

NOVEL FLAME RETARDANT POLYMERS & BLENDS

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ABSTRACT

Various halogenated chloral biphenyl monomers additives and polymers have been blended with thermoplastic polymers ABS and HIPS to impart flame retardancy to what are otherwise flammable plastics. Our current focus is to synthesize and test novel flame retardant polymers. Initial testing of some of these polymers has provided useful data that may lead to a new class of flame retardant materials.

INTRODUCTION

The initial approach of our research was the preparation of flame retardant additives. Blending Sb_2O_3 and these halogen-containing monomers with thermoplastic polymers like ABS and HIPS, we have imparted flame retardancy to what are otherwise flammable plastics. While Sb_2O_3 /halogen-compound additive systems are currently employed 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.

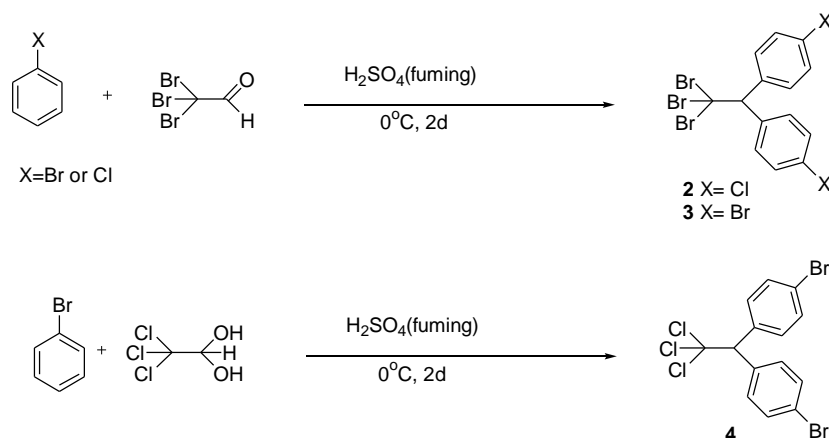
As an adjunct to our additive project we have also synthesized and tested flame retardant polymers and blends. By using functional groups on the polymer (i.e. halogens) or by incorporating certain elements (i.e. boron or phosphorous) into the backbone of the polymer chain, we hope to create a polymer that is flame retardant. Flame propagation is a thermodynamically driven process; it has been our goal to design a polymer in its lowest energy state. Incorporation of functional groups to act as radical traps in the vapor phase and other moieties that will cross-link during the burn process should help increase the polymer's flame retardant capabilities. Copolymerizing these new monomers with flame retardant boron or phosphorous containing monomers might lead to promising new flame retarding polymers.

RESULTS AND DISCUSSION

Additives

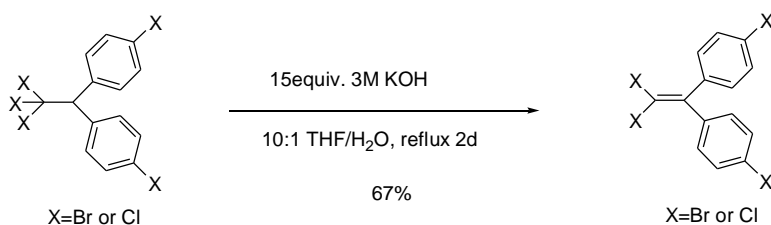
2,2-Bis(4-bromophenyl)-1,1-dichloroethylene (chloral biphenyl ethylene monomer) has successfully given V-0 results as an additive in both ABS and HIPS. The addition of 10 wt % (based on the weight percent of halogen) of the various chloral monomers with 4 wt % antimony oxide and 1 wt % of an anti-drip additive (PTFE) gave a UL-94 V-0 result in both ABS and HIPS. The brominated and chlorinated version of these monomers have been synthesized by a condensation reaction of tribromoacetaldehyde (bromal) or trichloroethanediol (chloral hydrate) with bromo or chlorobenzene in the presence of fuming sulfuric acid (Reactions 1 & 2).¹

Reaction 1 & 2



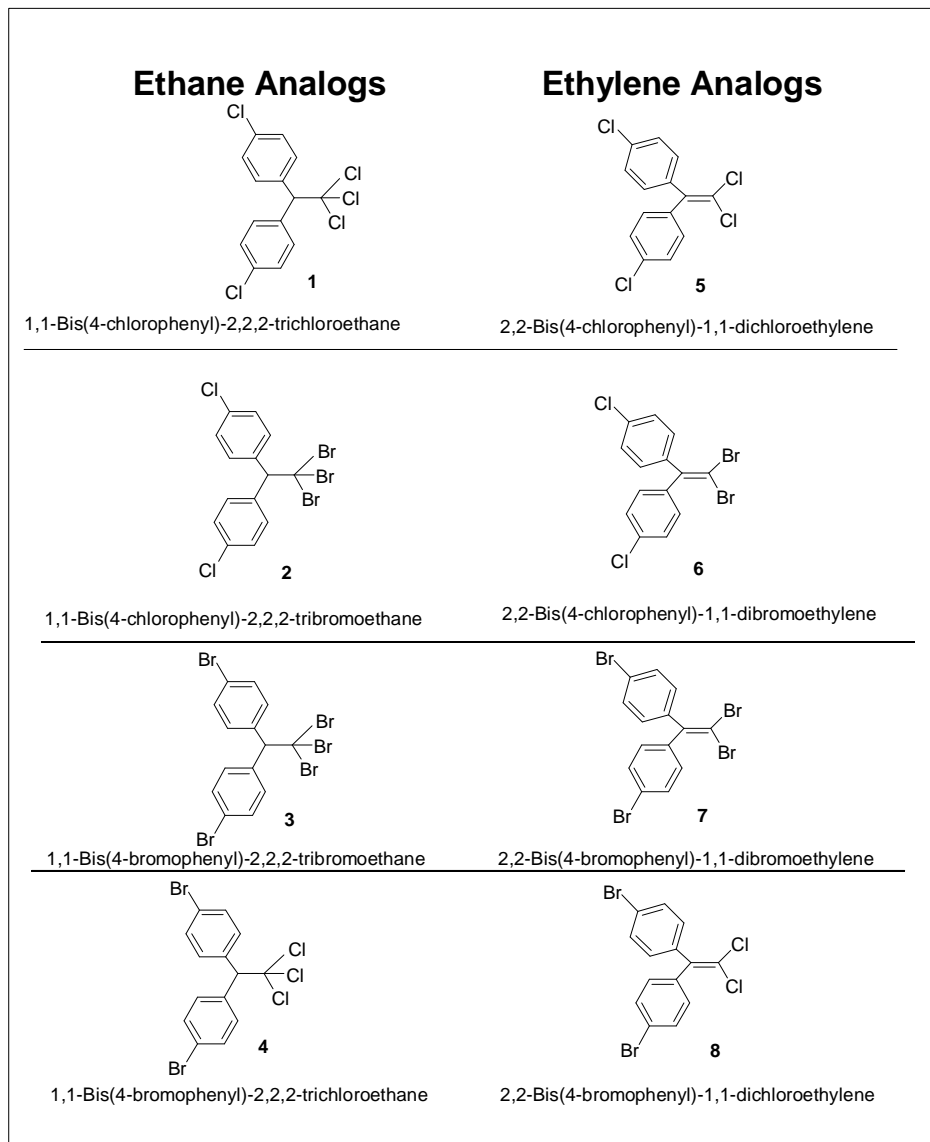
Dehydrohalogenation of the monomer was completed in two days in refluxing potassium hydroxide solution. (Reaction 3).

Reaction 3



The various chloral and bromal biphenyl ethane and ethylene analogs can be seen in table 3.

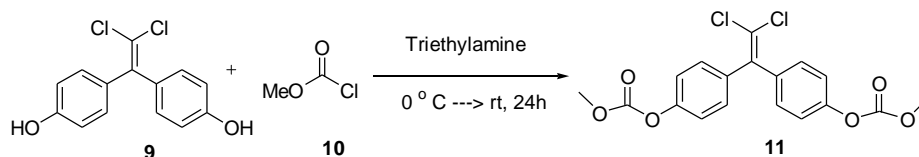
Table 1



Blends

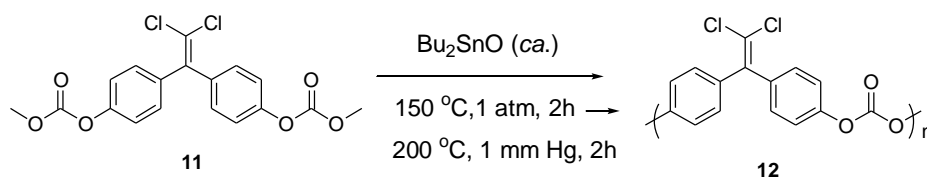
A bisphenol C polycarbonate has been prepared by G.E. and has been shown to increase flame resistance when it is co-polymerized with bisphenol A polycarbonate.² The production of polycarbonates in industry is synthesized by a condensation of bisphenol A and phosgene gas.³ Because of the high toxicity of this gas, we have used non-phosgene polymerizations. Bisphenol C (**9**) was transformed into its dicarbonate **11** by condensing with methyl chloroformate **10** (Reaction 4).⁴

Reaction 4



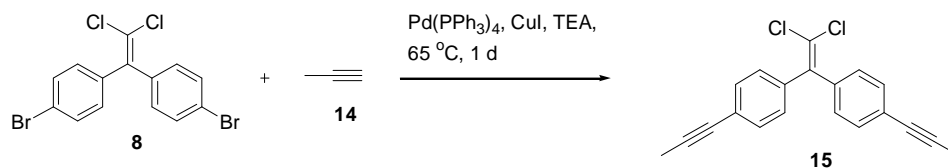
Polymerization of **11** resulted in low molecular weight polymer **12** (M_w : 14,600; M_n : 4,600). The focus was on making new materials not previously done by industry, so no further work was done optimizing this polymer (Polymerization 1).

Polymerization 1



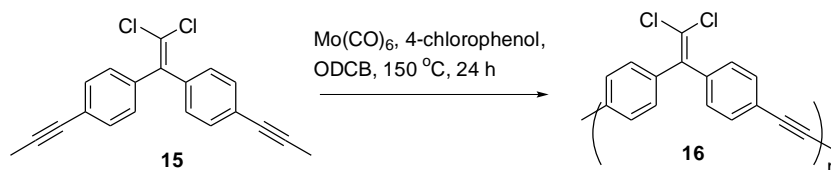
Changing our approach on polymerizing the chloral biphenyl ethylene monomers alkyne moieties were added to the monomer unit. With alkyne functional groups on the polymer, these materials can crosslink and form char in a flame. Unfortunately they also contribute energy to the system, causing these materials to have extended burn times as blends in ABS plastics.⁵ Building on the idea that the alkynes can cross-link during the combustion process, a polymer was synthesized from the functionalized biphenyl ethylene monomer. Starting with **8** using Buz's procedure for coupling with propyne (**14**), compound **15** was prepared.⁶ (Reaction 5)

Reaction 5



Monomer **15** was then polymerized using Buz's ADIMET process to produce polymer **16** (M_w : 3,950; M_n : 1,700) (Polymerization 2).⁷

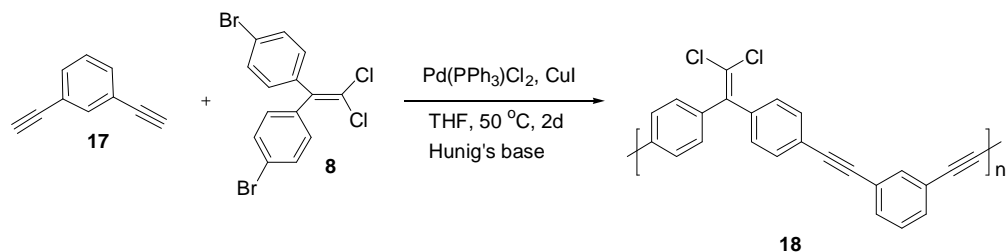
Polymerization 2



Due to its rigid structure it does not melt and cannot be used as a thermoplastic. Instead it was blended with ABS, where it led to extended burn times (Table 3).

Trying to decrease the rigidity of the polymer so it will melt, linker group 1,3-diethynylbenzene (**17**) was used. Polymer **18** was made by a Sonogashira⁸ coupling of (**17**) with **8** (Polymerization 3).

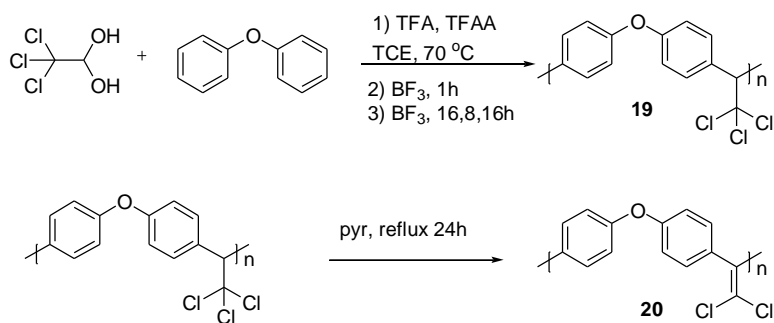
Polymerization 3



Due to the polymer's high level of cross-linking during polymerization, it was not soluble in any solvent making characterization difficult. Fortunately, we were able to obtain IR data. This polymer also suffered extended burn times, which hinders its use as a blend in ABS. Burn results from the compounds tested are listed in Table 3.

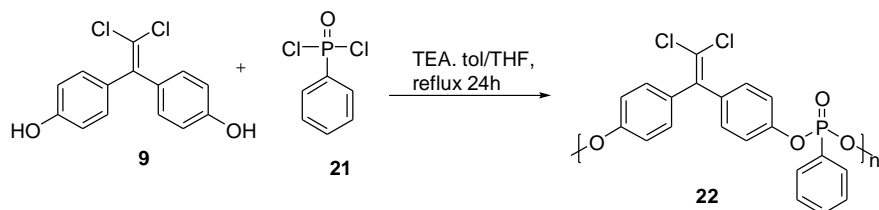
Investigating other G.E. literature procedures, another chloral condensation polymer was prepared. Using chloral hydrate and diphenylether produced poly (diphenyl ether-chloral) **19**; a subsequent dehydrohalogenation reaction produced the more stable dichlorovinylidene **20** (M_w : 9,350: M) (Polymerization 2).⁹ The use of this polymer as a viable flame retardant is being evaluated.

Polymerization 4



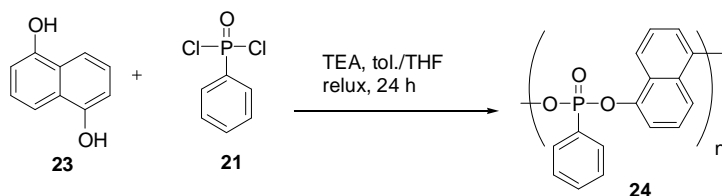
It has been theorized in the literature that phosphorus acts both in the solid and vapor phase to stop burning.¹⁰ Polymers with phosphorous in the backbone are currently being synthesized utilizing chloral base monomers such as bisphenol C (**9**) and phenylphosphonic dichloride (**21**) to yield polymer **22**. (Polymerization 5)

Polymerization 5



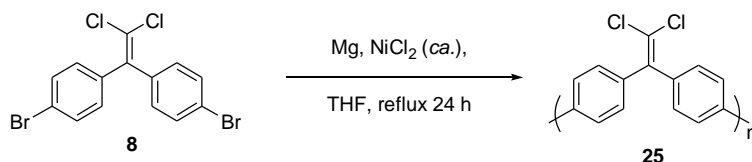
Due to the low molecular weight of the material (M_w : 3,750; M_n : 2,000) and whole bar could not be made in tested in the HVUL-94. Studies are underway to make high molecular weight polymer, so that it can be tested for its flame retarding capabilities. It is important to note that when a piece of this polymer is held in and above the flame of a Bunsen burner it does not burn. To test the integrity of this polymerization method another diphenol (1,5-dihydroxynaphthalene) **23** was polymerized under the same conditions to yield the naphthalene polymer **24** (Polymerization 6). Preliminary results indicated that this polymer also had a low molecular weight (M_w : 4,150; M_n : 2,150) so a blend was made with ABS. As seen with the other polymers, extended burn times were experienced with **24** (Table 3).

Polymerization 6

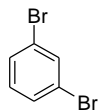


The latest approach to making polymers with the chloral biphenyl ethylene monomer is by direct aromatic polymerizations using aryl-aryl coupling procedures. The reaction that yielded high molecular weight polymer has been the polymerization of analog **8** catalyzed by nickel chloride and magnesium (Polymerization 7).¹¹

Polymerization 7

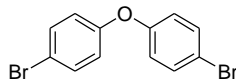


High molecular weight polymer has been achieved, but due to its rigid structure and lack of solubility this polymer does not melt. Several linkers were investigated to help these factors, but none thus far has resulted in making this polymer processible. In light of this fact, the polymer was pressed together using a Carver pellet press and a piece of it was held in and above the flame of a Bunsen burner, and after removing the plastic from the ignition source the flame went out. Current research in the laboratory is involved with making this polymer into a true thermoplastic. Several different linker groups have been co-polymerized to help break up the stiffness in the polymer and lower the melting point (Table 2).

Table 2

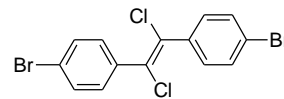
1,3-dibromobenzene

5 mol % 10 mol %
M_w : 16,000 **M_w** : 65,300
M_n : 2,300 **M_n** : 54,300



4,4'-dibromodiphenyl ether

5 mol % 10 mol %
M_w : 8,500 **M_w** : 8,600
M_n : 2,600 **M_n** : 2,500

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

20 mol %
M_w : 102,100
M_n : 68,000

Table 3

Additive	First ^a Ignition(sec)	Observed Dripping ^b	Second ^a Ignition(sec)	Observed Dripping ^b	UL-94 Rating
1, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	<1, 3	No, No	V-0, V-0
1, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	3, 0	No, No	4, 8	No, No	V-0, V-0
2, 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 0	No, No	V-0, V-0
2, 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; HIPS	0, 1	No, No	0, 0	No, No	V-0, V-0
3, 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; ABS	1, 0	No, No	0, 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, 2wt%; PTFE, 1wt%; ABS	0, 0	No, No	1, 1	No, No	V-0, V-0
4, 10wt%*; Sb2O3, 2wt%; PTFE, 1wt%; HIPS	9, 1, 0	No, No, No	50, 0, 0	Yes, No, No	?, V-0, V-0
6, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	1, 0	No, No	V-0, V-0
6, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	<1, <1	No, No	1,1	No, No	V-0, V-0
7, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; ABS	0,0	No, No	1,1	No, No	V-0, V-0
7, 10wt%*; Sb2O3, 4wt%; PTFE, 1wt%; HIPS	1,0	No, No	2,1	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%*; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; HIPS	38, 0, 10	No, No, No	0, 2, 1	No, No, No	V-1, V-0, V-0
16, 10wt%*; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	198, 195	No, Yes	281 ^d , 615 ^d	No, No	?, ?
18, 10wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	175, 192	No, No	113 ^d , 90 ^d	No, Yes	?, ?
22, 10wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	277, 169	Yes, Yes	X, 83	No, No	?, ?
24, 10wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	127, 127	Yes ^c , Yes ^c	82, 72	Yes, Yes	?, ?
25, 10wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	40, 275	Yes ^c , No	X, 7 ^d	No, No	?, ?
25, 10wt%; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; HIPS	30, 29	Yes ^c , Yes ^c	19, X	Yes, No	?, ?
25, 10wt%*; Sb ₂ O ₃ , 4wt%; PTFE, 1wt%; ABS	0, 0	No, No	143 ^d , 45 ^d	No, No	?, V-1

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.

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. 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. Hexane and methylene chloride were distilled. Unless otherwise stated, all other reagents were used as received. Mass spectrometry work was done by Dr. Terry Marriot in the Rice University mass spectrometry laboratory.

Instrumentation 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 from 30 to 900 °C at 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 using a 50 to 450 °C scanning window at 10 °C/min. under nitrogen. Melting points were obtained using a Büchi melting point apparatus. The bulk polymer blending was done in a Brabender Prep-Center using a 6/2 mixer head. Additional blending and molding

was done with a Custom Scientific Instruments CSI-183MMX Mini Max Blender/Extruder. An Atlas Electronic HVUL-94 flame test station was used for the UL-94 flame tests.

General Procedure for Plastic Blending/Molding Reagents were added by weight percent of total weight (chlorinated compounds were added by weight percent chlorine per total weight to maintain a constant halogen content) of plastic batches to yield 22.05 g batches of ABS-based plastics or 21.95 g batches of HIPS plastics (the total weight used being dependent upon the constant volume of the mixer and the density of the polymer used). The polymer (ABS or HIPS) was first added to the Brabender mixer and then blended at 100 rpm with 1 weight % PTFE (a commonly used anti-drip additive) for 10-15 min. The initial processing temperatures were 225 °C and 210 °C for ABS and HIPS, respectively. Sb_2O_3 was then added and blended at 150 rpm for 30 min. The blended plastic was then removed from the Brabender and put into the CSI-183MMX Mini Max where it was molded into bars to be used in the UL-94 flame test.

General Procedure for the Modified UL-94 Burn Test Two 1/8" thick x 1/2" wide x 3" long plastic (polymer + additive) rectangular bars (made with the CSI-183MMX Mini Max) were used for this test. The plastic bars were suspended in the Atlas Electronic HVUL-94 flame test station 70 mm above a Bunsen burner. The calibrated Bunsen burner flame height was 125 mm. To ignite the bar, the lit Bunsen burner was brought directly underneath the plastic bar via a sliding rail system. All test bars underwent two trials, each trial consisting of ignition for 10 sec, followed by flame removal and the time to self-extinguishing was recorded. As part of the flame test, the bar of plastic was suspended above a cotton patch prior to ignition. Cotton ignition was noted if polymer dripping occurred during the test.

CONCLUSION

Several additives based on the chloral biphenyl ethylene monomers have been synthesized and give V-0 results when blended in both ABS and HIPS. Additionally several polymers have also been prepared, and initial results show good to excellent flame retardant properties. These novel additives and polymers represent a new direction in flame retardant materials. It is important to note that though the processing of these polymers as thermoplastics is still under investigation they can be an important class of flame retardants.

ACKNOWLEDGEMENTS

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