then sealed with a septum and heated to 150 °C under a steady stream of nitrogen for 24 h. The mixture was then dissolved in methylene chloride and precipitated in methanol. The mixture was then dissolved in THF and precipitated in hexanes. Solvent was removed from the polymer in a vacuum desiccator for 24 h. ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.41 (m, 4 H), 7.28-7.21 (m, 4 H). FTIR (KBr). 3032.3, 1600.6, 1511.5, 1401.5, 1018.6, 970.3, 863.0, 831.6, 782.7, 728.4, 686.7, 570.8, 522.5. Mn- 4650, Mw- 28600.

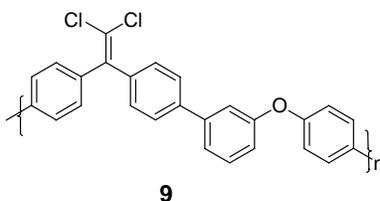


Poly[*p*-2,2-diphenyl-1,1-dichloroethylene] (7, JLJ-II-145, 147, 195, 203, 207). To a 250 mL three necked round bottom flask equipped with a stir bar and reflux condenser and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, magnesium turnings, and anhydrous nickel (II) chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3 ×). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 hours. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et₂O. The polymer was dried in

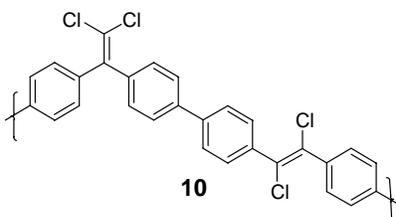
the vacuum oven 60 °C overnight. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8-7 (m, 8 H). FTIR (KBr) 3416.8, 2359.3, 1901.8, 1628.9, 1581.7, 1484.7, 1390.6, 1069.9, 1008.4, 969.1, 854.6. M_w : 110,000; M_n : 68,950.



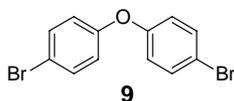
Poly[(2,2-diphenyl-*m*-phenyl)-1,1-dichloroethylene] [8, JLJ-II-169(5 mol %), 177 (10 mol%)]. To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condenser and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, 1,3-dibromobenzene (5 or 10 mol %), magnesium turnings, and anhydrous nickel(II)chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3 \times). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 hours. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O . The polymer was dried in the vacuum oven 60 °C overnight. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8-7 (m, 12 H). FTIR (KBr). (5 mol%) M_w : 16,000; M_n : 2300. (10 mol%) M_w : 65,300; M_n : 54,300.



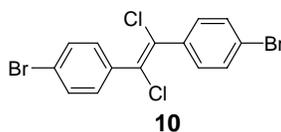
Poly[(2,2-diphenyl-*p*-diphenylether)-1,1-dichloroethylene] [9, JLJ-II-185(10 mol%), 193(5 mol%)]. To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condenser and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, 4,4'-dibromophenyl ether (5 or 10 mol %), magnesium turnings, and anhydrous nickel(II)chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3 \times). THF (100 mL) was added via syringe. The reaction was heated to reflux for 24 hours. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et_2O . The polymer was dried in the vacuum oven 60 °C overnight. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8-7 (m, 16 H). FTIR (KBr). (5 mol%) M_w : 8500; M_n : 2600. (10 mol%) M_w : 8600.; M_n : 2500.



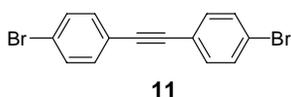
Poly[(2,2-diphenyl-p-1,2diphenyl-1,2-dichloroethylene)-1,1-dichloroethylene] [10, JLJ-III-5 (20 mol%), 21 (100 mol%)]. To a 250 mL three necked round bottom flask, equipped with a stir bar and reflux condenser and purged with argon, was added 2,2-bis(4-bromophenyl)-1,1-dichloroethylene, **1**, 1,2-bis(4-bromophenyl)-1,2-dichloroethylene (20 or 100 mol %), magnesium turnings, and anhydrous nickel (II) chloride. The flask was then sealed under argon with a septa, evacuated and backfilled with argon (3 ×). THF (100 mL) was added via syringe. The reaction was heated at reflux for 24 hours. The reaction mixture was then allowed to cool to room temperature, then poured into a vigorously stirred flask of MeOH (400 mL) to precipitate the polymer. This was followed by filtration of the polymer in a fritted funnel (medium porosity). The polymer was washed with copious amounts of MeOH and Et₂O. The polymer was dried in the vacuum oven 60 °C overnight. FTIR (KBr). (20 mol%) M_w: 102,100; M_n: 68,000. (100 mol%)M_w: 8700.; M_n: 2700.



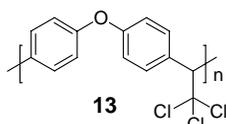
4,4'-Dibromodiphenylether (9, JLJ-II-173, 174). To a 100 mL round bottom flask equipped with a stir bar and purged with nitrogen was added diphenyl ether and a crystal of iodine. Methylene chloride (10 mL) was added to the flask and the mixture was stirred until the solid dissolved. Bromine was added drop-wise via syringe and the reaction was allowed to stir for 6 h. The reaction was then diluted in methylene chloride and water. The organic layer was washed with sodium bisulfite (1 M) and extracted with methylene chloride (3 ×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was removed via rotary evaporation and the solid residue was dried in vacuo overnight. ¹H NMR (400 MHz, CDCl₃) δ 7.4 (dt, J = 9, 2.8 Hz, 4 H), 6.9 (dt, J = 9, 2.7 Hz, 4 H). FTIR (KBr).



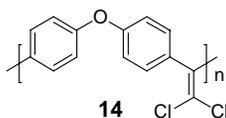
1,2-Bis(4-bromophenyl)-1,2-dichloroethylene (10, JLJ-II-172, 191, III-3). To a 100 mL three neck round bottom flask equipped with a stir bar, gas inlet and outlet, was added dibromotolane **11** and chloroform (50 mL). The reaction mixture was placed in an ice bath and chlorine was bubbled into the reaction (at a rate of approximately 1 bubble a second) for 40 min. The reaction was then diluted in methylene chloride and water. The organic layer was washed with sodium bisulfite (1 M) and extracted with methylene chloride (3 ×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was removed via rotary evaporation and the solid residue was dried in vacuo overnight. ¹H NMR (400 MHz, CDCl₃) δ [cis] 7.6 (dt, J = 8.7, 2.2 Hz, 4 H), 7.5 (dt, J = 8.7, 2.2 Hz, 4 H); [tran] 7.3 (dt, J = 8.7, 2.2 Hz, 4 H), 7.1 (dt, J = 8.7, 3.3 Hz, 4 H). FTIR (KBr).



Dibromotolane (11, JLJ-II-171, 187). To a 250 mL round bottom flask equipped with a stir bar was added 2,2-bis(4-bromophenyl)-1,1-dichloroethane, **1**. The flask was sealed with a septa, then evacuated and backfilled with nitrogen (3 ×). Diethyl ether (100 mL) was added to the flask via syringe, and cooled to -40 to -50 °C. Phenyl lithium (1.8 M) was added to the reaction flask drop-wise via syringe. The reaction was stirred at -40 to -50 °C for 2 hours, and then allowed to warm to room temperature overnight. The precipitate was filtered off and saved. The remaining ethereal filtrate was washed with water and extracted with ether (3 ×). The organic layers were combined and dried over magnesium sulfate, and filtered through filter paper. Solvent was removed via rotary evaporation. The filter cake and the remaining solids after rotary evaporation were combined and dried in vacuo overnight. ^1H NMR (400 MHz, CDCl_3) δ 7.5 (dt, $J = 8.7, 2.1$ Hz, 4 H), 7.4 (dt, $J = 8.7, 2.0$ Hz, 4 H). FTIR (KBr). HRMS calc'd for $\text{C}_{14}\text{H}_8\text{Br}_2\text{Cl}_2$: 405.8348. Found: 405.8347. 0.27 ppm error.



Poly(diphenylether-chloral) (12, JLJ-II-7, 19) To a 250 mL three neck round bottom flask, equipped with a stir bar, addition funnel, gas inlet, reflux condenser and purged with nitrogen, was added chloral hydrate **12** (1.654 g/10 mmol). The flask was then sealed with septa, evacuated, and backfilled with nitrogen (3×). Trifluoroacetic acid (10 mL) was added *via* syringe, and trifluoroacetic anhydride (1.41 mL/10 mmol) was added dropwise *via* an addition funnel over 1.5 h and stirred. To a separate 50 mL round bottom flask equipped with a stir bar was added diphenylether **9** (1.702 g/ 10 mmol). The flask was then sealed with septa, evacuated, and backfilled with nitrogen (3×). Tetrachloroethane (10 mL) was added to the flask and allowed to stir. After the diphenylether dissolved, the solution was added drop-wise to the 250 mL flask *via* cannula. An additional 10 mL of tetrachloroethane was added to the 50 mL flask and was added drop-wise *via* cannula to the 250 mL flask. The mixture was heated to 70 °C for 2.5 h and allowed to stir. The reaction was allowed to cool to room temperature and BF_3 (gas) was bubbled into the mixture (approximately 1 bubble per second) for one hour and heated to 70 °C overnight. The addition of BF_3 (gas) was done for (approximately 1 bubble per second) an hour twice a day (morning and night) for 3 days. The reaction was then dissolved in chloroform and the solids precipitated with methanol. Solvent was removed from the polymer in a vacuum desiccators for 24 h. ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.53 (m, 4 H), 6.98-6.94 (m, 4 H), 5.01 (s, 1 H). FTIR (KBr) 3053.8, 1596.3, 1500.1, 1242.3, 1171.6, 1015.5, 872.1, 792.1, 764.1, 715.2, 666.9, 566.8. Mn-3500, Mw-9400.



Polydichlorovinylidene (14, JLJ-II-15). To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen, was added poly(diphenylether-chloral) **13** (2.0 g). The flask was sealed with a septum, evacuated, and backfilled with nitrogen

(3×). Pyridine (40 mL) was added to the flask via syringe and heated to reflux for 24 h. The cooled reaction was quenched in water and then the solids filtered, and washed with hot water (5×). The resulting polymer was dried in the vacuum oven 50 °C for 24 h. ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.24 (m, 4 H), 6.97-6.90 (m, 4 H). FTIR (KBr) 3035.5, 2358.6, 1592.8, 1498.4, 1240.1, 1166.7, 1015.2, 971.4, 874.4, 795.3, 750.5, 581.5. Mn-3500, Mw-9400.

4.1 Novel Flame Retardant Polymers of Bisphenol C

The use of flame retardant additives for making commercial polymers flame resistant consumes 909,000 tons/yr of additives.[#41] While increasing the flame resistance of the polymers, these additives are known to compromise the polymers' physical and mechanical characteristics, such as decreasing the strength and stress modulus. The impetus of the polymer industry is the design of a low-cost flame retardant polymer that does not require additives yet still has favorable physical and mechanical properties. New flame resistant polymers that have been commercialized are used in specialty applications, and are referred to as "engineering plastics"; for example, polyarylsulfone and polyetheretherketone (PEEK). These polymers work as heat/flame resistant polymers, but due to high cost of production and poor processibility, their commercial use has been limited. Furthermore, a polymer system is sought that does not burn even when it is exposed to a constant flame source. Currently there is no such polymer available.

The compound that we have explored as a backbone for the flame retardant polymers is commonly called bisphenol C (BPC) or 1,1-dichloro-2, 2-bis(4-hydroxy-phenyl)ethylene. It is derived from an acid catalyzed condensation of chloral hydrate and phenol, followed by a dehydrohalogenation reaction to yield BPC. As has been shown by many research groups, BPC can be used as a blendable additive in a commercial plastic or as part of a polymer back bone to effectively impart flame resistance to certain polymeric materials. When thermally decomposed, BPC exothermically produces volatile products such as HCl and CO₂. It is these pyrolysis by-products and the high char forming nature of BPC that cause flame resistance in these polymers and blends.

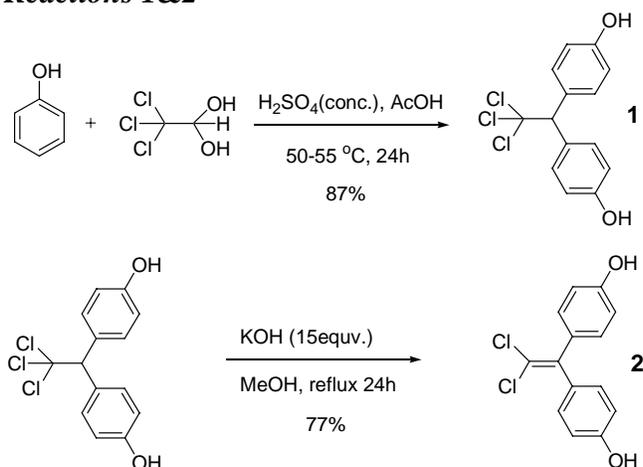
The thrust of our research has been to incorporate the BPC moiety into a polymer backbone that can impart flame retardancy without additives. The incorporation of this monomer into a thermoplastic has been approached several ways including the following: nucleophilic aromatic polymerizations, nucleophilic displacement under Phase Transfer Conditions (PTC), diene metathesis (ADMET), and lastly urethane chemistry.

4.2 Results and Discussion- Bisphenol C and BPC polycarbonate

The original research into the BPC molecule was done by the Ex-Lax Inc. in Brooklyn New York. It was believed from other sources that these bisphenolic compounds would have laxative properties, so they synthesis of BPC was pursued. The synthesis of BPC was carried out by condensing phenol with chloral to produce 1,1,1-Trichloro-2,2-bis(p-hydroxyphenyl)ethane **1**

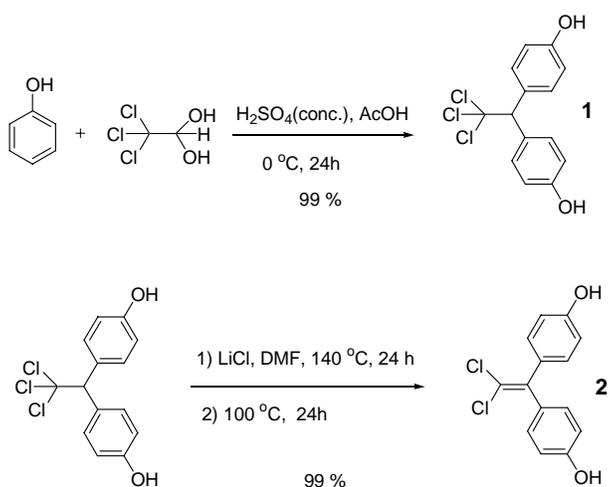
followed by a dehydrohalogenation to give the corresponding dehydrohalogenated compound 1,1-dichloro-2,2-bis(p-hydroxyphenyl)ethylene or BPC **2** (Reactions 1 & 2).

Reactions 1&2



The improved synthesis of bisphenol C has been obtained from the thesis of Jennifer Stewart at the University of Massachusetts and her procedure for synthesizing BPC has resulted in higher yields. Using her reaction conditions the bisphenol C monomer can be made in quantitative crude yield (Reaction 2 & 3). Several decolorizing and recrystallizations are then needed to obtain material that is suitable for condensation polymerizations, but overall this procedure requires less workup time and better yields.

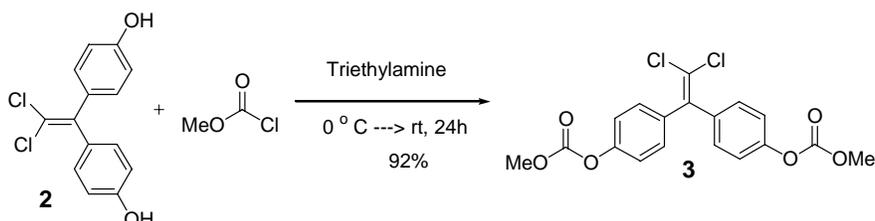
Reaction 2 & 3



The use of BPC as a flame retardant additive or a polymer was not developed until the late 70's by General Electric.[Mark, 1980 #45;Factor, 1980 #9] In this paper and patent they had improved the flame-resistant properties of polycarbonate, by co-polymerizing BPC with

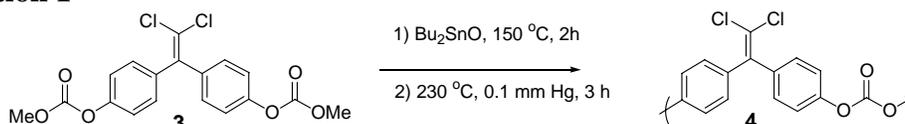
biphenol A (BPA).[Mark, 1980 #45;Factor, 1980 #9] In the G.E. polymerizations they do their synthesis with the aid of phosgene gas. Because of the high toxicity of this gas, we have used a non-phosgene polymerizations procedure.[Haba, 1999 #40] In the route to making polycarbonate monomers, bisphenol C was transformed into the dicarbonate by condensing with methyl chloroformate to give bisphenol C bis(methyl carbonate) **3** (Reaction 5).

Reaction 5



The polymer was made with the bis(methyl carbonate) **3** of bisphenol C **4** that was then polymerized using dibutyltin oxide as a catalyst, with high heat and vacuum (Polymerization 1).

Polymerization 1

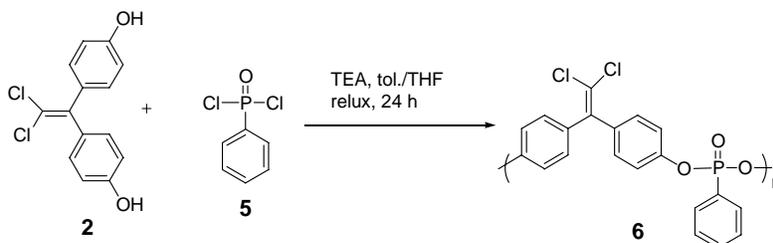


As a result of the high heat and vacuum used in this method a lot of the monomer sublimed resulting in low molecular weight polymer. The synthesized polymer was sent to FAA for further testing.

4.3 Results and Discussion- Phosphorous and BPC polymers

The next type of polymer that has been synthesized in the lab contains phosphorus. It has been theorized in the literature that phosphorus acts both in the solid and vapor phase to stop burning. The first polymer that incorporated phosphorus in the backbone and copolymerized with BPC was done by a condensation with phenylphosphonic dichloride **5** to yield polymer **6** (Polymerization 2).

Polymerization 2

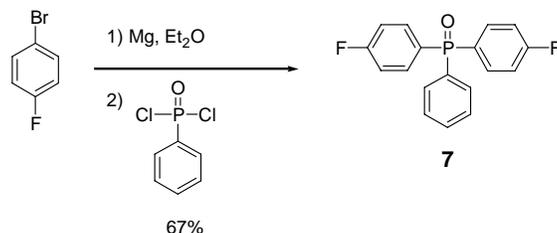


Several different polymerization procedures were tried but resulted in a brittle low molecular weight material. A full bar could not be made and tested in the HVUL-94, but in the improvised pellet test this polymer did not burn.

Another approach to incorporating phosphorous with the bisphenol C moiety was done utilizing a different condensation polymerization method. In order to make this new polymer the nucleophilic aromatic substitution reaction was utilized. Bis(4-fluorophenyl)phenylphosphine

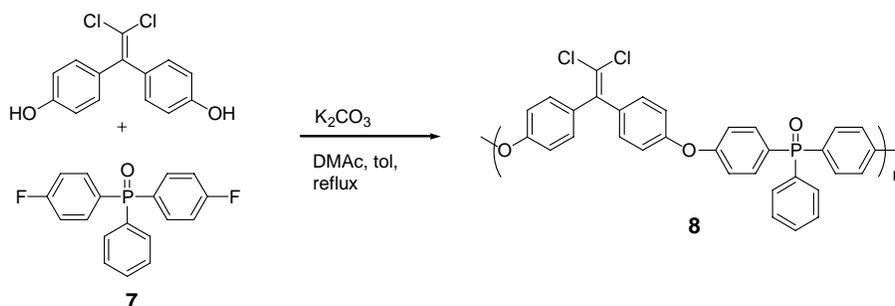
oxide **7** was synthesized by reacting the Grignard of 1-bromo-4-fluoro benzene with dichlorophenylphosphine oxide to give co-monomer for the ensuing polymerization (Reaction 3).

Reaction 3



The polymer was achieved by reacting **7** with the BPC monomer under basic conditions to yield a new polyphosphoroether **8** (Polymerization 3).

Polymerization 3



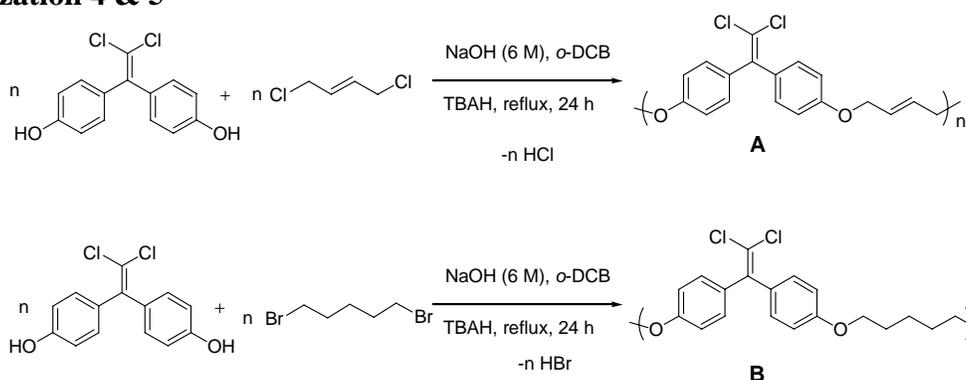
This polymer was obtained in low molecular weight (M_w : 4000; M_n : 3500) but with improvised burn test (making a pellet) the resulting polymer did not burn.(Table 2).

4.4 Results and Discussion- BPC Polyarylethers

The inflexibility of these highly aromatic polyethers has been a problem with several of the polymers that have been made in our lab. In order to make flexible polymers that have distinct melting points aliphatic and olefinic groups had to be part of our polymeric backbone. The quandary of using these types of functional groups is that theoretically they should increase the amount of “fuel” for the fire, and therefore the flammability of the polymer. It is also known in flame retardant chemistry that olefins can cross-link during the burning process and increase char formation. In addition Wagner describes some of his unsaturated polyethers as having high degree of thermal stability as measured by thermogravimetric analysis.

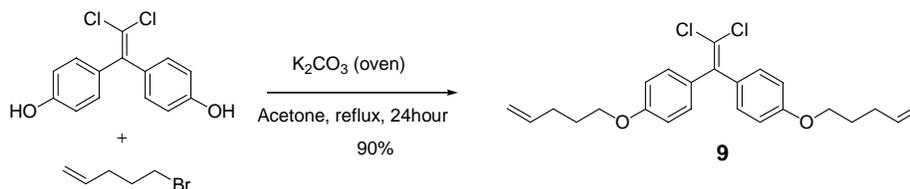
The first of these types of polymers was done by a nucleophilic displacement of chloride by phenolate. A common polyether that has been made by several groups is the addition of bisphenol A with 1,4-dichloro-2-butene under phase transfer conditions (PTC). Using this procedure we synthesized a polymer with bisphenol C and 1,4-dichloro-2-butene(DCB) and 1,5-dibromobutane under PTC to yield polyether **A & B** (Polymerization 4 & 5). The burn results for these two polymers are summarized on **Table 1**.

Polymerization 4 & 5



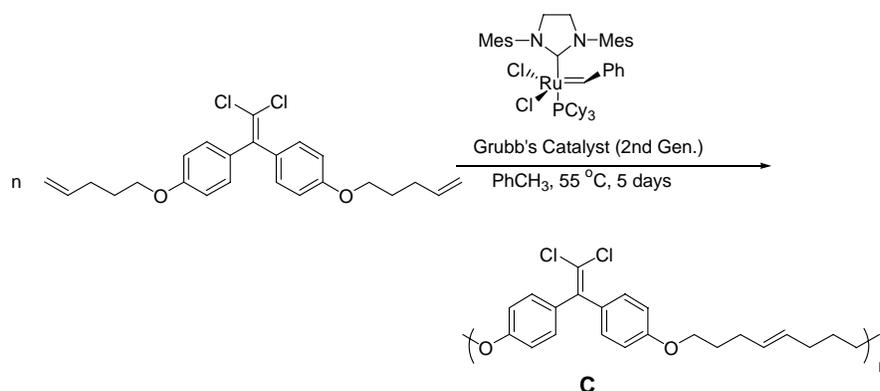
The next approach at obtaining high molecular weight polymers was to explore Acyclic Diene Metathesis polymerizations (ADMET). The aim was to achieve high molecular weights flame resistant polymers. In our pursuit to these types of polymers we used several aliphatic diene monomers such as, 1,5-hexadiene and 1,9-decadiene, as test polymerizations to achieve optimized conditions. Following Wagener's procedures using Grubb's catalyst (2nd Generation) we obtained an aliphatic polymer. Due to GPC problems, refractometer is not working, we could not obtain molecular weight information. At this point we decided to functionalize the bisphenol C with an olefin. Wagener has also done considerable work on the influence of the neighboring group effect. His studies have concluded that atoms such as, oxygen and sulfur act as Lewis Bases, therefore they complex with the metal (Ru) and hinder the metathesis reaction from occurring. In order to circumvent this problem we have incorporated three methylene "spacers" into the monomer. This was achieved by condensing bisphenol C with 5-bromo-1-pentene under basic conditions to yield monomer **9** (Reaction 4).

Reaction 4



After purification of this monomer through multiple recrystallizations in methanol we polymerized this molecule using Grubb's Catalyst (2nd Generation) in toluene, at 55 °C with a positive flow of argon for 5 days to yield polyether C. (Polymerization 6).

Polymerization 6

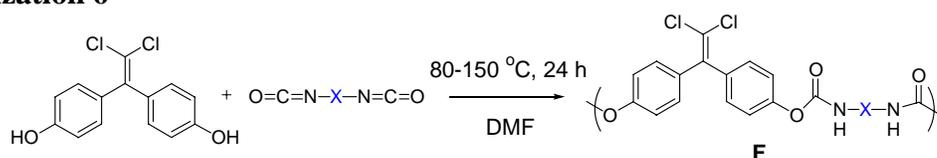


The flammability of these three polyarylethers was measured using the standard UL-94 test for plastic flammability. All three samples obtained a V-0 rating when two sample bars were exposed to two, 10-second flame ignitions. All sample were mixed with 1 wt % PTFE as an anti-drip additive. It is important to note that the samples were tested without anti-drip additive, and did not burn but dripped excessively, making characterization impossible. It is because of this reason that an anti-drip additive was used. The polymer samples all give good results without the need for a synergist such as antimony oxide to impart flame retardancy. It was observed that while these polymers were subjected to prolonged exposure to the Bunsen burner flame, the fire never consumed them. The UL-94 sample results can be seen **Table 1**.

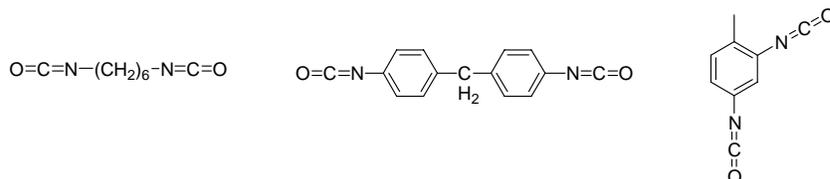
4.5 Results and Discussion- BPC Polyurethanes

The latest approach to making flexible flame retardant thermoplastics has been to utilize urethane chemistry. Polyurethanes have found uses in many such as flexible foams and coatings. They are generally not considered good flame-retardants but co-polymerizing them with bisphenol C could yield a flexible flame-resistant polymer. Two different polymerizations methods were tried. The first was a solution polymerization of various diisocyanate (HDI, MDI, TDI) and bisphenol C in dimethylformamide to make polyurethane **F** (Polymerization 6).

Polymerization 6



X = HDI (hexamethylenediisocyanate), **MDI** (methylenediisocyanate), **TDI** (toluenediisocyanate)



These polymerization resulted in medium to low molecular polymers. The next method for making the urethane polymer was a melt polymerization of the different diisocyanate and bisphenol C. This method gave a hard and virtually insoluble polymer, therefore GPC measurements are not accurate. The flame resistant properties of these polymers were tried on the urethane polymers copolymerized with both MDI and HDI and both showed good flame

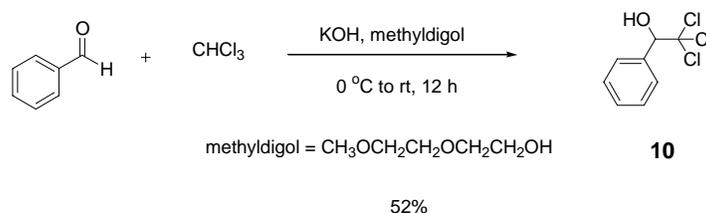
retardant characteristics. The polyurethane made with BPC and MDI showed the best results, being that it did not ignite after the flame was removed. The PCFC results are summarized in Table 2.

4.6 Results and Discussion- Flame Retardant Asymmetrical Bisphenol C Polymers (ABPC)

The incorporation of flexible linkers for making processible polymers, which are found in vinyl addition polymers, are not usually considered flame resistant, and therefore is not usually a suitable options for flame retardant polymers. Due to the excellent flame retardant characteristics of bisphenol C (BPC) molecule we have made new asymmetric BPC (ABPC) monomers with an easily polymerized acrylate functional group. Acrylic polymers are known for their resistance to heat, sunlight, and weathering which makes them an excellent candidate for flame retardant polymers. The approach to making these acrylate polymers was to incorporate the flame retardant BPC as a pendant group hanging off the acrylate skeleton. This has produced a flame retardant and processible polymer that can be melted and molded into a new flame resistant material.

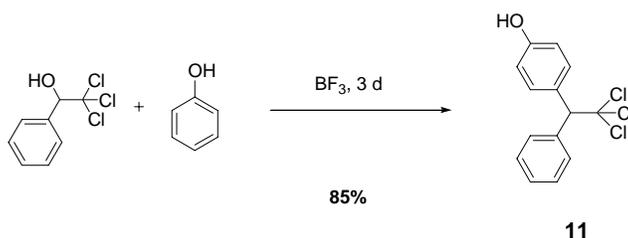
The new asymmetric bisphenol C (ABPC) structures are made from cheap and readily available starting materials. The first step is to produce the trichloroethanol product often referred to as the carbinol **10**. The carbinol is synthesized by slowly adding a solution of potassium hydroxide and methylidigol (diethylene glycol monomethylether) to a stirring solution of benzaldehyde and chloroform chilled at 0 °C (Reaction 5).

Reaction 5

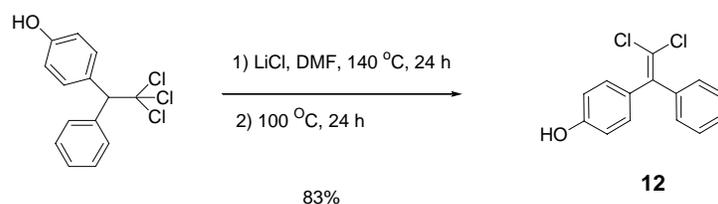


The resulting carbinol **10** is purified by vacuum distillation and reacted with phenol in the presence of BF_3 gas over several days to yield the asymmetrical DDT **11** molecule. This process takes several daily additions of BF_3 and mechanical stirring to afford the dark viscous mixture, which is then purified by column chromatography (Reaction 6).

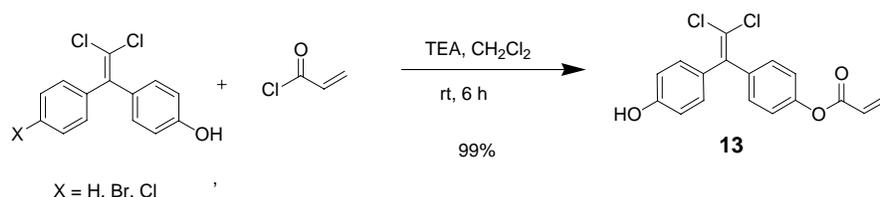
Reaction 6



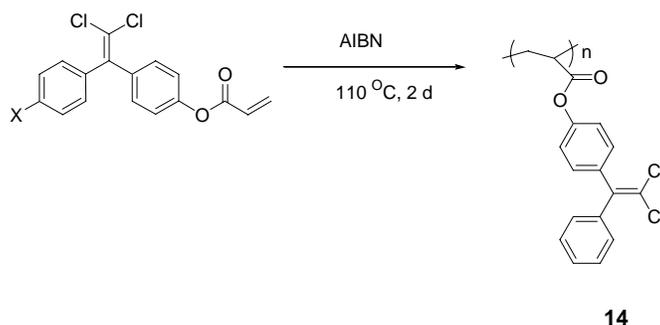
The dehydrohalogenation of the ABPC is done using the standard procedure of Lithium Chloride in DMF at 140 °C for 24 hours then slowly decreasing the heat to 100 °C, to yield the asymmetrical BPC analog **12** (Reaction 7).

Reaction 7

The final step to afford the acrylate monomer is the addition of acryloyl chloride to a solution of the ABPC, triethylamine and in methylene chloride to produce the acrylate monomer **13** (Reaction 8).

Reaction 8

The acrylate polymer **14** is made by a bulk polymerization with 2,2'-azobisisobutyronitrile (AIBN) at 110 °C for 2 d (Polymerization 7)

Polymerization 7

The burn results concluded that this polymer works well as a flame retardant material without the need for a synergist. The polymer dripped but did not ignite the cotton when it subjected to the HVUL-94 flame test and with the addition of 1 wt% PTFE did not drip at all. The polymer is considered to be a V-0 material according to the UL-94 test for flammability of plastic materials.

Table 1. HVUL-94 Burn Results

Additive	First Ignition ^a (sec)	Observed Dripping ^b	Second Ignition ^a (sec)	Observed Dripping ^b	UL-94 Rating
Polyarylether A, 1wt % PTFE	3, 0	No, No	0, 0	No, No	V-0

Polyarylether B , 1wt % PTFE	1, 6	No, No	3, 0	No, No	V-0
Polyarylether C , 1wt %PTFE	6, 0	No, No	0, 2	No, No	V-0
Polyarylether A , 10wt % CIPE	2, 5	No, No	6, 9	No, No	V-0
Polyacrylate 14	0, 0	No, No	1, 1	No, Yes	V-0
Polyacrylate 14 , 1wt % PTFE	0, 0	No, No	0, 0	No, No	V-0

a Time to self-extinguishing in seconds after 1st, 2nd, 3rd 10 sec ignition. **b** Indicates that molten ABS did (Y) or did not (N) drip on to cotton patch underneath ignited bar during UL-94 test. **c** Indicates ignition of cotton patch underneath ignited bar of plastic. **d** Indicates time that only glowing, not flame occurred after re-application of flame. X indicates not enough bar remaining for 2nd ignition. * Wt % based on halogen content.

Table 2 PCFC Results.

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)
Polyarylether A	37	8	58
Polyarylether B	205	13	37
Polyarylether C	146	18	20
Polyethylene	1676	42	0
Polystyrene	927	39	0

4.7 Experimental

General Procedures: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^1H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Bruker Avance 400 spectrometer. ^1H chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. IR spectra were obtained on a Nicolet Avatar 360 FTIR. Gas chromatography experiments were performed on a Hewlett-Packard GC model 5890A. Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer TGA7 or TA Q 50 from 30 - 900 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 or TA Q 10 using a 30 - 450 $^\circ\text{C}$ scanning window at 10 $^\circ\text{C}/\text{min}$. under nitrogen. Polymer blending/extrusion was done with a Custom Scientific Instruments CSI-183MMX Mini-Max Blender/Extruder or with a Brabender Prep-Center using a type 6/2 mixer head or Thermo Haake Mini lab Rheomex CTW5. An Atlas Electric HVUL-94 flame test station was used for the UL-94 flame tests. Melting points were obtained using a Büchi melting point apparatus. Reagent grade tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Dry benzene, toluene, methylene chloride, and triethylamine were distilled over calcium hydride and under nitrogen. The molecular weights of the polymers have been analyzed on either a Waters GPC 150 C and/or a Polymer Laboratory GPC 220, using THF (40 $^\circ\text{C}$, 1 mL/min) as the eluent. The GPC samples were analyzed by both refractive index and UV absorption. The synthesized polymers were compared with polystyrene standards with known molecular weights of 1000000, 900000, 435500, 96000, 30300, 22000, 5050, 1250, and 580. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was obtained from the Rice University Mass Spectrometry Laboratory.

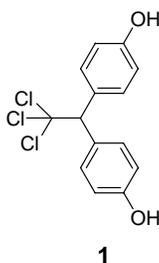
General Procedure for Blending Flame Retardant Plastics & Additives in either the Brabender 30 ml Type 6/2 Mixing bowl or the Thermo Haake Mini lab Rheomex CTW5 – Prep Center. The additives and plastics were weighed out in their respective amounts according to the wt % of additive. Heating temperatures for the blending bowl varied depending on the material involved. After the bowl had heated to the necessary processing temperature, the sample was poured quickly through the top opening of the Brabender while the blades were rotating at 50 RPM. The opening was then closed with the weighted handles and the sample was blended according to the type of flame retardant added. If a melt-blendable additive was used, the plastic and additives were blended for 10 min at 100 RPM. If a non-melt blendable additive was used the plastic and additives were blended for 10-30 min at 150 RPM. If fibrillare PTFE (Dupont PTFE 30, 60 % PTFE in an aqueous suspension; density = 1.3 g/mL) was used as an anti-drip additive, the resin and the PTFE were blended first for 10 min at 150 RPM. The flame-retardant additives were added and the plastic was blended again for 10 min at 150 RPM. After the blending was complete and the blades were stopped, the bowl was opened and molten plastic with the additives were removed with a bronze spatula. The plastic was then blended in the CSI-183MMX blender and extruded to give bars for the UL-94 test.

General Procedure for Extruding Plastic in the UL-94 Test Bars. The plastic removed from the Brabender mixing center was then broken into smaller pieces and inserted into the heated cup of the CSI-183MMX blender until the cup was full. The plastic and additives were heated until molten and extruded into a heated 1/8" thick \times 1/2" wide \times 3" long rectangular

bar mold. Heating temperatures for the blend cup and the extrusion mold varied depending on the material involved.

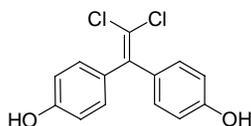
General Procedure for the HVUL-94 Burn Test. The flame resistance of the new polymers was tested using the horizontal and vertical Underwriters Laboratory test for flammability of plastic materials (HVUL-94). Two 1/8 inch thick \times 1/2 inch wide \times 3 inches long plastic (polymer + anti-drip additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The methane tank pressure regulator was set to 20 psi. The pressure regulator on the HVUL-94 test station was set to 4.5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. The flame is blue with an intense blue inner cone with a flow rate 90 cc/min. All test bars underwent two trials; each trial consisting of ignition for 10 seconds followed by flame removal and a recording of the time for the bar to be considered self-extinguished.

General Procedure for the Pyrolysis Combustion Flow Calorimetry (PCFC, done at FAA Lab) PCFC measurements were taken using 0.1-0.2 mg of the polymer sample with an interface temperature just below the onset of decomposition. The samples were pyrolyzed to a temperature of 930 °C at 4.3 °C/s in a nitrogen atmosphere. The polymer was then completely combusted at 900 °C. The sample results are an average of five measurements. The PCFC is a new method used to characterize the potential flame retardancy of a polymeric material. It gives three important data points that are used to evaluate the materials performance: 1. Heat Release Capacity, a calculated variable derived from the polymeric structure, this is a true material property which is dependent upon thermodynamic state variables, independent of sample size and heating rate. 2. Total Heat Release, is measured value that is derived from the controlled pyrolysis of the polymer in an inert gas (to avoid oxidizing the char), the fuel gas is then mixed with oxygen at elevated temperatures (900 °C) and the heat of combustion is measured. 3. Char yields are important because char does not burn and helps to add an insulating layer between the flame front and the polymeric fuel. It has been shown that the data obtained from PCFC measurements and correlates well with other pyrolysis methods such as, Cone Calorimetry, UL-94 test for flammability of plastic materials, and oxygen bomb calorimetry.



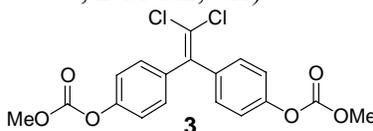
2,2-Bis(p-hydroxyphenyl)-1,1,1-Trichloroethane (1). To a 1 L round bottom flask, equipped with a mechanical stirrer, thermometer, addition funnel, and purged with nitrogen, was added phenol (131 g/ 1.3 mol), chloral hydrate (104 g/ 0.63 mol) and acetic acid (120 mL). The reaction was sealed under nitrogen with a septum and placed in a cooling bath at 0 °C, concentrated sulfuric acid (60 mL) and acetic acid (60 mL) was added drop-wise via the addition funnel, over 90 min period. Then an additional 150 mL of sulfuric acid was added to the

reaction mixture dropwise at a rate so that the internal temperature of the reaction never reached above 5 °C. The reaction was then allowed to warm to room temperature overnight (12 h). The reaction mixture was then quenched with ice and water and diluted to twice its volume. The precipitated powder was then filtered through a fritted filter and washed with copious amounts of water (3 L) to remove all excess acid. The resulting solid was then dried for 24 h in a vacuum oven at 95 °C. MP 204-206 °C. FTIR (KBr) 3215, 1894, 1606, 1510, 1449, 1369, 1246, 1179, 1113, 1020, 827, 751, 710, 576, 540. ¹H NMR (400 MHz, CD₃OD) δ 7.45 (dt, J = 8.62, 2.43 Hz, 4 H), 6.74 (dt, J = 8.73, 2.54 Hz, 4 H), 4.28 (s, 1 H).



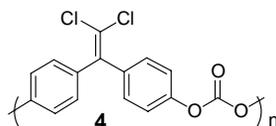
2

2,2-Bis(p-hydroxyphenyl)-1,1-dichloroethylene (2). To a 2 L round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen was added 2,2-bis(p-hydroxyphenyl)-1,1-Trichloroethane 1, LiCl (0.5 equivalents), and DMF (1 L). The flask was then sealed under nitrogen with a septum and heated to 140 °C for 16 h. The reaction was then cooled to 100 °C for another 16 h. The heat was then removed and the reaction was then allowed to cool to room temperature. The reaction mixture was then diluted with a large amount of water (2-3× its volume) to precipitate the product. The resulting solid was then filtered through a fritted funnel and washed with copious amounts of water (2 – 3 L) to remove the DMF. The product was then dried in a vacuum oven for 24 at 60 °C. FTIR (KBr) 3129, 1594, 1507, 1437, 1229, 1169, 973, 863, 833, 772, 592, 556. ¹H NMR (400 MHz, CD₃OD) δ 7.07 (dt, J = 8.77, 2.12 Hz, 4 H), 6.74 (dt, J = 8.76, 2.11 Hz, 4H).



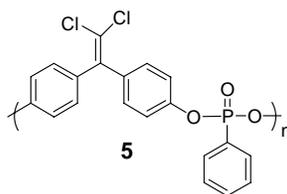
3

2,2-Bis(p-methylphenylcarbonate)-1,1-dichloroethylene (3) To a 250 mL round bottom flask equipped with a stir bar and purged with nitrogen was added 2,2-bis(p-hydroxyphenyl)-1,1-dichloroethylene (2.81 g/ 10 mmol). The flask was then sealed under nitrogen with a septum and cooled to 0 °C. Triethylamine (3.09 mL/ 40 mmol) and dry THF (100 mL) were added via syringe. Methyl chloroformate (3.09 mL/40 mmol) was added slowly, drop-wise, via syringe to the reaction. The reaction was allowed to warm to room temperature and stirred for 24 h. The reaction was then poured through filter paper and the filtrate was condensed via rotary evaporation. The residue was introduced drop-wise into 500 mL of water and stirred for 1 h. The resulting precipitate was then collected by filtration. This solid was dried in vacuo for 24 h. FTIR (KBr) 2960, 1758, 1598, 1508, 1441, 1407, 1267, 1217, 1058, 1014, 933, 863, 778, 743, 697, 623, 539, 510. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (dt, J = 8.78, 2.32 Hz, 4 H), 7.16 (dt, J = 8.81, 2.36 Hz, 4 H), 3.91 (s, 6 H).

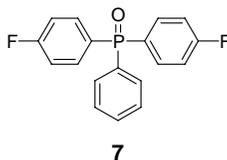


4

Poly[2,2-bis(*p*-phenylcarbonate)-1,1-dichloroethylene] (4). To a 50 mL round bottom flask equipped with a stir bar and purged with nitrogen was added 2,2-bis(*p*-methylphenylcarbonate)-1,1-dichloroethylene **3** (3.692 g/ 9.28 mmol) and dibutyltin oxide (0.011 g/0.0464 mmol). The flask was then sealed under nitrogen with a septum. The reaction was then heated to 160 °C. After 2 h the mixture was then evacuated (0.5 mm Hg) and the temperature was to 230 °C for 2.5 h. The mixture was then dissolved in a minimum amount of chloroform and precipitated with methanol. Methanol was removed from the polymer by placing the product in a vacuum desiccators for 24 h. FTIR (KBr) 1774, 1504, 1223, 1189, 1160, 1017, 862, 768, 515. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.31 (m, 4 H), 7.27-7.25 (m, 4 H). Mn: 4650; Mw: 14600.

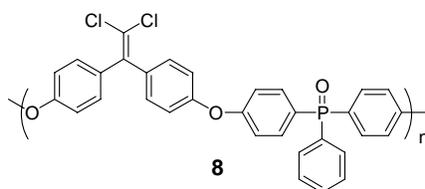


Poly[2,2-bis(*p*-phenylphosphate)-1,1-dichloroethylene] (5) To a 250 mL round bottom flask equipped with a stir bar and reflux condenser and purged with nitrogen was added bis(*p*-hydroxyphenyl)ethylene **2** (7.035 g/ 25 mmol). The flask was then sealed with a septum, evacuated, and backfilled with nitrogen (3 ×). Triethylamine (6.21 mL/52.5 mmol), toluene (70 mL), and THF (30 mL) were added via syringe and allowed to stir at room temp for an hour. To a separate 25 mL pear shaped flask that was sealed with a septum, evacuated, and backfilled with nitrogen (3 ×) was added phenylphosphonic dichloride and toluene (15 mL). This solution was then added to the 250 mL flask drop-wise via cannula. An additional (15 mL) of toluene was added to the pear shaped flask. This rinse was added drop-wise to the 250 mL flask via cannula. The reaction was heated to reflux for 24 h. The cooled mixture were dissolved in methylene chloride and precipitated as a resin in methanol. The methanol was decanted off and the resin was redissolved in methylene chloride and transferred to a clean flask. The solvent was removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3059, 1599, 1502, 1273, 1196, 1164, 1129, 920, 742, 692, 591, 508. ¹H NMR (400 MHz, CDCl₃) δ 7.96-7.91 (m, 2 H), 7.60-7.51 (m, 4 H), 7.49-7.46 (m, 4 H), 7.24-7.11 (m, 4 H). Mn: 3000; Mw: 6800.

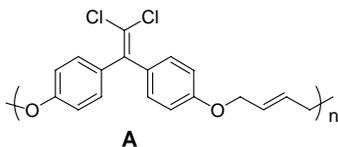


Bis(4-fluorophenyl)phenylphosphine oxide (7). To a 100 mL 3 neck round bottom flask equipped with stir bar and reflux condenser with argon was sealed with septa, then flame dried, evacuated and backfilled with argon (3 ×). Magnesium (100 mmol, 2.435 g) was added to the flask and the septum was replaced and the reaction flask was evacuated and back filled to

replace the atmosphere (3 ×). Diethyl ether (50 mL) was added to the flask via syringe and then 1-bromo-4-fluorobenzene (50 mmol, 8.75 g) was added to the reaction flask with constant stirring. The reaction mixture bubbled vigorously. An ice bath was used to keep the reaction mixture from bubbling over. After the bubbling had decreased, the reaction mixture was heated to reflux for 30 minutes. The reaction was then allowed to cool to room temperature. To a separate 25 mL pear shaped flask that was evacuated and backfilled with argon (3 ×) was added dichlorophenylphosphonate (100 mmol, 14.2 mL) and diethyl ether (20 mL, 2 ×). This mixture was then added to the 100 mL reaction flask slowly drop-wise via cannula at in an ice bath at 0 °C. After the vigorous mixture slowed down the reaction was heated to reflux for an hour. The reaction was quenched with water and diluted with ether. The two layers were separated and the organic layer was washed with water and brine solution (3 ×). The organic layer was dried over magnesium sulfate and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via column chromatography (10:1, chloroform: ethyl acetate). FTIR (KBr) 3450, 3058, 1909, 1666, 1587, 1491, 1432, 1393, 1194, 1113, 1006, 828, 710, 621, 478. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (m, 5 H), 7.55 (m, 1 H), 7.49 (m, 2 H), 7.21 (m, 4 H).

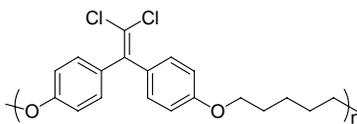


Polyphosphoroether (8). To a 250 mL three neck round bottom flask equipped with a mechanical stirrer, claisen adapter, dean stark trap, and condenser was added bisphenol C (10 mmol, 2.814 g), Bis(4-fluorophenyl)phenylphosphine oxide (10 mmol, 3.143 g), and potassium carbonate (11.5 mmol, 1.589) in the dry box. The reaction flask was removed from the dry box and setup in the hood. N, N-Dimethylacetamide (57 mmol, 54 mL) and toluene (50 mL) was added via syringe. The reaction was heated to reflux for 2 days to azeotrope the water from the reaction. The reaction was then cooled to room temperature and precipitated in methanol. FTIR (KBr) 3401, 3047, 1588, 1496, 1238, 1168, 1112, 865, 830, 694, 541. ¹H NMR (400 MHz, CDCl₃) δ 7.61(m), 7.38 (m), 7.22 (m), 7.0 (m). Mw: 4000; Mn: 3500.

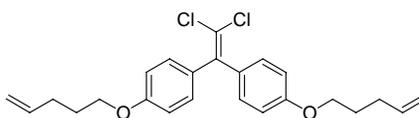


Polyether (A). It is important to note that the order of addition of the reagents is critical for optimum reaction conditions. To a 500 mL three neck round bottom flask equipped with a mechanical stirrer and a reflux condenser was added bisphenol C (10 mmol, 2.813 g) and sodium hydroxide solution (6 M, 33 mL), tertiarybutylammonium hydrogen sulfate (TBAH) (2 mmol, 0.679 g), *o*-dichlorobenzene (33 mL), and finally 1,4-dichloro-2-butene (10 mmol, 1.057 mL). The reaction was heated to reflux for 2 days. The reaction was then cooled and separated into

two layers and diluted with toluene. The organic layer was washed with slightly acidic aqueous solution (HCL 0.1 N) and with water (2 ×). The organic layer was then precipitated in MeOH. FTIR (KBr) 3427, 3036, 2862, 1603, 1506, 1296, 1237, 1171, 1084, 1010, 972, 828, 611. ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.5 Hz, 4 H), 6.85 (d, *J* = 8.5 Hz, 4 H), 6.06 (s, 2 H), 4.55 (s, 4 H). Mw: 27,000; Mn: 5800. T_g: 80 °C.

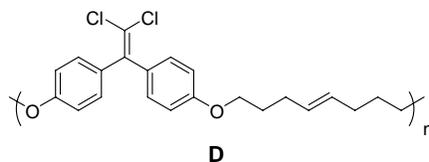
**B**

Polyether (B). It is important to note that order of addition of the reagents is critical for optimum reaction conditions. To a 500 mL three neck round bottom flask equipped with a mechanical stirrer and a reflux condenser was added bisphenol C (10 mmol, 2.813 g) and sodium hydroxide solution (6 M, 33 mL), tertiarybutylammonium hydrogen sulfate (TBAH) (2 mmol, 0.679 g), *o*-dichlorobenzene (33 mL), and finally 1,5-dibromopentane (10 mmol, 1.057 mL). The reaction was heated to reflux for 2 days. The reaction was then cooled and separated into two layers and diluted with toluene. The organic layer was washed with slightly acidic aqueous solution (HCL 0.1 N) and with water (2 ×). The organic layer was then precipitated in MeOH. FTIR (KBr) 3427, 2939, 1605, 1508, 1244, 1172, 1025, 831, 611, 461. ¹H NMR (400 MHz, CDCl₃) δ 7.1 (d, *J* = 8.8 Hz, 4 H), 6.8 (d, *J* = 8.7, 4 H), 3.9 (t, *J* = 6.4), 1.8 (m, 4 H), 1.6 (m, 2 H). Mw: 27,000; Mn: 6800. T_g: 69 °C.

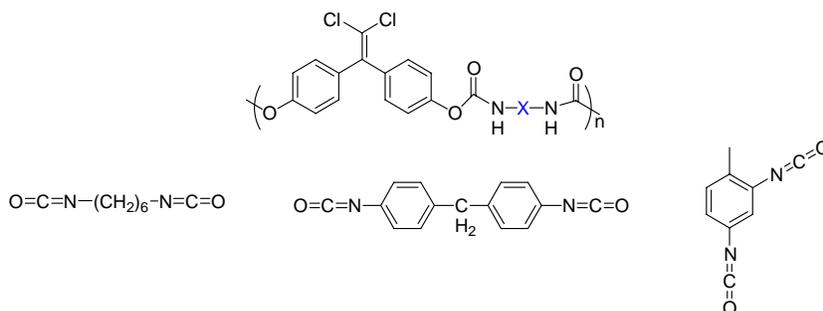
**9**

1,1-dichloro-2,2-bis(*p*-oxy-4-pentenophenyl)ethylene (9). To a 500 mL round bottom flask equipped with a stir bar and reflux condenser was added bisphenol C (40 mmol, 11.255 g), potassium carbonate (200 mmol, 27.642 g). The reaction was sealed with a septa under nitrogen. The reaction mixture was then evacuated and backfilled with nitrogen (3 ×). Acetone (250 mL) and 5-bromo-1-pentene (100 mmol, 11.8 mL) was added via syringe. The reaction was heated to reflux for 24 hours. The reaction was then diluted with ethyl acetate and the organic layer was washed with water (3×). The organic layer was then dried over magnesium sulfate and filtered through filter paper. The solvent was then removed via rotary evaporation and dried *in vacuo* overnight. The product was purified in MeOH several times.). FTIR (KBr) 2938, 2868, 1603, 1509, 1464, 1397, 1243, 1169, 1117, 1022, 910, 850, 773, 627, 528. ¹H NMR (400 MHz, CDCl₃) δ 7.2 (dt, *J* = 8.9, 2.5 Hz, 4 H), 6.8 (dt, *J* = 8.9, 2.5, 4 H), 5.85 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 2 H), 5.06 (dtd, 17.1, 1.7, 1.7 Hz, 2 H), 4.9 (dtd, *J* = 10.2, 1.6, 1.6 Hz, 2 H), 3.9 (t, *J* = 6.4 Hz, 4 H), 2.2 (q, *J* = 7.3 Hz, 4 H), 1.8 (quin, *J* = 6.9 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ

158.6, 139.8, 137.8, 131.9, 130.8, 117.5, 115.2, 114.0, 67.1, 30.1, 28.4. HRMS Calc'd for $C_{24}H_{26}Cl_2O_2$: 416.130986. Found: 416.130986. 0.42 ppm error. Mp 62 °C

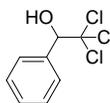


Polyether (D). To a 100 mL shlenk flask equipped with a stir bar and reflux condenser, was added 2 (20 mmol, 8.326 g) and Grubb's catalyst (2nd Generation; 0.2 mmol, 170 mg) in the dry box. The reaction hardware was sealed with a septa and removed from the dry box and setup in the hood then evacuated and backfilled with nitrogen (3 ×). Toluene (20 mL) was added via syringe and the reaction was heated to 55 °C for 5 days under a positive pressure of argon to remove ethylene. Opening the flask to air and diluting with toluene quenched the reaction. The polymer mixture was then precipitated in MeOH. FTIR (KBr) 3429, 3034, 2934, 2538, 2358, 1888, 1604, 1507, 1466, 1389, 1249, 1172, 969, 827, 725, 610, 525. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (m), 6.82 (m), 5.84 (m), 5.50 (m), 5.03 (m), 3.95 (m), 2.50 (m), 2.22 (m), 1.83 (m). Mw: 19000; Mn: 8500. T_g: 42 °C.



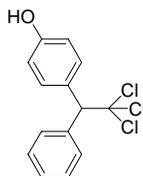
X = **HDI** (hexamethylenediisocyanate), **MDI** (methylenediisocyanate), **TDI** (toluenediisocyanate)

General Procedure for BPC Polyurethanes. To a 250 mL round bottom flask equipped with a stir bar was added bisphenol C (10 mmol, 2.813 g). The flask was then sealed with a septa then, evacuated and backfilled with nitrogen (3 ×). Dimethylformamide (50 mL) and the diisocyanate HDI, MDI, or TDI; 10 mmol, 1.65 mL) were. The reaction mixture was heated to 80-155 °C for two days. The reaction was then precipitated in methanol. X = HDI, FTIR (KBr) 3415, 2324, 1741, 1660, 1504, 1386, 1199, 858. X = MDI, FTIR (KBr) 3413, 1741, 1601, 1497, 1406, 1309, 1191, 1003, 851, 808, 751, 505. X = TDI, FTIR (KBr) 3297, 2929, 2359, 1741, 1622, 1602, 1539, 1501, 1414, 1198, 1100, 1005, 856. ¹H NMR (400 MHz, CDCl₃) δ Not soluble. X = HDI, Mw: 39,000; Mn: 12,200. X = MDI, Mw: 27,800; Mn: 11,150. X = TDI, Mw: 6,400; Mn: 2,175.



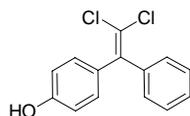
10

2,2,2-Trichloro-1-phenylethanol (10). To a 250 mL three necked round bottom flask equipped with a stir bar, addition funnel, and purged with nitrogen was added benzaldehyde and chloroform. Potassium hydroxide (1.2 equivalents) (KOH) dissolved in diethylene glycol monomethyl ether (methyl digol) was added dropwise via the addition funnel. The reaction mixture was cooled to 0 °C while the KOH and methyl digol was added slowly over 6 h. The reaction was then allowed to warm to room temperature with stirring for 12 h. The reaction was then poured into cold water and diluted with methylene chloride. The two layers were separated and the organic layer was washed with HCl (0.1 N), and H₂O (2 x). The organic layer was dried over magnesium and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via vacuum distillation 85 – 110 °C (1 atm). ¹H NMR (400 MHz, CDCl₃) δ 7.6 (m, 2H), 7.4 (m, 3H), 5.2 (s, 1H), 3.2 (s, 1H).



11

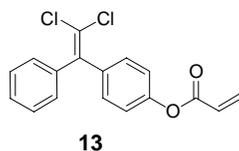
2-(p-hydroxyphenyl)-2'-(phenyl)-1,1,1-Trichloroethane (11). To a 100 mL three necked round bottom flask, equipped with a stir bar, mechanical stirrer and a gas inlet tube was added **10** and phenol (0.98 equivalents), the flask was sealed with a septa and boron trifluoride (BF₃) was bubbled into the solution for 20 m with constant stirring. The thick solution was stirred vigorously and BF₃ was bubbled into the reaction mixture every 12 h for 3 to 5 days. The reaction was then poured into cold water and diluted with ethyl acetate. The two layers were separated and the organic layer was washed with K₂CO₃ (1 M, 2 x) and H₂O (2 x). The organic layer was dried over magnesium and filtered through filter paper. Solvent was removed via rotary evaporation. The final product was isolated via column chromatography (9:1; Hexane/Ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.6 (dt, *J* = 6.9, 1.5 Hz, 2H), 7.4 (dt, *J* = 8.7, 2.5 Hz, 2H), 7.3 (m, 3H), 6.8 (dt *J* = 8.7, 2.6, 2H), 5.0 (s, 1H), 4.7 (s, 1H).



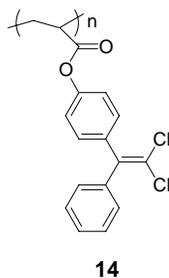
12

2-(p-hydroxyphenyl)-2'-(phenyl)-1,1-Dichloroethane (12). To a 250 mL round bottom flask, equipped with a stir bar and reflux condenser and purged with nitrogen, was added 2-(p-hydroxyphenyl)-2'-(phenyl)-1,1,1-Trichloroethane, KOH (7 equivalents), and MeOH (150 mL). The flask was then sealed under nitrogen with a septum and heated to reflux for 24 h. The

reaction mixture was then diluted with ethyl acetate. The organic layer was washed with H₂O (3×) and the aqueous layer was then extracted with ethyl acetate (3×). The organic layers were combined and dried over magnesium sulfate and filtered through filter paper. Solvent was then removed via rotary evaporation and the resulting solid was dried *in vacuo* for 24 h. FTIR (KBr) 3153, 2357, 1600, 1504, 1439, 1243, 1211, 1171, 970, 855, 740, 698, 629, 570. ¹H NMR (400 MHz, CDCl₃) δ 7.3 (m, 5H), 7.1 (dt, *J* = 8.8, 2.5 Hz, 2H), 6.8 (dt, *J* = 8.8, 2.5 Hz, 2H), 4.8 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ. HRMS Calc'd for C₁₄H₁₀Cl₂O₁:



Acrylic acid [2-(*p*-hydroxyphenyl)-2'-(phenyl)-1,1-Dichloroethane] ester (13**).** To a 100 mL round bottom flask equipped with a stir bar and purged with nitrogen was added the acrylate monomer **13**. The reaction flask was evacuated and backfilled with nitrogen (3 ×). Methylene chloride and triethylamine (1.5 equivalents) were added to the flask via syringe and cooled on an ice bath. Acryloyl chloride (1.1 equivalents) was slowly added drop-wise via syringe. The ice bath was removed and the resulting solution was allowed to warm to room temperature and stirred for 12 h. The reaction was then quenched by opening the flask to air, and the reaction mixture was rotovaped to dryness. The final product was isolated via column chromatography (9:1; Hexane/Ethyl acetate). FTIR (KBr) ¹H NMR (400 MHz, CDCl₃) δ 7.3(m, 7H), 7.1 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.6 (dd, *J* = 17.4, 1.2 Hz, 1H), 6.3 (q, *J* = 9.2 Hz, 1 H), 6.0 (dd, *J* = 10.4, 1.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ. HRMS Calc'd for C₁₇H₁₂Cl₂O₂:



Polyacrylate (14**).** To a 100 mL round bottom flask equipped with a stir bar was added the acrylate monomer and 2,2'-azobisisobutyronitrile (AIBN: 1000/1; monomer/initiator) and sealed with a septa under nitrogen. The reaction flask was evacuated and backfilled with nitrogen (3 ×). The reaction mixture was then placed in an oil bath at 110 °C and stirred for 2 d. The reaction was then cooled to room temperature, dissolved in chloroform and precipitated in methanol. FTIR (KBr) ¹H NMR (400 MHz, CDCl₃) δ 7.2 (m, 4H), 6.9 (m, 5H), 2.8 (m, 1H), 2.3 (m, 1H), 1.9 (m, 1H). Mw: 607,300; Mn: 321,200. T_g: 70 °C

5. Flame Retardant Polymers

Flame retardant additives have been used for many years to provide flame resistant properties to bulk plastics. However, because they are simply added to the polymers and not

covalently bound, there is a chance that these additives may leach out of the material and cause environmental damage, or worse, lessen the flame resistant properties of the polymer. Work has been done here to create inherently flame retardant polymers that need no additives and do not lose their ability to inhibit combustion through leaching.

In order to fully describe the process of creating a flame retardant polymer, first it is necessary to understand how polymer combustion occurs and how various flame retardants work. Polymer combustion occurs when the polymer has suffered enough thermal degradation to volatilize flammable decomposition species, such as monomer and polymer fragments, which then combine with oxygen for combustion upon the application of an ignition source. Once combustion begins, the oxygen is consumed at the flame front, and heat from the flame radiates back down to the polymer, assisting in additional polymer thermal degradation, melting, and fuel pyrolysis. The process continues until the flame is extinguished or the fuel is completely consumed (Figure 1).¹

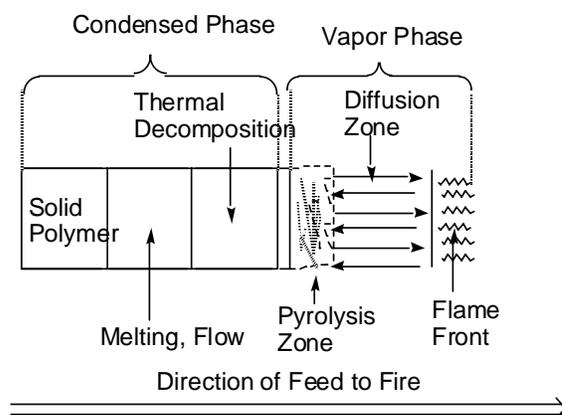


Figure 1. Pyrolysis of combustible material. Condensed and vapor phase shown to illustrate methods of combustion.

To provide flame retardancy to the polymer, there are three main mechanisms which all flame retardants use, although some flame retardants use more than one mechanism to be effective. The first mechanism is by altering the gas phase or combustion chemistry. Additives that work by this mechanism are referred to as vapor phase flame retardants (see Figure 1) during combustion. Halogenated and some phosphorus flame retardants work by this route by reducing heat from combustion through the scavenging of reactive free radicals in either a catalytic or stoichiometric manner.

The second mechanism is by cooling the system through endothermic decomposition. These materials are usually metal hydroxides or carbonates that release non-flammable gases, such as water or CO_2 , which cool the polymer and dilute the total amount of fuel going to the flame front.

The last mechanism by which flame retardancy is achieved is through cross-linking, or char formation in the condensed phase. There are a variety of flame retardants that rely on this mechanism through numerous chemical pathways. It works by preventing fuel release through cross-linking of the polymer matrix or by inducing the formation of high thermal stability chemical bonds. The inhibition of fuel release prevents combustion, which in turn slows down the rate of flame growth and polymer decomposition. Additionally, as char forms, it may become thermally stable enough to act as an insulator to prevent heat from transmitting to non-

decomposed polymer, thus providing extinguishment of the flame and protection to non-heat exposed polymer (Figure 2).² An additional benefit to char formation is that it will keep the heat release rate of the polymer low during burning. This will lower the fire risk to other items near the burning polymer because low heat release rates have much lower chances of propagating fire to non-flame retardant objects (Figure 3).³

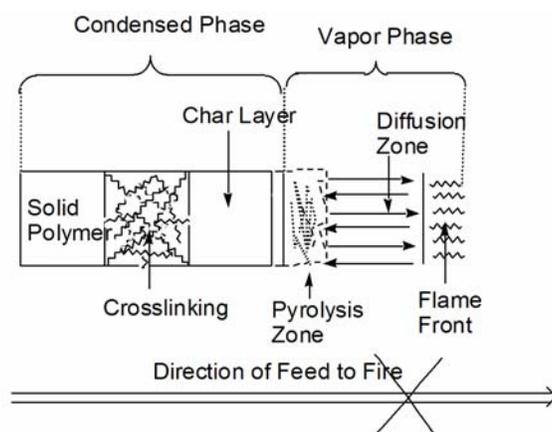


Figure 2. Inhibited pyrolysis through crosslinking in condensed phase.

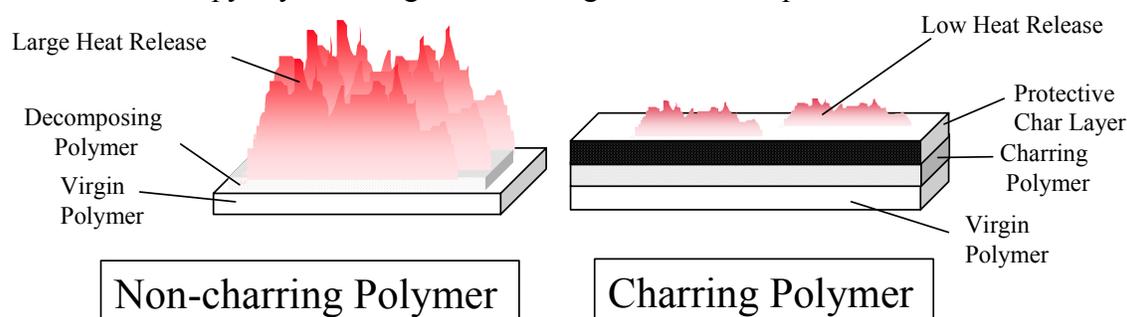


Figure 3. Schematic showing condensed phase char formation and the resulting low heat release of the burning polymer.

Bisphenol C (BPC) (1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene) has been shown by many research groups to serve as a flame retardant and blendable additive as well as a monomer for producing flame retardant polymer materials.⁴⁻⁶ When BPC decomposes thermally, it releases HCl gas and forms a polycyclic aromatic decomposition product that serves as a char layer.⁷ This unique ability to fight the flame front in both the gas phase and condensed phase is helpful in creating materials with excellent fire resistance properties.⁸ Most flame retardant polymers are highly rigid structures containing large amounts of aromatic char-forming functionality. These polymers tend to be hard to process and have high melting temperatures that result in elevated cost and rigorous processing requirements. The incorporation of flexible linkers for making polymers easier to process, an approach commonly used in making vinyl addition polymers, has not been considered a viable approach to making flame retardant polymers since the flexible linkers tend not to be flame resistant. Polymers made using BPC-based chain growth systems, contain both the flexibility of a vinyl backbone and the fire resistance qualities inherent in BPC. By creating these chain-growth polymers, it is possible to overcome the processing difficulties of other BPC polymers while still retaining the ability to create a V-0 compound as tested by UL-94 standards.

2. Synthesis and Testing

The step-wise synthesis of BPC compounds allows the ability to create a molecule that is bi-functional and provides an opportunity for selective coupling of reactive polymerizable units. These units, whether acryloyl or styrenyl, allow BPC to be incorporated into a polymer chain through vinyl polymerization. The target monomer compounds were synthesized in order to create a polymer that has the BPC moiety pendant to the main vinyl backbone which facilitates high molecular weights and easy processing of the polymer. The target polymers can be seen in Figure 4.

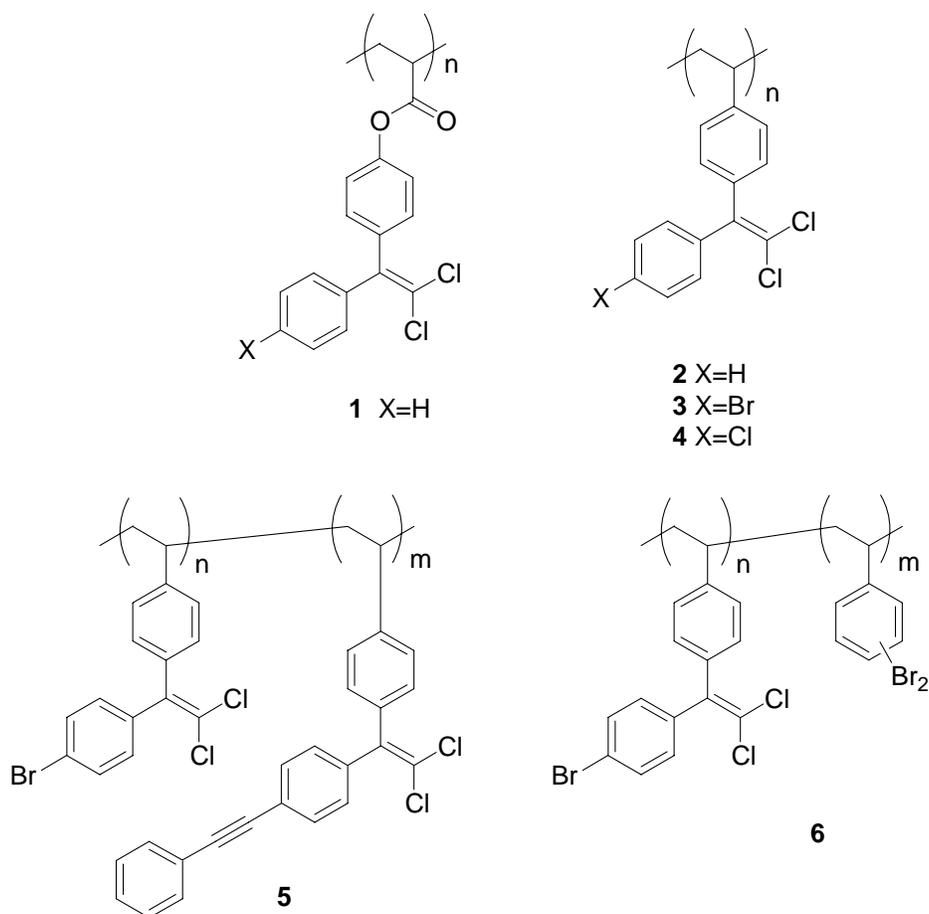
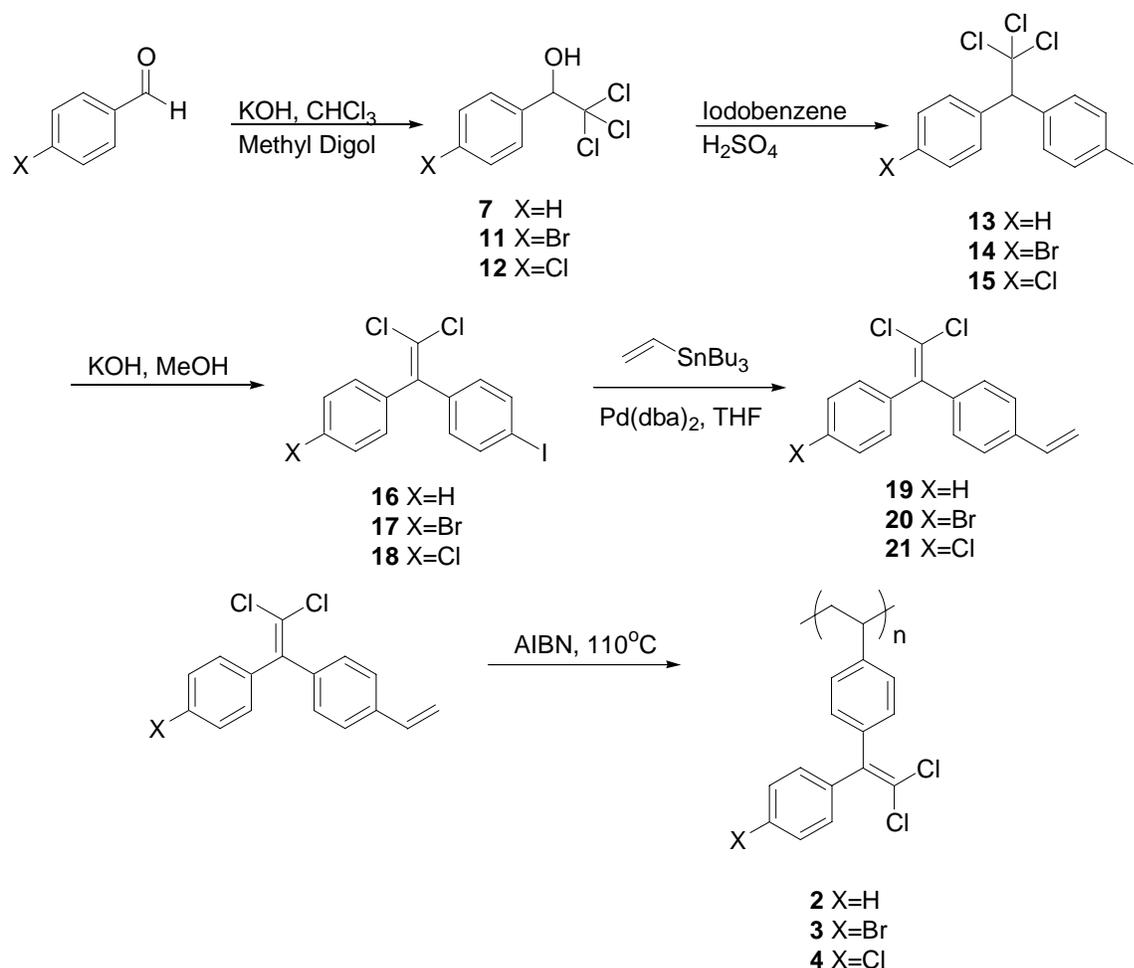


Figure 4. Polymer targets for inherently flame retardant compounds

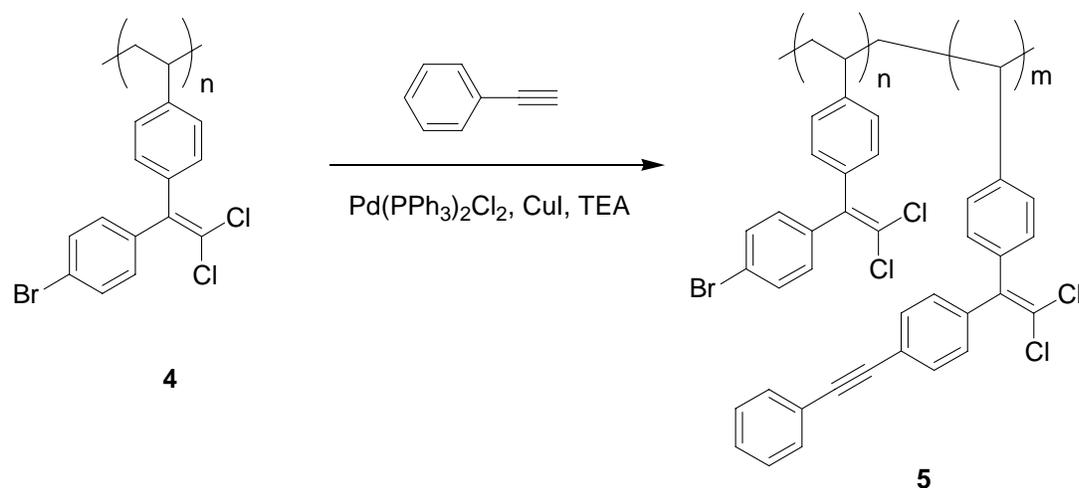
The synthesis of **1** is shown in Scheme 1. Starting with commercially available benzaldehyde, chloroform is added in the presence of base to form the trichlorocarbonyl **7**. Then electrophilic aromatic substitution is performed with phenol to form the DDT compound **8** which can be dehydrohalogenated with base to form the nonsymmetric DDE compound **9**.⁹ After coupling with acryloyl chloride, a monomeric DDE compound **10** is available for vinyl polymerization. Compound **10** is then heated neat in an oil bath to 110 °C with AIBN as a radical initiator for polymerization to form polymer **1** (M_w 300,000; M_n 110,000; T_g 70 °C).



Scheme 2. Synthesis of nonsymmetrical styrene BPC polymers

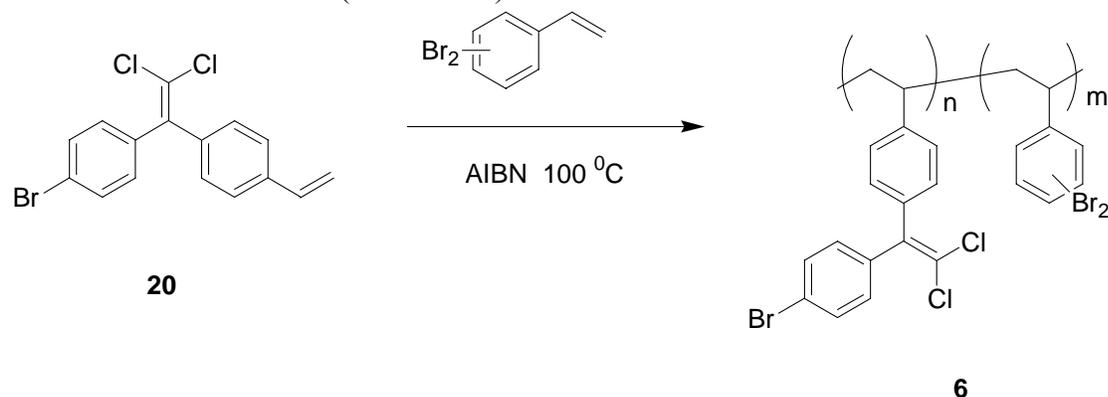
The synthesis of styrene based flame retardant polymers come from an obvious need to achieve a level of flame resistance in a commodity, high volume plastic. By synthesizing a polymer based on the styrene unit, it more closely resembles that of the base polymer polystyrene. Processing and molding of the polystyrene BPC are very similar to that of styrene yet afford the unique property of flame resistance. Each of the three polymers, **2** (M_w 848,000; M_n 398,000; T_g 110 °C), **3** (M_w 862,000; M_n 560,000; T_g 110 °C), and **4** (M_w 338,000; M_n 133,000; T_g 110 °C) shows a UL-94 rating of V-0. Due to the lack of synthesized monomer, enough polymer was not produced to make a full testing sample of nearly 5 g. However, each polymer showed great enhancement in char formation as well as its ability to not ignite or drip.

Copolymer **5** (M_w 1,180,000; M_n 574,000; T_g 110 °C) was synthesized by functionalizing polymer **4**. Taking the bulk polymer and treating it with phenylacetylene in THF with a palladium catalyst produced a functionalized polymer that included brominated BPC pendants as well as diphenyl acetylene moieties off the main chain.¹³ By adding the phenylacetylene unit, it was possible to increase the level of char that remained when the polymer burned. By increasing the level of char, it is possible to insulate the base polymer from the flame front and thus provide greater flame resistance. Scheme 3 shows the method whereby **5** was synthesized.



Scheme 3. Synthesis of polymer **5**.

The synthesis of polymer **6** (M_w 325,000; M_n 150,000; T_g 110 °C) shown in Scheme 4 was done using a BPC monomer **20** copolymerized with commercially available dibromostyrene (DBS) from Great Lakes Chemicals in a 10:1 ratio (DBS:BPC). The use of BPC monomer as a copolymer in an otherwise commercial plastic showed an increase from 2% char created by polyDBS to over 6% char when adding in a 10% equivalent of BPC monomer **20**. By adding the BPC compound to the polymer backbone there would be no risk of the flame retardant agent leaching out of the base polymer and causing health or fire risks. Each of the copolymers **5** and **6** showed enhancement of the base polymer however the neat polymers **1-4** showed the greatest effect of flame resistance (see Table 1).



Scheme 4. Synthesis of polymer **6**.

Table 1 contains the tabulated data from each polymer as it was tested in the HVUL flame hood. The flammability is measured using the standard UL-94 test for plastic flammability and all polymers achieved this rating after being subjected to a 10 second flame ignition. Each polymer gave a rating of V-0 which is the highest standard for flame resistance assigned by this test.

Polymer	First Ignition ^a (s)	Observed Dripping ^b	Second Ignition ^a	Observed Dripping ^b	UL-94 Rating
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Polyacrylate 1	0, 0	No, No	1, 1	No, Yes ^d	V-0
Polystyrene 2	0, 0 ^c	No, No ^c	0, 0 ^c	No, No ^c	V-0 ^c
Polystyrene 3	0, 0 ^c	No, No ^c	0, 0 ^c	No, No ^c	V-0 ^c
Polystyrene 4	0, 0 ^c	No, No ^c	0, 0 ^c	No, No ^c	V-0 ^c
Copolymer 5	0, 0 ^c	No, No ^c	1, 0 ^c	No, No ^c	V-0 ^c
Copolymer 6	1, 1 ^c	No, No ^c	1, 2 ^c	Yes, Yes ^c	V-0 ^c

Table 1 Data from HVUL-94 testing. (a) Time to self-extinguish after ignition. The two numbers are for two separate tests on two separate samples. (b) Indicates that molten polymer did (Yes) or did not (No) drip onto a cotton patch underneath the ignited bar during UL-94 test. (c) Preliminary tests were performed on smaller samples than dictated by UL-94 standards. (d) The dripping did not ignite the cotton.

Along with the UL-94 data, our collaborators at the FAA provided thermal data on polymers **1**, **3**, **4** and **6**. Table 2 shows data for heat release capacity (J/gK), total heat release (kJ/g) and char percent for polymers **1**, **3**, **4** and **6** as well as for commercially available polyDBS for a direct comparison to polymer **6**.

Polymer	HR Capacity (J/gK)	Total HR (kJ/g)	Char (%)
1	185	12	17
3	263	8.4	26
4	320	15.6	20
6	308	9.3	6
Polydibromostyrene	184	9.2	2

Table 2. Heat release (HR) data for polymers **1**, **3**, **4**, **6** and PolyDBS received from the FAA testing laboratories.

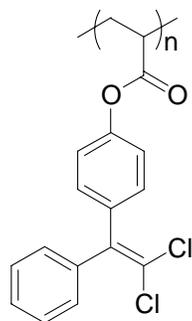
3. Summary

We have shown that inherently flame retardant polymers can be synthesized using asymmetrical BPC analogues. Utilizing the technology and chemistry known about BPC as a flame retardant compound, we have found a way to incorporate the BPC analogue as a pendant group on a vinyl backbone chain polymer. This affords the higher molecular weight polymers not typically seen with condensation polymerizations using BPC as well as the easily processed acrylate and styrene based polymers. By incorporating the BPC unit as a pendant group to these types of vinyl polymers, we have maintained the V-0 rating used to determine flame resistance in polymers while improving the range of use for these BPC-based polymers.

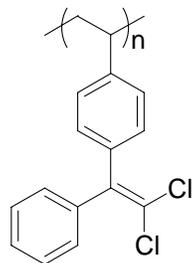
4. Experimental

General Procedures:

All commercially available reagents were used as received. CH_2Cl_2 and TEA were distilled over CaH_2 . Reagent grade THF, Et_2O , MeOH, and EtOAc were used without further distillation. All reactions were performed under an atmosphere of nitrogen unless otherwise stated. Silica TLC plates were 250 μm thick, 40 F254 grade from EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. ^1H NMR spectra were observed at 400 MHz and ^{13}C NMR spectra were observed at 100 MHz on a Bruker Avance 400 spectrometer. ^1H chemical shifts are reported in ppm downfield from tetramethylsilane. IR Spectra were obtained on a Nicolet Avatar 360 FTIR. All polymer molecular weights (number average and weight average) were determined using Polymer Laboratories GPC 220. Samples were prepared in THF and eluted at 1.0 mL/min across size exclusion columns and compared to standardized polystyrene. Beilstein autonom was used in the naming of the compounds listed.

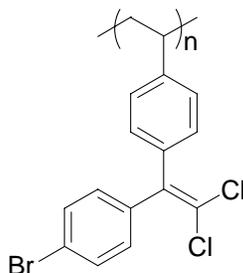


Poly(1-phenyl,1-(4-acrylic-acid-phenyl-ester)-2,2-dichloro-ethene) (1).¹⁴ To a 100 mL round bottom flask equipped with a stir bar was added **10** (2.2 g, 6.9 mmol) with AIBN (0.5 mg, 0.0034 mmol). The flask was purged with nitrogen and put into an oil bath at 110 °C and allowed to stir for 12 h. After 12 h the reaction mixture was cooled to room temperature and dissolved in chloroform. The polymer was precipitated by adding the chloroform solution to 200 mL of methanol and the solid was removed by filtration. 2.1 g (95%) of polymer was recovered. ^1H NMR (400 MHz, CDCl_3) δ 7.2 (m, 4H), 6.9 (m, 5H), 2.8 (m, 1H), 2.3 (m, 1H), 1.9 (m, 1H). M_w 300,000; M_n 110,000; T_g 70 °C.

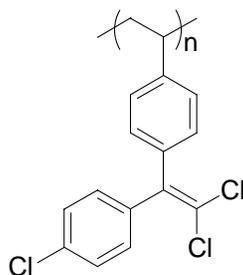


Poly(1,1-diphenyl-2,2-dichloro-ethene) (2). To a 100 mL round bottom flask equipped with a stir bar was added **19** (2.8 g, 10 mmol) with AIBN (0.001 g, 0.01 mmol). The flask was purged with nitrogen and put into an oil bath at 110 °C and allowed to stir for 12 h. After 12 h the reaction mixture was cooled to room temperature and dissolved in chloroform. The polymer was precipitated by adding the chloroform solution to 200 mL of methanol and the solid was removed by filtration. 2.5 g (89%) of polymer was recovered. IR (KBR) 3507.2, 3417.9,

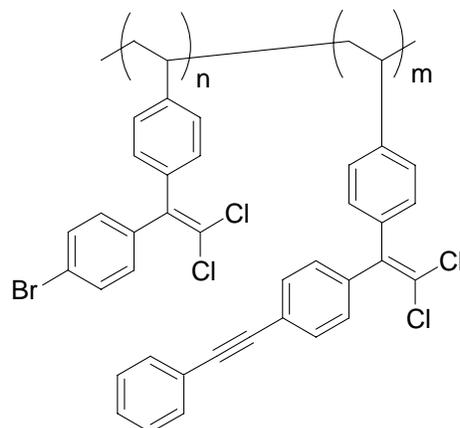
3148.7, 3079.9, 3055.7, 3023.1, 2969.7, 2942.13, 2850.0, 2356.9, 2335.7, 1950.0, 1907.0, 1881.4, 1805.5, 1703.5, 1691.1, 1681.4, 1649.4, 1628.4, 1597.9, 1584.7, 1556.2, 1506.0, 1492.1, 1462.6, 1442.4, 1413.1, 1401.9, 1388.0, 1353.0, 1313.5, 1292.1, 1270.0, 1206.6, 1185.6, 1167.9, 1157.6, 1113.0, 1073.4, 1061.5, 1008.3. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35-7.15 (m, 5H), 7.05-6.75 (m, 2H), 6.60-6.10 (m, 2H), 2.0-1.60 (m, 1H), 1.50-1.15 (m, 2). M_w 848,000; M_n 398,000; PD 2.1; T_g 110 $^\circ\text{C}$.



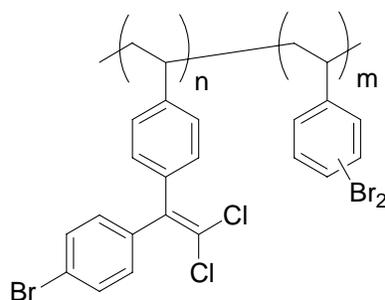
Poly(1-(4-bromophenyl)-1-phenyl-2,2-dichloro-ethene) (3). To a 100 mL round bottom flask equipped with a stir bar was added **20** (2.4 g, 6.7 mmol) with AIBN (0.001 g, 0.006 mmol). The flask was purged with nitrogen and put into an oil bath at 110 $^\circ\text{C}$ and allowed to stir for 12 h. After 12 h the reaction mixture was cooled to room temperature and dissolved in chloroform. The polymer was precipitated by adding the chloroform solution to 200 mL of methanol and the solid was removed by filtration. 2.1 g (88%) of polymer was recovered. IR (KBR) 3446.5, 3077.5, 3044.5, 3023.3, 3001.5, 2921.9, 2846.5, 1900.6, 1781.7, 1683.5, 1654.3, 1647.3, 1605.4, 1584.7, 1557.8, 1506.5, 1485.6, 1448.0, 1413.1, 1391.9, 1352.0, 1313.0, 1262.1, 1178.9, 1165.0, 1102.1, 1070.8, 1012.3. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48-7.32 (m, 2H), 7.13-7.00 (m, 2H), 7.00-6.75 (m, 2H), 6.55-6.20 (m, 2H), 1.90-1.60 (m, 1H), 1.55-1.25 (m, 2H). M_w 862,000; M_n 560,000; PD 1.5; T_g 110 $^\circ\text{C}$.



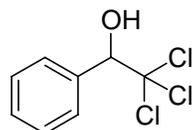
Poly(1-(4-chlorophenyl)-1-phenyl-2,2-dichloro-ethene) (4). To a 100 mL round bottom flask equipped with a stir bar was added **21** (3.1 g, 10 mmol) with AIBN (0.001 g, 0.01 mmol). The flask was purged with nitrogen and put into an oil bath at 110 $^\circ\text{C}$ and allowed to stir for 12 h. After 12 h the reaction mixture was cooled to room temperature and dissolved in chloroform. The polymer was precipitated by adding the chloroform solution to 200 mL of methanol and the solid was removed by filtration. 2.7 g (87%) of polymer was recovered. IR (KBR) 3448.5, 3078.1, 3023.5, 3001.1, 2919.5, 2848.5, 2603.5, 2570.6, 2359.1, 2281.5, 1899.2, 1780.6, 1605.2, 1589.2, 1559.6, 1504.8, 1487.2, 1447.2, 1412.1, 1395.9, 1350.5, 1312.1, 1262.9, 1165.6, 1089.9, 1015.7. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.3-7.2 (m, 2H), 7.2-7.0 (m, 2H), 7.0-6.7 (m, 2H), 6.6-6.1 (m, 2H), 1.7-1.5 (m, 1H), 1.5-1.2 (m, 2H). M_w 338,000; M_n 133,000; PD 2.5; T_g 110 $^\circ\text{C}$.



Polymer (5). To a 100 mL round bottom flask equipped with a stir bar was added **3** (0.3 g, 0.8 mmol) and the solid was dissolved in THF (30 mL) and phenylacetylene (0.09 mL, 0.84 mmol), Pd(Cl)₂(PPh₃)₂ (0.03 g, 0.042 mmol), triethylamine (0.5 mL, 3.4 mmol) and copper(I) iodide (0.003 g, 0.02 mmol) were added and the reaction mixture was heated to 80 °C for 5 h to couple the phenylacetylene groups onto the polymer. The polymer was precipitated by adding the THF solution to 200 mL of methanol and the solid was removed by filtration. 0.3 g of polymer was recovered. IR (KBR) 3446.5, 3358.8, 3118.1, 3077.1, 3047.1, 3023.0, 2920.5, 2848.9, 2361.9, 1899.7, 1781.4, 1701.0, 1654.5, 1647.9, 1584.5, 1557.5, 1506.7, 1485.4, 1442.5, 1412.8, 1391.7, 1352.3, 1312.5, 1261.5, 1230.6, 1178.1, 1164.7, 1101.8, 1070.6, 1012.1. ¹H NMR (400 MHz, CDCl₃) δ 7.6-7.5 (m, 0.3H), 7.5-7.2 (m, 2H), 7.2-7.0 (m, 2H), 7.0-6.7 (m, 2H), 6.6-6.2 (m, 2H), 1.7-1.5 (m, 2H), 1.5-1.2 (m, 1H). *M_w* 1,180,000; *M_n* 574,000; PD 2.0; *T_g* 110 °C.

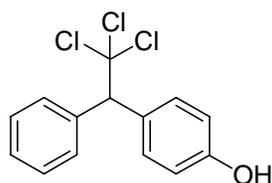


Polymer (6). To a 100 mL round bottom flask equipped with a stir bar was added **20** (0.20 g, 0.56 mmol), dibromostyrene (1.5 g, 5.6 mmol) and AIBN (0.001g, 0.01 mmol). The flask was purged with nitrogen and put into an oil bath at 110 °C and allowed to stir for 12 h. After 12 h the reaction mixture was cooled to room temperature and dissolved in chloroform. The polymer was precipitated by adding the chloroform solution to 200 mL of methanol and the solid was removed by filtration. 1.9 g (88%) of polymer was recovered. *M_w* 325,000; *M_n* 150,000; PD 2.0; *T_g* 115 °C.

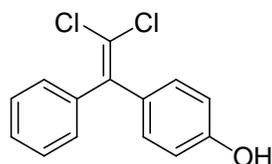


1-Phenyl-2,2,2-trichloro-ethanol (7).¹⁴ To a three-necked 500 mL round bottom flask equipped with a stir bar, benzaldehyde (38.2 g, 360 mmol) along with CHCl₃ (200 mL) was

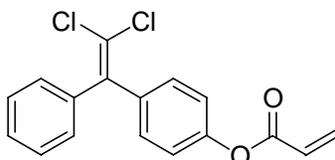
added and the mixture was placed in an ice bath at 0 °C. To a separate Erlenmeyer flask was added KOH (24.1 g, 430 mmol) and methyl digol (150 mL) and the mixture was allowed to stir until all the KOH was dissolved. Once the KOH was dissolved in methyl digol, the solution was transferred into a 250 mL addition funnel and attached to the chilled three-necked flask. This KOH solution was then added dropwise to the benzaldehyde solution over 4 h while stirring. After the KOH solution has been added, the reaction was allowed to stir at 0 °C for 3 h, and then allowed to warm to room temperature. Once at room temperature, the reaction mixture was poured into cold H₂O (300 mL) and subsequently washed with HCl (300 mL, 1 M), H₂O (300 mL), and NaHSO₄ (300 mL, 1 N). The organic layer was then dried with MgSO₄ and the solvent removed by rotary evaporation to give 43 g (53%). ¹H NMR (400 MHz, CDCl₃) δ 7.6 (m, 2H), 7.4 (m, 3H), 5.2 (s, 1H), 3.2 (s, 1H).



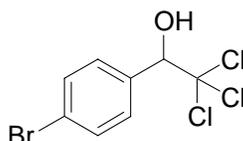
1-Phenyl-1-(4-hydroxyphenyl)-2,2,2-trichloro-ethane (8).¹⁴ To a 100 mL three-necked round bottom flask was added **7** (22.3 g, 98.8 mmol) and phenol (9.00 g, 95.8 mmol) and the flask was equipped with a mechanical stirrer. The flask was evacuated and backfilled with nitrogen. BF₃ gas was then bubbled into the solution for 20 min, twice a day for 5 d. The reaction was allowed to stir for a total of 1 week before adding H₂O (50 mL) and diluted with EtOAc (50 mL). The two layers were separated and the organic layer was washed with aqueous K₂CO₃ (1 L, 1 M) to remove the excess phenol. The organic layers were combined, dried with MgSO₄ and the solvent was removed by rotary evaporation. The final product was isolated by silica column chromatography (9:1 Hex:EtOAc) to obtain 22.5 g (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.6 (d, *J* = 6.9, 2H), 7.4 (d, *J* = 8.7, 2H), 7.3 (m, 3H), 6.8 (d, *J* = 8.7, 2H), 5.0 (s, 1H).



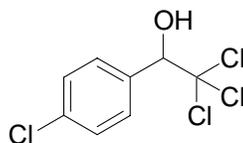
1-(4-Hydroxyphenyl)-1-phenyl-2,2-dichloro-ethene (9).¹⁴ To a 1L round bottom flask equipped with a stir bar and reflux condenser was added **8** (12.1 g, 40 mmol), KOH (16.9 g, 300 mmol), and MeOH (350 mL). The reaction was then heated to reflux using a heating mantle for 24 h. After 24 h the reaction was allowed to cool to room temperature and the insoluble salts were filtered, then the MeOH was removed by rotary evaporation. H₂O (200 mL) was added with HCl (100 mL, 1 M) to neutralize excess KOH. The aqueous layer was extracted with ethyl ether (200 mL, 3x) and the organic layers were then combined, dried with MgSO₄ and the solvent was removed by rotary evaporation. The final product was isolated by silica column chromatography (9:1 Hex:EtOAc) to give 6.4 g (61%). ¹H NMR (400 MHz, CDCl₃) δ 7.3 (m, 5H), 7.1 (d *J* = 8.8, 2H), 6.8 (d, *J* = 8.8, 2H), 4.8 (s, 1H).



Acrylic acid 4-(2,2-dichloro-1-phenyl-vinyl)-phenyl ester (10).¹⁴ To a 250 mL round bottom flask equipped with a stir bar was added **9** (2.1 g, 7.8 mmol) then purged and sealed with nitrogen. Distilled CH_2Cl_2 (40 mL) and distilled triethylamine (2.4 mL, 17.3 mmol) was then added to the flask and the solution became clear. The reaction was then set in an ice bath at $0\text{ }^\circ\text{C}$ and allowed to stir. After 10 min, acryloyl chloride (1.2 mL, 15.7 mmol) was added dropwise by syringe over 10 min and the solution was maintained at $0\text{ }^\circ\text{C}$. After 4 h, the reaction was allowed to warm to room temperature. The final acrylated product was purified using silica column chromatography (9:1 Hex:EtOAc) to give 2.4 g (99%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.3(m, 7H), 7.1 (d, $J = 8.8$, 2H), 6.6 (d, $J = 17.4$, 1H), 6.3 (dd, $J = 17.4$, 10.4 Hz, 1 H), 6.0 (d, $J = 10.4$, 1 H).

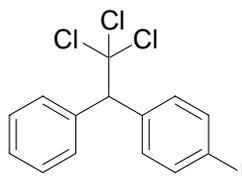


1-(4-Bromophenyl)-2,2,2-trichloroethanol (11).⁹ To a three-necked 250 mL round bottom flask equipped with a stir bar, 4-bromobenzaldehyde (9.25 g, 50 mmol) along with CHCl_3 (70 mL) was added and the mixture was placed in an ice batch at $0\text{ }^\circ\text{C}$. To a separate Erlenmeyer flask was added KOH (3.36 g, 60 mmol) and methyl digol (60 mL) and the mixture was allowed to stir until all the KOH was dissolved. Once the KOH was dissolved in methyl digol, the solution was transferred into a 125 mL addition funnel and attached to the chilled three-necked flask. This KOH solution was then added dropwise over 4 h while stirring. After the KOH solution has been added, the reaction was allowed to stir at $0\text{ }^\circ\text{C}$ for 3 h, and then allowed to warm to room temperature. Once at room temperature, the reaction mixture was poured into cold H_2O (150 mL) and subsequently washed with HCl (150 mL, 1 M), H_2O (150 mL), and NaHSO_4 (150 mL, 1 N). The organic layer was then dried with MgSO_4 and the solvent removed by rotary evaporation to give 9.2 g (60%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54-7.48 (m, 4H), 5.2 (s, 1H), 3.4 (s, 1H).

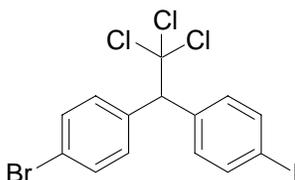


1-(4-Chloro-phenyl)-2,2,2-trichloroethanol (12).⁹ To a three-necked 250 mL round bottom flask equipped with a stir bar, 4-chlorobenzaldehyde (7.0 g, 60 mmol) along with CHCl_3 (70 mL) was added and the mixture was placed in an ice batch at $0\text{ }^\circ\text{C}$. To a separate Erlenmeyer flask was added KOH (3.36 g, 60 mmol) and methyl digol (60 mL) and allowed to stir until all the KOH was dissolved. Once the KOH was dissolved in methyl digol, the solution was transferred into a 125 mL addition funnel and attached to the chilled three-necked flask. This KOH solution was then added dropwise over 4 h while stirring. After the KOH solution has been added, the reaction was allowed to stir at $0\text{ }^\circ\text{C}$ for 3 h, and then allowed to warm to room

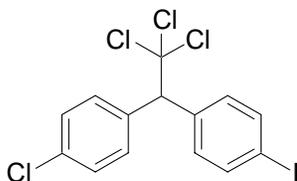
temperature. Once at room temperature, the reaction mixture was poured into cold H₂O (150 mL) and subsequently washed with HCl (150 mL, 1 M), H₂O (150 mL), and NaHSO₄ (150 mL, 1 N). The organic layer was then dried with MgSO₄ and the solvent removed by rotary evaporation to give 7.5 g (58%). ¹H NMR (400MHz, CDCl₃) δ 7.56-7.49 (m, 4H), 5.2 (s, 1H), 3.4 (s, 1H).



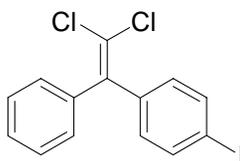
1-Phenyl-1-(4-iodophenyl)-2,2,2-trichloroethane (13). To a 100 mL round bottom flask equipped with a stir bar was added compound **7** (11.19 g, 49.62 mmol), iodobenzene (6.7 mL, 60 mmol), and concentrated H₂SO₄ (25 mL). The reaction was allowed to stir 12 h. After 4 h a visible brown precipitate had formed. After 12 h the reaction mixture was poured into H₂O (200 mL) and ether (200 mL). The ether layer was washed 2 more times with H₂O (200 mL) then dried with MgSO₄ and dried with rotary evaporation to a yellow oil which crystallized under vacuum. Crystals were washed with ethanol and filtered and dried in vacuum oven at 60 °C to yield 10.3 g (50%). IR (KBR) 3444.2, 3062.5, 3027.3, 2913.9, 1958.1, 1914.1, 1891.4, 1652.8, 1582.6, 1484.4, 1452.5, 1401.3, 1342.0, 1295.6, 1262.1, 1242.45, 1174.1, 1123.9, 1110.0, 1079.0, 1065.1, 1033.6, 1007.13 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ 7.67 (d, *J* = 4.6 Hz, 2H), 7.57 (m, 2H), 7.31 (m, 5H), 5.00 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.2, 138.0, 137.8, 132.3, 130.36, 128.8, 128.5, 101.3, 94.2, 70.9. HRMS observed mass 409.8887, calculated mass 409.8893.



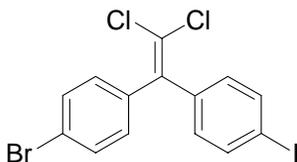
1-(4-Bromophenyl)-1-(4-iodophenyl)-2,2,2-trichloroethane (14). To a 100 mL round bottom flask equipped with a stir bar was added compound **11** (8.93 g, 29.6 mmol), iodobenzene (3.7 mL, 33 mmol), and concentrated H₂SO₄ (30 mL). The reaction mixture was allowed to stir 12 h. After 4 h a visible brown precipitate had formed. After 12 h the reaction mixture was poured into H₂O (200 mL) and ether (200 mL). The ether layer was washed 2 more times with H₂O (200 mL) then dried with MgSO₄ and dried with rotary evaporation to a yellow oil which crystallized under vacuum. The crystals were washed with ethanol and filtered and dried in a vacuum oven at 60 °C to obtain 7.5 g (45%). IR (KBR) 3442.5, 3068.5, 3045.8, 2915.8, 1901.3, 1583.7, 1485.7, 1458.2, 1400.3, 1420.7, 1342.3, 1263.0, 1241.9, 1201.9, 1118.2, 1110.7, 1075.7, 1066.0, 1008.6 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.45 (m, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.97 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.0, 137.7, 137.0, 132.2, 132.0, 131.9, 131.4, 122.9, 94.6, 70.2. HRMS observed mass 487.7991, calculated mass 487.7998.



1-Chlorophenyl-1-(4-iodophenyl)-2,2,2-trichloroethane (15). To a 100 mL round bottom flask equipped with a stir bar was added compound **12** (13.0 g, 50 mmol), iodobenzene (6.7 mL, 60 mmol), and concentrated H₂SO₄ (25 mL). The reaction was allowed to stir 12 h. After 4 h a visible brown precipitate had formed. After 12 h reaction was poured into H₂O (200 mL) and ether (200 mL). The ether layer was washed 2 more times with H₂O (200 mL) then dried with MgSO₄ and dried with rotary evaporation to a yellow oil which crystallized under vacuum. The crystals were washed with ethanol and filtered and dried in a vacuum oven at 60 °C to yield 10.9 g (49%). ¹H NMR (400MHz, CDCl₃) δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.76 Hz, 2H) 7.31 (m, 4H), 4.98 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 137.6, 136.3, 134.5, 132.0, 131.5, 128.8, 100.8, 94.4, 70.0.

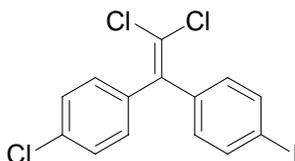


1-(4-Iodophenyl)-1-phenyl-2,2-dichloroethene (16). To a 1 L round bottom flask equipped with a stir bar and reflux condenser was added compound **13** (9.3 g, 23 mmol), KOH (2.7 g, 47 mmol), and THF:MeOH (100 mL, 1:3 vol:vol). The reaction was then heated to reflux using a heating mantle for 24 h. After 24 h the reaction mixture was allowed to cool to room temperature and EtOH (40 mL) was added, then the solution was poured into H₂O (100 mL). A precipitate formed and was filtered and dried in vacuum oven at 60 °C to give 6.6 g (78%). IR (KBR) 3444.1, 3081.0, 3052.6, 3020.9, 1973.4, 1952.2, 1903.6, 1884.2, 1809.8, 1761.0, 1664.4, 1620.4, 1592.9, 1578.17, 1552.7, 1490.7, 1480.7, 1440.6, 1386.1, 1341.4, 1299.8, 1290.5, 1258.1, 1202.6, 1165.4, 1158.7, 1115.8, 1098.2, 1073.1008.4 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ 7.67 (d, *J* = 8.57 Hz, 2H), 7.34-7.24 (m, 5H), 7.03 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.9, 139.3, 137.9, 131.6, 129.7, 128.8, 128.6, 120.4, 94.4. HRMS observed mass 373.9130, calculated mass 373.9126.

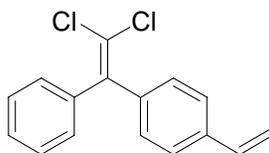


1-(4-Bromophenyl)-1-(4-iodophenyl)-2,2-dichloroethene (17). To a 1 L round bottom flask equipped with a stir bar and reflux condenser was added compound **14** (15.6 g, 32.0 mmol), KOH (3.9 g, 70 mmol), and THF:MeOH (75 mL, 1:3 vol:vol). The reaction was then heated to reflux using a heating mantle for 24 h. After 24 h the reaction mixture was allowed to cool to room temperature and EtOH (40 mL) was added, then the solution was poured into H₂O (100 mL). A precipitate formed and was filtered and dried in a vacuum oven at 60 °C to give 1.2 g (83%). IR (KBR) 3443.8, 3078.8, 3059.2, 2570.2, 2358.98, 2287.6, 1903.4, 1786.6, 1714.3,

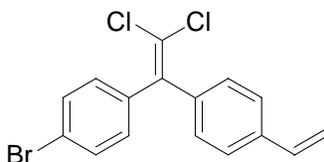
1671.3, 1650.8, 1580.2, 1552.8, 1482.5, 1460.7, 1434.7, 1388.1, 1345.1, 1303.2, 1256.8, 1182.6, 1104.1, 1069.2, 1059.6, 1005.7 cm^{-1} . ^1H NMR (400MHz, CDCl_3) δ 7.68 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 7.01 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 138.2, 138.0, 132.0, 131.5, 131.4, 122.9, 94.7. HRMS observed mass 451.8227, calculated mass 451.8231.



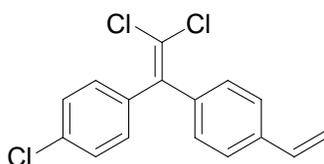
1-(4-Chlorophenyl)-1-(4-iodophenyl)-2,2-dichloroethene (18). To a 1 L round bottom flask equipped with a stir bar and reflux condenser was added compound **15** (9.0 g, 20.1 mmol), KOH (2.5 g, 45 mmol), and THF:MeOH (100 mL, 1:3 vol:vol). The reaction mixture was then heated to reflux using a heating mantle for 24 h. After 24 h the reaction was allowed to cool to room temperature and EtOH (40 mL) was added, then the solution was poured into H_2O (100 mL). A precipitate formed and was filtered and dried in vacuum oven at 60 $^\circ\text{C}$ to give 6.4 g (78%). IR (KBR) 3055.6, 2360.0, 2287.4, 1902.4, 1784.6, 1715.7, 1668.8, 1652.0, 1620.0, 1579.6, 1560.3, 1550.3, 1488.2, 1481.9, 1464.5, 1442.8, 1388.1, 1346.5, 1303.0, 1281.4, 1257.0, 1219.3, 1183.1, 1165.6, 1149.4, 1105.7, 1087.4, 1060.0, 1013.0, 1006.2 cm^{-1} . ^1H NMR (400MHz, CDCl_3) δ 7.67 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.00 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 138.8, 138.0, 137.7, 134.7, 131.5, 131.2, 129.1, 120.9, 94.8. HRMS observed mass 407.8742, calculated mass 407.8736.



1-Phenyl-1-(4-vinylphenyl)-2,2-dichloroethene (19). To a 100 mL round bottom flask equipped with a stir bar was added **15** (0.8 g, 2.2 mmol) with THF (15 mL) to form a solution. To this solution tributyl(vinyl)tin (0.7 mL, 2.2 mmol), triphenylarsine (0.04 g, 0.12 mmol) and $\text{Pd}(\text{dba})_2$ (0.04 g, 0.06 mmol) was added dropwise via solution in THF (15 mL). The solution was allowed to react for 3 h at 0 $^\circ\text{C}$ and then warmed to room temperature. The solution was then poured into a saturated solution of KF (100 mL) and the aqueous phase was extracted with ether. The combined ethereal phase was then subsequently washed with two more portions of KF (100 mL). The organic layer was dried with MgSO_4 and the solvent removed by rotary evaporation. The final product was purified using silica column chromatography (9:1 Hex:EtOAc) to give 0.48 g product (80%). IR (KBR) 3417.9, 30082.2, 3057.6, 3029.3, 3002.8, 1953.8, 1912.1, 1884.5, 1814.5, 1760.5, 1683.0, 1682.0, 1589.2, 1555.9, 1505.5, 1488.7, 1442.2, 1421.4, 1400.3, 1291.9, 1270.3, 1204.8, 1168.9, 1158.6, 1112.8, 1073.7, 1031.2, 1016.8, 1007.6 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.30 (m, 9H), 6.68 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.74 (d, $J = 17.6$, 1H), 5.5 (d, $J = 10.9$, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 139.8, 139.2, 137.9, 137.7, 136.6, 131.6, 129.7, 128.7, 128.4, 126.5, 115.0. HRMS observed mass 274.0313, calculated mass 274.0316.



1-(4-Bromophenyl)-1-(4-vinylphenyl)-2,2-dichloroethene (20). To a 100 mL round bottom flask equipped with a stir bar was added **17** (1.0 g, 2.2 mmol) with 15 mL of THF to form a solution. To this solution tributyl(vinyl)tin (0.7 mL, 2.2 mmol), triphenylarsine (0.04 g, 0.12 mmol) and Pd(dba)₂ (0.04 g, 0.06 mmol) was added via solution dropwise in THF (15 mL). The solution was allowed to react for 3 h at 0 °C and then warmed to room temperature. The solution was then poured into a saturated solution of KF (100 mL) and the aqueous phase was extracted with ether. The combined ethereal layer was then subsequently washed with two more portions of KF (100 mL). The organic layer is then dried with MgSO₄ and the solvent was removed by rotary evaporation. The final product was purified using silica column chromatography (9:1 Hex:EtOAc) to give 0.56 g product (72%). IR (KBR) 3448.4, 3060.1, 3034.8, 2986.5, 2921.8, 1901.5, 1839.2, 1782.4, 1685.2, 1655.2, 1629.0, 1581.0, 1552.9, 1507.5, 1484.5, 1421.8, 1400.5, 1390.3, 1353.0, 1318.2, 1287.6, 1260.0, 1205.9, 1164.9, 1117.0, 1102.9, 1067.3, 1010.6 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.27-7.18 (m, 4H), 6.74 (dd, *J* = 16.8, 10.8 Hz, 1H), 5.79 (d, *J* = 16.8 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 139.5, 138.7, 137.9, 136.5, 131.9, 131.5, 130.0, 126.5, 122.7, 120.3, 115.3. HRMS observed mass 351.9419, calculated mass 351.9421.



1-(4-Chlorophenyl)-1-(4-vinylphenyl)-2,2-dichloroethene (21). To a 100 mL round bottom flask equipped with a stir bar was added **17** (1.0 g, 2.2 mmol) with 15 mL of THF to form a solution. To this solution tributyl(vinyl)tin (0.7 mL, 2.2 mmol), triphenylarsine (0.04 g, 0.12 mmol) and Pd(dba)₂ (0.04 g, 0.06 mmol) was added via solution dropwise in THF (15 mL). The solution was allowed to react for 3 h at 0 °C and then warmed to room temperature. The solution was then poured into a saturated solution of KF (100 mL) and the aqueous phase was extracted with ether. The combined ethereal layer was then subsequently washed with two more portions of KF (100 mL). The organic layer was dried with MgSO₄ and the solvent was removed by rotary evaporation. The final product was purified using silica column chromatography (9:1 Hex:EtOAc) to give 0.54 g product (80%). IR (KBR) 3443.9, 3061.4, 3034.0, 2986.7, 1899.9, 1841.6, 1778.5, 1687.8, 1659.3, 1629.7, 1584.4, 1562.8, 1555.5, 1507.6, 1486.4, 1422.2, 1400.4, 1394.8, 1317.5, 1288.3, 1260.4, 1206.4, 1166.7, 1116.9, 1086.0, 1015.0 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.33-7.24 (m, 4H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (d, *J* = 17.6 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H). NMR (100 MHz, CDCl₃) δ 139.5, 138.8, 138.2, 137.9, 136.5, 134.5, 131.2, 130.0, 129.0, 126.5, 120.4, 115.3. HRMS observed mass 307.9920, calculated mass 307.9926.

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