Novel Flame Retardant Polymers & Blends

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Introduction

- An Estimated 8.9 billion dollars in property damage and 4,035 civilian fatalities due to fires occurred in 1998. -NFPA 1999 report.

- 1.7 million fires occurred in 1998 and out of that 381,000 of these fires occurred in vehicles (planes, cars, trains, etc…). -NFPA 1999 report.

- The focus of the research in the laboratory, funded by the FAA, is on the flame retardancy of the plastics used in commercial aircraft.

- Approximately 20% of the 1153 fatalities on U.S. transport airlines (1981-1990) occurred in impact survivable accidents involving fire. -FAA personal communication.

- It has been estimated that the amount of plastic currently in the aircraft cabins has a fire potential equivalent to the weight of aviation fuel. The material gives off the same amount of energy per kilogram. -Science News, vol. 155,**1999**, 40.

Primary Research Objectives

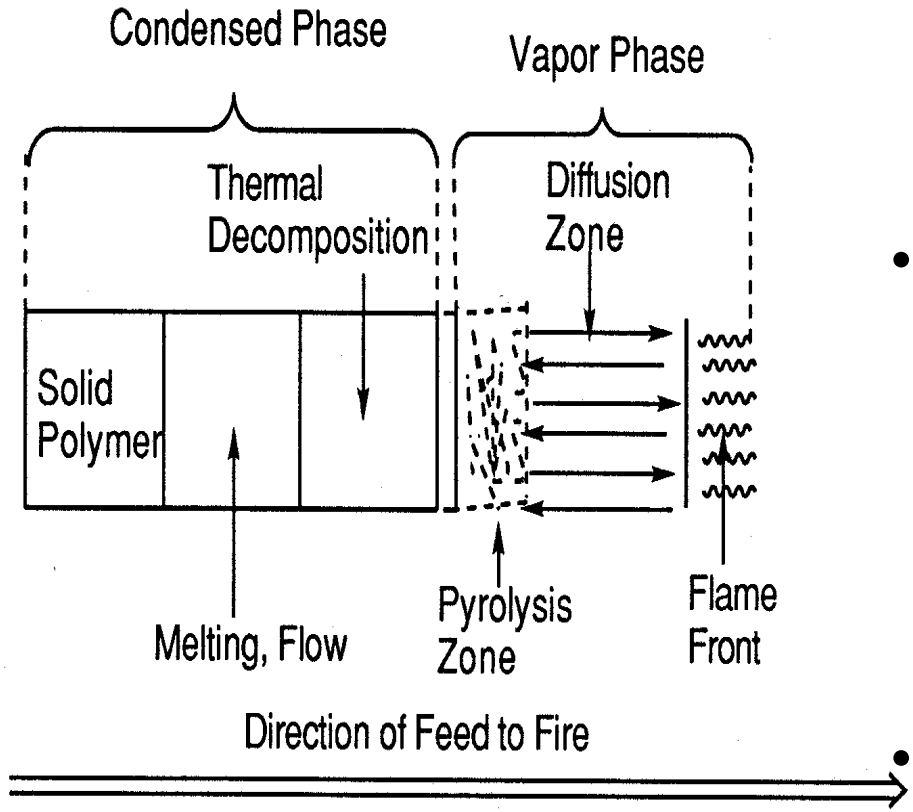
•To develop an effective low cost flame retardant polymer that can be used in industry.

- To synthesize, process, and test potential flame retardant polymers and additives which can be used in currently existing polymeric materials, such as ABS (Acrylonitrile-Butadiene-Styrene), HIPS (High Impact Poly Styrene) and HDPE (High Density Poly Ethylene).

- To fully understand the synergism between organic structures and how it affects the process of polymer combustion.

- **To Save Lives!**

Schematic of Polymer Combustion



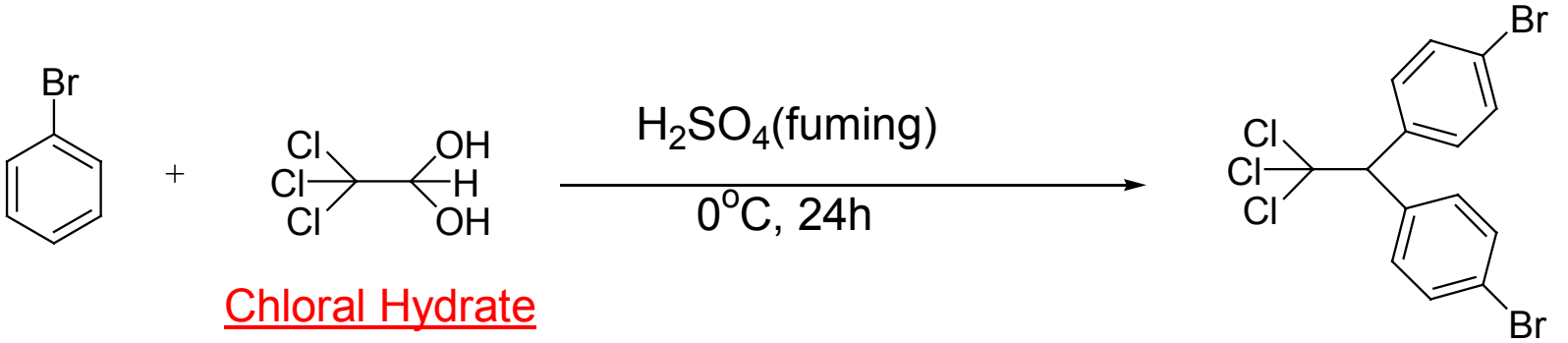
Stevens, M.P.; Polymer Chemistry: An Introduction, 3rd ed. Oxford, NY; Oxford University Press 1999. p 111.

- Vapor Phase- halogenated compounds act as free radical traps which interrupt the burn cycle.
- Condensed Phase- high char forming and cross-linking materials can prevent fuel molecules from reaching the flame front and further depolymeriztion of the plastic.
- Current research in the Laboratory focuses on both areas of polymer combustion.

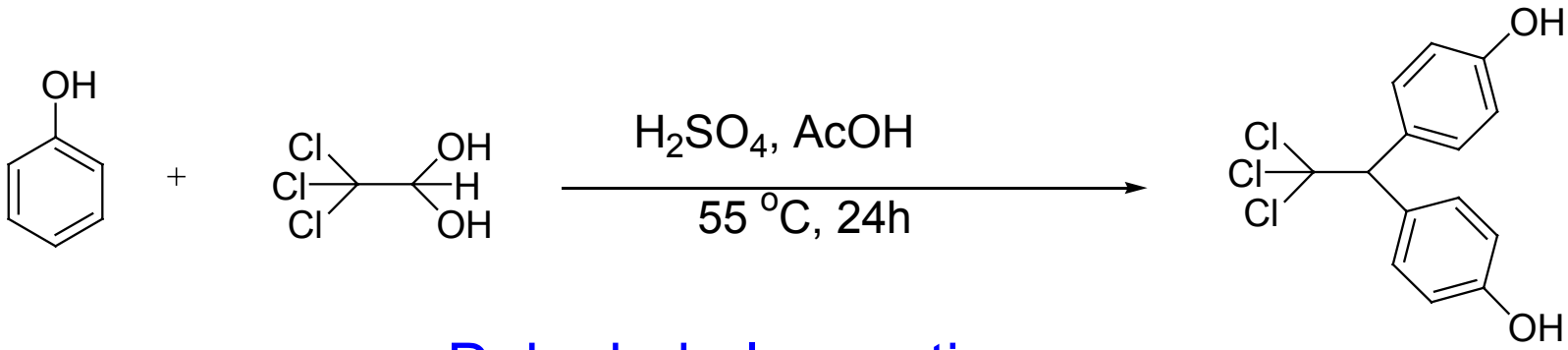
Halogenated Flame Retardants

- Advantages
  - Highly efficient.
  - Relatively low loadings required (4-20%).
  - Less Impact on physical properties of the plastic.
  - Thermally stable
- Disadvantages
  - Relatively high cost/pound of flame retardant
  - Corrosive smoke
  - Environmental concerns, due to halogen and dioxin/furan issues.

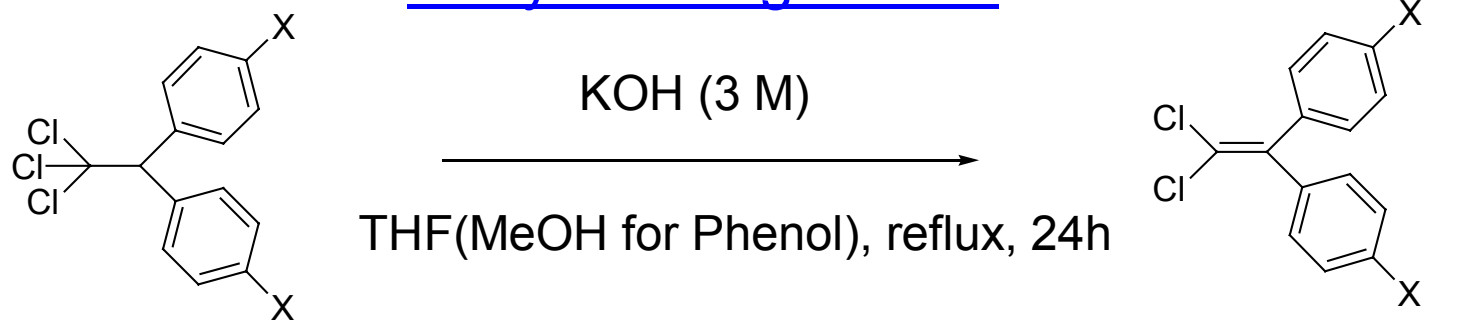
Synthesis of the Biphenyl Ethylene Monomers



Chloral Hydrate



Dehydrohalogenation

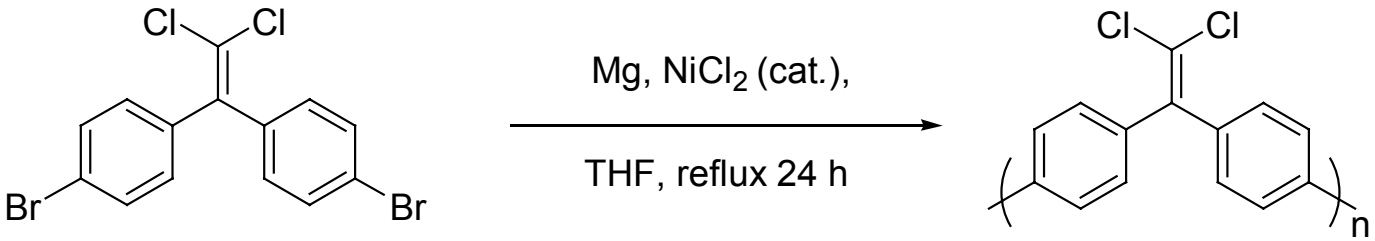


Ethane analog

X=Br or OH

Ethylene analog

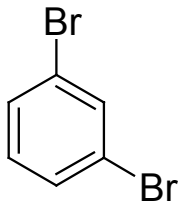
Polymerization of the Chloral Biphenyl Ethylene monomers



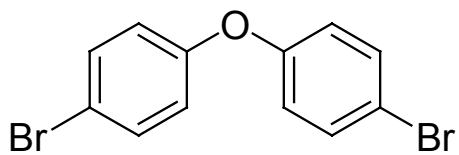
$\mathbf{M_w}$:128,600

$\mathbf{M_n}$: 76,400

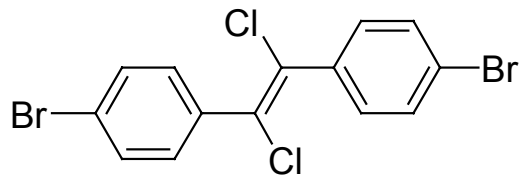
Linker groups used to break up polymer rigidity and increase solubility.



1,3-dibromobenzene



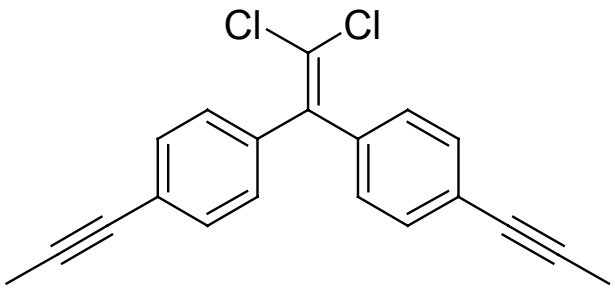
4,4'-dibromodiphenyl ether



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

5 mol %	10 mol %	5 mol %	10 mol %	20 mol %
$\mathbf{M_w}$: 16,000	$\mathbf{M_w}$: 65,300	$\mathbf{M_w}$: 8,500	$\mathbf{M_w}$: 8,600	$\mathbf{M_w}$: 102,100
$\mathbf{M_n}$: 2,300	$\mathbf{M_n}$: 54,300	$\mathbf{M_n}$: 2,600	$\mathbf{M_n}$: 2,500	$\mathbf{M_n}$: 68,000

Synthesis of the Alkynyl Chloral Biphenyl Ethylene Monomers and Polymerization

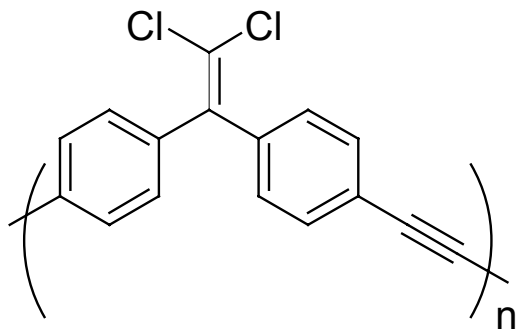


$Mo(CO)_6$

4-chlorophenol,

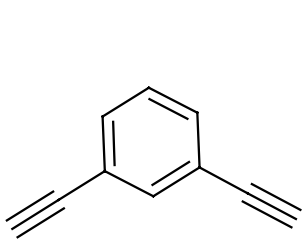
o-dichlorobenze

150 ^{o}C, 24 h



$\mathbf{M_w}$: 3,950

$\mathbf{M_n}$:1,700



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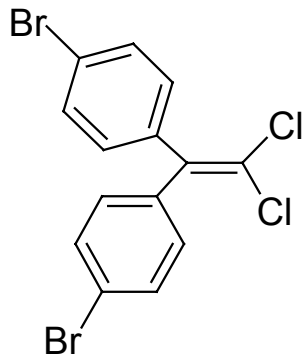
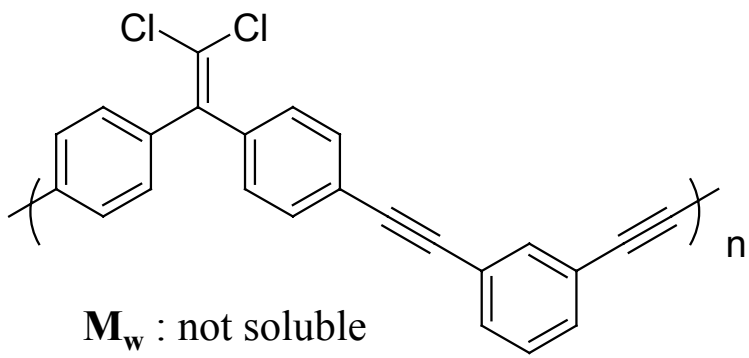


$Pd(PPh_3)_2Cl_2$, CuI

THF, 50 ^{o}C, 2d

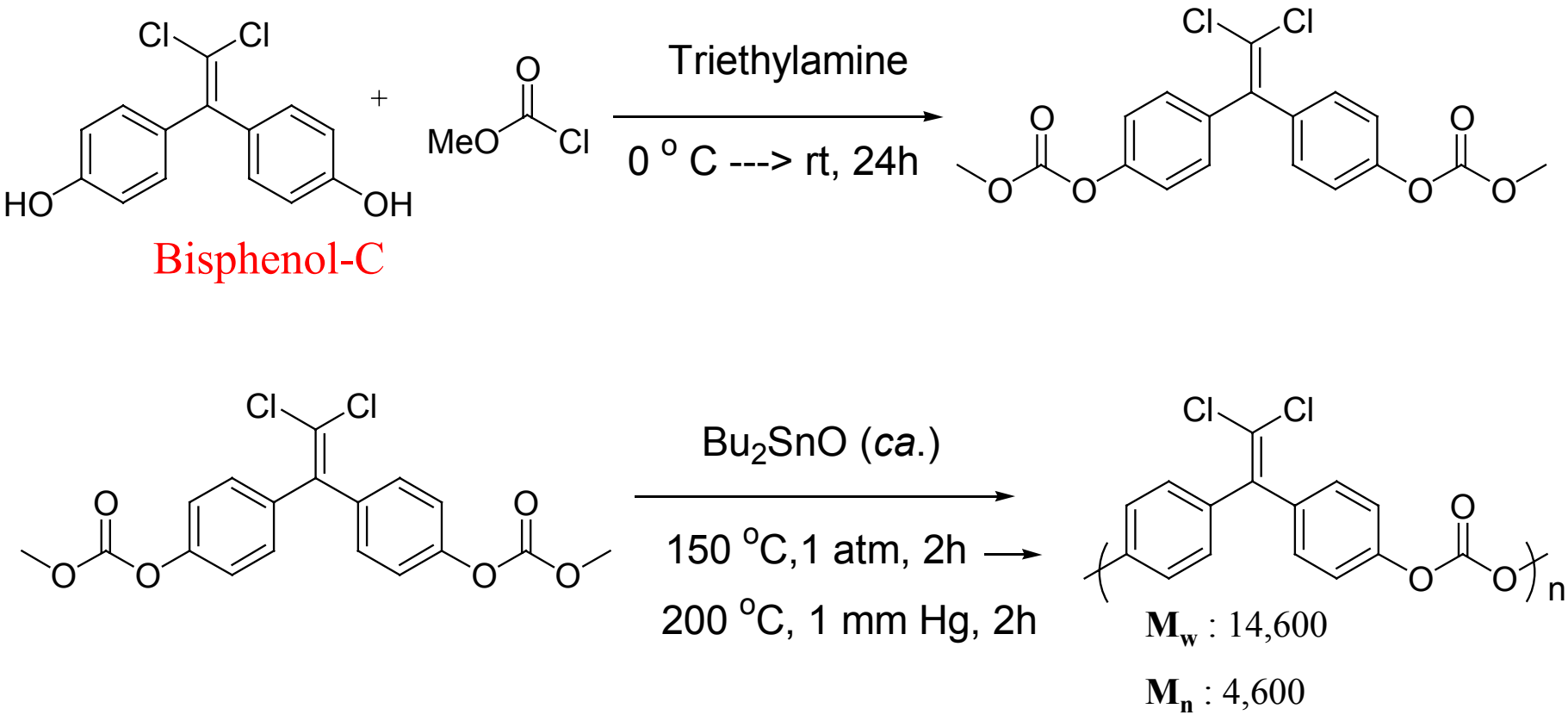
Hünig's base



$\mathbf{M_w}$: not soluble

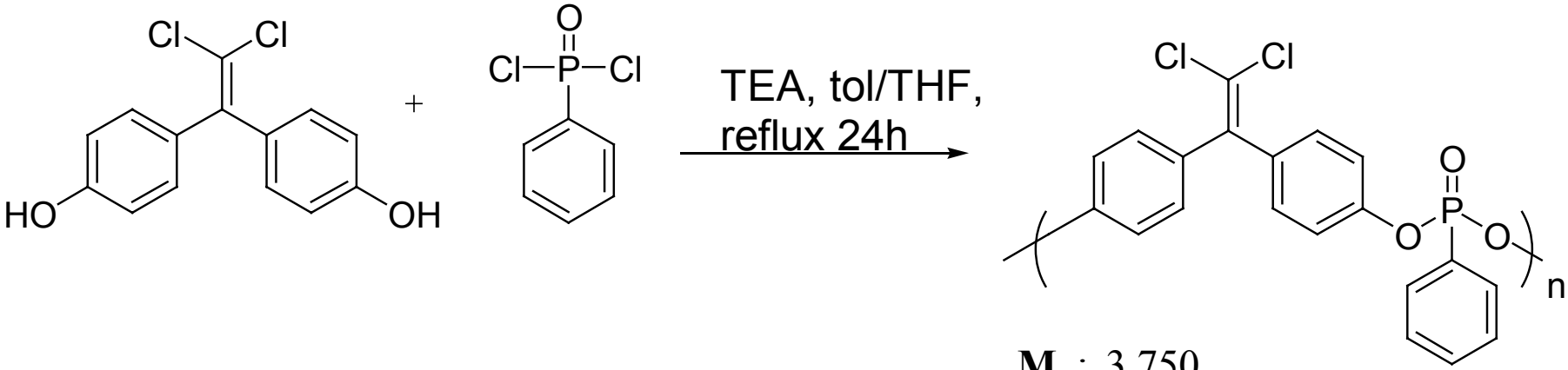
$\mathbf{M_n}$: not soluble

Polymerization of other Biphenyl Ethylene Monomer



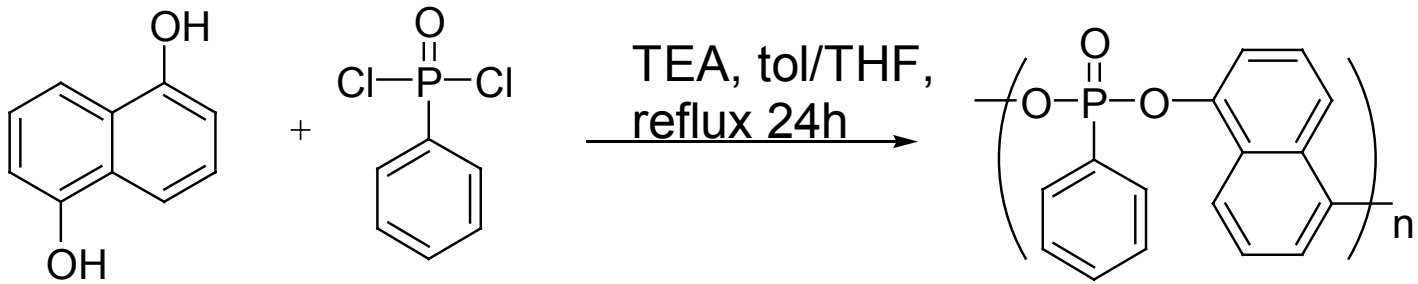
Bisphenol-C polycarbonate-General Electric Company; U.S. Patent 4,182,838. 1980.

Synthesis of Chloral and Phosphorous Based Polymers



$\mathbf{M_w}$: 3,750

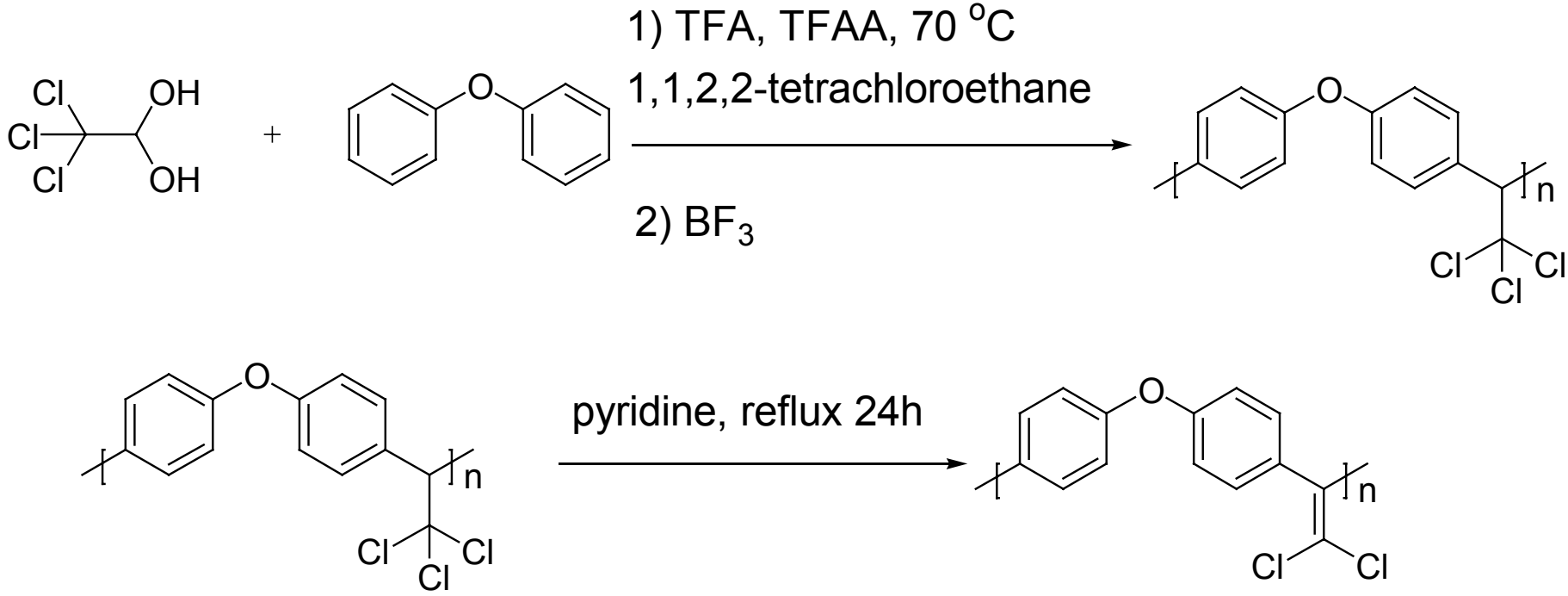
$\mathbf{M_n}$: 2,000



$\mathbf{M_w}$: 4,150

$\mathbf{M_n}$: 2,150

Polymerization of Chloral w/ Diphenyl Ether



$\mathbf{M_w}$: 9,350

$\mathbf{M_{n-}}$: 3,300

Flame Retardant Blending and Testing Procedures for the UL-94 Test

- Thermoplastic blending was achieved with the Brabender Prep-Center system, blending the plastic in batches. All extrusion molding was accomplished with the CSI-183MMX Mini-Max extruding system.

- All ABS/HIPS/HDPE blends contained 1 wt% fibrillar PTFE as an anti-drip additive.

- Flame retardant testing of the materials synthesized was investigated using HVUL-94 Flame Test Station.

- Two bars of each additive and plastic were made with the CSI-183MMX Mini Max extruding system and both were subjected to the UL-94 Flame Test.

- The UL-94 Test exposes the plastic to two 10 second ignitions. After the ignition, the flame is removed and the amount of time to extinguish is recorded. If the plastic self extinguishes in less than 10 seconds with no dripping onto a piece of cotton it is considered to be a V-0 material.

Summary of Burn Results for Biphenyl Ethane Analogs

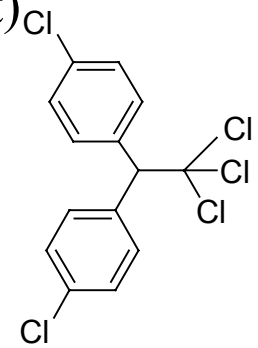
(10 wt% based on Halogen Content)

ABS + Analog **1**/Sb_2O_3 → V-0

HIPS + Analog **1**/Sb_2O_3 → V-0

HDPE + Analog **1**/Sb_2O_3 → V-2

1

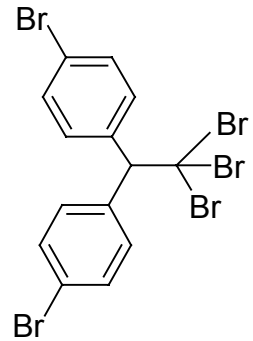


1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane

ABS + Analog **2**/ Sb_2O_3 → V-0

HIPS + Analog **2**/ Sb_2O_3 → V-0

2

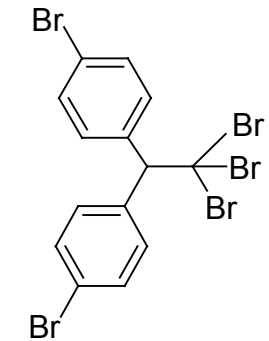


1,1-Bis(4-bromophenyl)-2,2,2-tribromoethane

ABS + Analog **3**/ Sb_2O_3 → V-0

HIPS + Analog **3**/ Sb_2O_3 → V-0

3



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

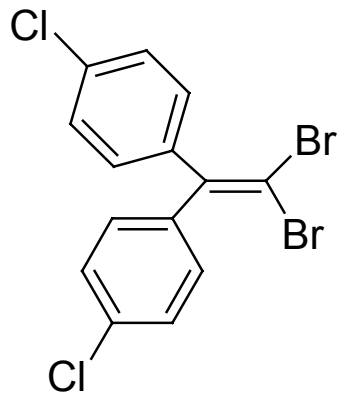
Summary of Burn Results for Biphenyl Ethylene Analogs

(10 wt% based on Halogen Content)

ABS + Analog **4**/ Sb_2O_3 → V-0

HIPS + Analog **4**/ Sb_2O_3 → V-0

4

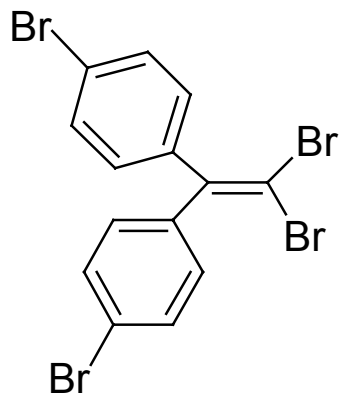


2,2-Bis(4-chlorophenyl)-1,1-dibromoethylene

ABS + Analog **5**/ Sb_2O_3 → V-0

HIPS + Analog **4**/ Sb_2O_3 → V-0

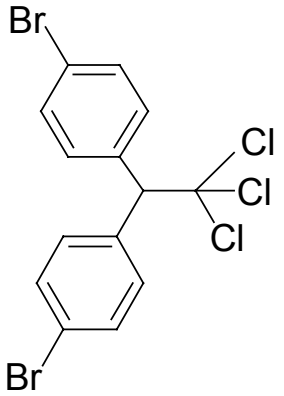
5



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

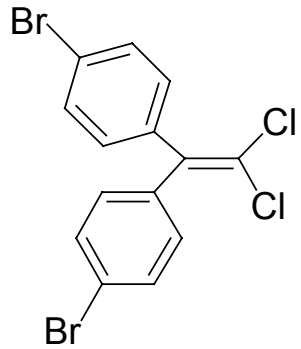
Burn Results for Biphenyl Monomers

6



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

7



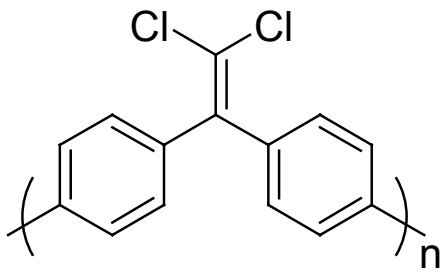
2,2-Bis(4-bromophenyl)-1,1-dichloroethylene

Additive	First [a] Ignition(sec)	Observed Dripping [b]	Second [a] Ignition(sec)	Observed Dripping [b]	UL-94 Rating
6, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; **ABS**	0, 0	No, No	1, 1	No, No	V-0, V-0
6, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; **HIPS**	9, 1, 0	No, No, No	50, 0, 0	Yes ,No, No	?, V-0, V-0
7, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; **ABS**	0, 1	No, No	0, 1	No, No	V-0, V-0
7, 10wt%*; Sb_2O_3, 2wt%; PTFE, 1wt%; **HIPS**	38, 0,10	No, No	0, 2, 1	No, No	?, V-0, V-0

a Time to self-extinguishing in seconds after 1st and 2 nd, 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. * Indicates that weight percent is based on halogen weight percent.

Burn Results for Biphenyl Ethylene Polymer

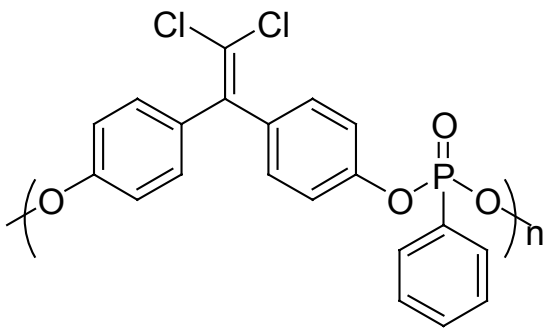
8

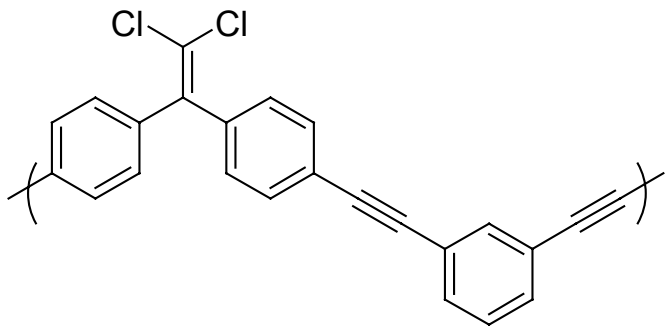


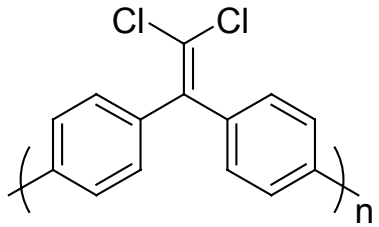
Additive	First [a] Ignition(sec)	Observed Dripping [b]	Second [a] Ignition(sec)	Observed Dripping [b]	UL-94 Rating
8, 10wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; **ABS**	40, 275	Yes [c], No	X, 7 [d]	No, No	?, ?
8, 10wt%; Sb_2O_3, 4wt%; PTFE, 1wt%; **HIPS**	30, 29	Yes [c], Yes [c]	19, X	Yes, No	?, ?
8, 10wt%*; Sb_2O_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 and 2 nd, 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. * Indicates that weight percent is based on halogen weight percent.

Modified Burn Procedure and Results







- Due to processing difficulties the above polymers where pressed on a Carver pellet press.
- 5-10 Minutes, 150 ^{o}C; 10,000 lbs. of force was applied to make a pellet.
- Pellet was held above the flame(3-5 sec;2×) flame went out **immediately**.
- Pellet was held in the flame (3-5 sec; 2×) flame went out **immediately**.

Conclusion

- These chloral biphenyl polymers are too rigid to be used as thermoplastics (i.e. decompose before they melt).
- Need to develop a non-flammable, flexible linker group to break up the rigidity, so the polymer will melt.
- Blending 10 wt % (based on halogen content) of the monomer and its various analogs with commercial plastics will give a V-0 rating.
- The biphenyl ethylene polymers do not burn after it is ignited.

Future Direction

- Work on polymer processing.
- Develop a novel non-flammable thermoplastic that has comparable cost, physical, and mechanical properties to commercially available plastics, i.e. ABS, HIPS, etc…
- Fine tune the minimum amount of halogenated additive/polymer need to give a V-0.
- Investigate new directions in both the vapor phase and condensed phase flame retardant strategies (i.e. phosphorous, boron, silicon, etc…).

Acknowledgements

Federal Aviation Administration

Albemarle Corporation

Great Lakes Chemical Corporation

Dow Chemical Company