Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell

Sustainable Routes to Non-Halogenated Flame Retardants Based on Phenolic Monomers

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Academic Research Program

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University of Massachusetts Lowell

Sustainable Routes to Non-Halogenated Flame Retardants Based on Phenolic Monomers

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing to the Toxics Use Reduction Institute, University of Massachusetts Lowell, 600 Suffolk St, Wannalancit Mills, 5th Floor, Lowell, Massachusetts 01854.

Academic Research Program

The Academic Research program is a project of the Toxics Use Reduction Institute (TURI). The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies and, in some cases, evaluate and/or adopt processes and technologies resulting from research. Past projects supported by this program have focused on finding alternatives to the use of toxic chemicals in various plastics applications. These projects, which are described in more detail on TURI's website (www.turi.org and click on Industry, Research, Academic Research Program), include:

- 2008 – "Greener" Routes to Halogen Free Flame Retardants – Prof. Jayant Kumar and Asst. Prof. Ramaswamy Nagarajan, UMass Lowell Center for Advanced Materials.
- 2006 – Improved Lead-Free Wire and Cable Insulation Performance Using Nanocomposites – Asst. Prof. Daniel Schmidt and Noble Francis, UMass Lowell Department of Plastics Engineering.
- 2005 – Flame Retardancy Enhancement for EPDM Wire and Cable Coatings Using Nanoclays – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering.
- 2004 – Alternative Stabilizers and Surface Characterization (SEM/EDXS Analysis) of EPDM for Wire and Cable Applications – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering, and Changmo Sung, UMass Lowell Department of Chemical Engineering.
- 2003 – Analysis of Lead-Containing Wire Coating Materials – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering, and Changmo Sung, UMass Lowell Department of Chemical Engineering.
- 2003 – Innovative Materials for Wire and Cable Coating – Prof. Stephen McCarthy, UMass Lowell Department of Plastics Engineering and the Institute for Plastics Innovations.
- 2002 – Innovative Materials for Wire and Cable Coating – Prof. Stephen McCarthy, UMass Lowell, Department of Plastics Engineering and the Institute for Plastics Innovations.

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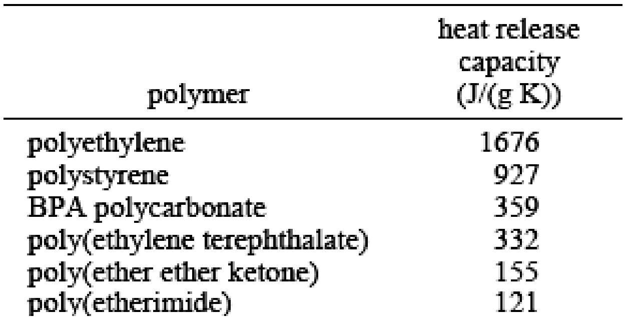
1. Background:

Flame retardant (FR) materials are used to control or reduce the risk[1] of fire and therefore play a major role in the safety of people using products that contain FRs. Commodity plastics are inherently flammable and release heat upon burning (have very high heat release capacities) as shown in Table 1. Thus, in order to ensure the safety of plastics products during their use in a variety of applications the addition of FR materials is inevitable.



polymer	heat release capacity (J/(g K))
polyethylene	1676
polystyrene	927
BPA polycarbonate	359
poly(ethylene terephthalate)	332
poly(ether ether ketone)	155
poly(etherimide)	121

Table 1: Heat Release Capacity of some commodity plastics

Halogenated compounds are one of the most commonly used class of FRs. However halogenated FRs are environmentally persistent and generate toxic, corrosive gases during combustion that threaten both air and water ecosystems. As a result several governments, from the European Union to states like Maine, Washington and Oregon, have created restrictions and/or bans on the use of specific halogenated FRs. There is therefore an immediate need to replace these halogenated FRs with more environmentally compatible alternative FR materials.

In 2007-2008 UML researchers investigated the possibility of substituting toxic halogenated FR materials with a new class of polyphenol based FR materials under a TURI funded project. The proof-of-concept studies were completed during the first year of this project. Subsequently in 2008-2009, our goal was to modify the synthetic strategies investigated in the first study and create a new class of non-halogenated flame retardant copolymers based on synthetic monomers as well as naturally occurring starting materials.

One of the important aspects of designing a new FR material includes understanding the reactions involved during burning of polymers. The chemical reactions often encountered when solid organic materials (polymers) burn are shown in Figure 1.

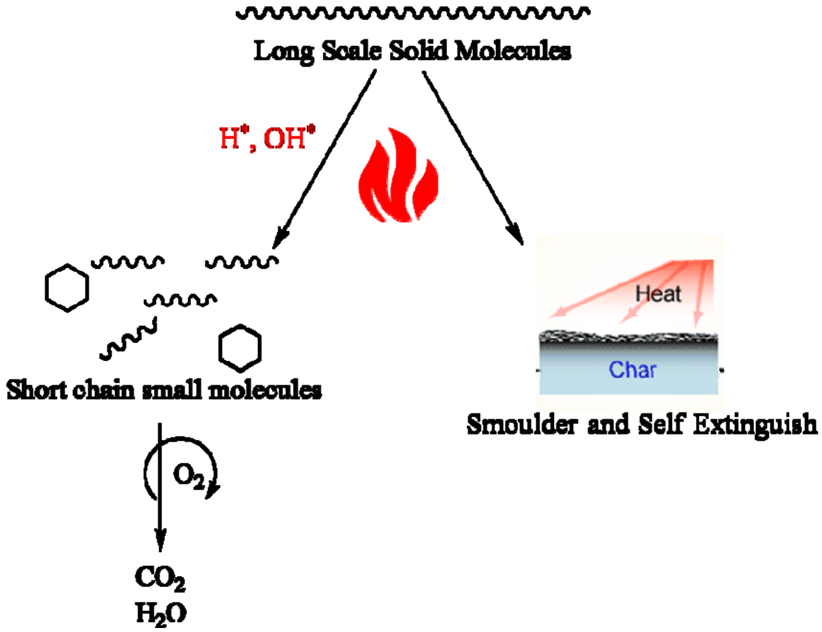


Figure 1: Burning of Polymers

Break down of the polymer backbone occurs through propagation of extremely reactive OH and H radicals. The mechanism of action of most FRs is based on abstraction of these very reactive radicals by the radicals formed from the FR materials. Another important mechanism for reducing the flammability of a material is to promote the generation of a layer of char on the surface of the polymer which quenches oxygen supply to the flame zone, thereby quenching the flame. Most polymers cannot intrinsically generate char and hence they require external addition of flame retardant materials. Radical quenching capability and char forming ability are two of the most important characteristics for FR materials.

Flame retardants (FR) classification

Flame retardant materials can be broadly classified into three major types based on their mechanism of action.

- **Physical action with FRs**

  The additives can form a shield with low thermal conductivity causing a reduction in the heat transferred from the heat source to the material. Some FRs degrade through an endothermal process reducing the heat generated in the system. Another mechanism is associated with a dilution effect due to incorporation of inert substances that eventually dilute the fuel in the gas phase thus lowering the ignition limit of the gas mixture. Examples of FRs that use physical action to induce flame retardancy include:

  - <u>Organophosphorous FRs</u>: Phosphorous-based compounds are well known for their inherent flame retardancy. Studies have indicated a significant improvement of flame retardance with the incorporation of these organophosphorous groups.[2] However some of them have the problem of high levels of carbon monoxide emission.[3]

  - <u>Inorganic FRs</u>: Metal hydroxides typically work based on the 'cooling effect'. That is, they reduce the effective heat generated in the flame zone by an endothermic degradation process. Antimony trioxide in synergy with phosphorous based FRs is a very effective fire retarder.

- **Chemical action in condensed phase:**

  The major portion of this type of FR is composed of intumescent materials. An intumescent material is one which expands in volume and reduces in density when heated. This provides a two way barrier, hindering the passage of the combustible gases and molten polymer to the flame as well as the shielding of the polymer from the heat of the flame. Nitrogen based organic FRs are one example of intumescent FR materials.

- **Chemical action in gas phase:**

  This type of FR works by quenching of reactive radical species in the gas phase of the flame zone as shown in Figure 2.

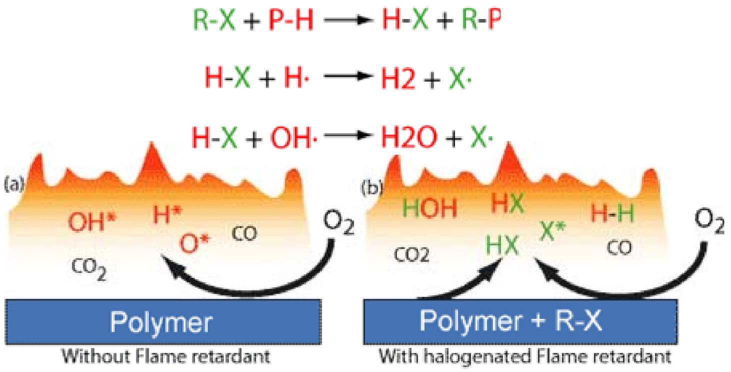


Figure 2: Mechanism of action of halogenated FR in flame

- Halogenated-organic FR: These are the preferred choice of FRs that work by this mechanism due to their extremely good radical scavenging ability and ease of incorporation into the polymer matrix. Some examples of this type of FR is provided in Figure 3.

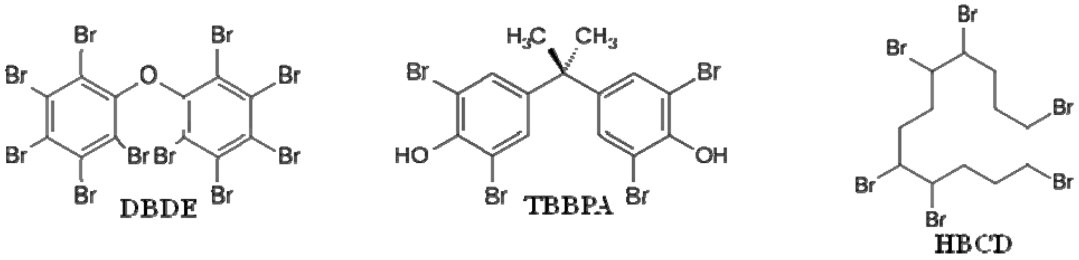


Figure 3: Structures of common halogenated FRs

The detection of these FRs in sperm whales, dolphins and humans, however, raises significant concerns about their impact on both environmental and human health. Halogenated FRs have been reported to be extremely toxic to both plant and animal life.

2. Motivation

2a. Deoxybenzoin based polymers

Polymers derived from the bisphenol of chloral, or 1,1-dichloro-2,2-(4-hydroxyphenyl)ethane (BPC), have been shown to exhibit exceptionally good fire resistance[45]. Investigations into decomposition pathways of BPC-containing polymers suggest that char formation may proceed through diphenylacetylene derivatives, arising from base-induced elimination of chlorine on BPC to give a carbene, which undergoes phenyl migration to diphenylacetylene derivatives. Thus, while chlorine in BPC sets up the rearrangement chemistry, the role of diphenylacetylene must be of considerable importance. It was also reported that there is a catalyzed conversion of deoxybenzoin to diphenylacetylene by flash vacuum pyrolysis at 300-500°C. The temperature range at which deoxybenzoin goes to diphenylacetylene suggests its potential utility to affect char in burning polymer materials.

More recently it has been recently reported that phenolic monomers (Figure 4.) such as 4,4’-bishydroxydeoxybenzoin (BHDB) when copolymerized with phenylphosphonic dichloride yield BHDB polyphosphonates that have highly desirable property of flame resistance with good solution processability[6]. However some phosphates have already banned in some countries because they have been shown to be carcinogenic. Phenol-formaldehyde polymers exhibit some FR properties but are synthesized by reacting phenolic monomers and formaldehyde. Formaldehyde is toxic and carcinogenic making this undesirable for continued use as FR. It is therefore desirable to develop methods to directly oligomerize phenolic monomers shown in Figure 4 directly to yield non-toxic FR.

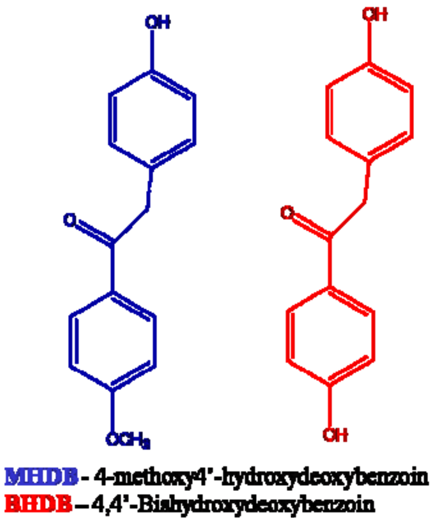


Figure 4: Structures of deoxybenzoin monomers

2b. Proof-of-concept studies on enzymatic polymerization of BHDB and MHDB (2007-2008)

We had explored the possibility of synthesizing oligomers of BHDB and MHDB using oxidoreductases under benign environment conditions in a TURI funded project during 2007-2008. The oligomers were characterized for their char yield upon heating in air using a TGA. The oligomers showed promising thermal stability as shown in Figure 5.

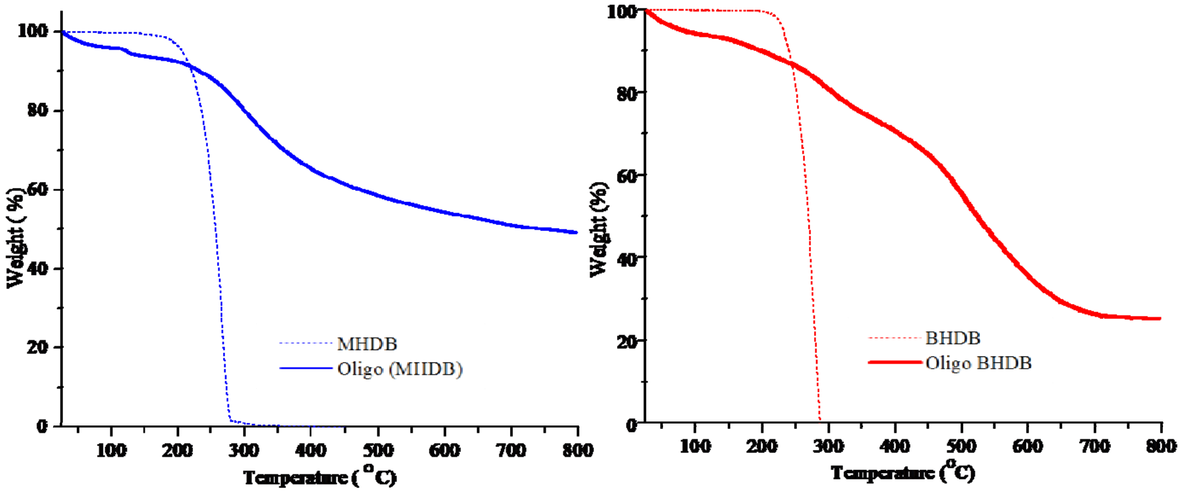


Figure 5: Thermogravimetric analysis for oligomers based on BHDB and MHDB

Beyond thermal stability studies, in order ascertain if indeed these oligomers have flame retardant characteristics it was also important to investigate the heat release capacity of these materials. A serious limitation of the synthetic protocol developed in our previous study was that the gravimetric yields of the oligomers were mediocre (around 40%) and needed improvement to be viable for commercial application. In addition the possibility of using these FR materials in specific applications had to be explored.

3. Research Goals and Objectives

The goal of this work was to create a new novel class of non-halogenated flame retardants with good char and heat release capacities by the use of biocatalytic enzymes in predominantly aqueous / benign solvent environment.

Another goal of this work was to explore the use of renewable raw materials (monomers and catalysts) for the synthesis of these FRs.

4. Relevance of the research to sustainability and toxic use reduction

Until recently the FR development process had not taken into account the toxicity of FR and their long term impact on or persistence in ecosystems. Flame retardant additives currently used consist of halocarbons like polybrominated diphenyl ether (PBDE), phosphorous and organophosphates or metal oxides. Studies show that these additives generate toxic, corrosive gases during combustion that are harmful to both air and water ecosystems. The presence of PBDEs in sperm whales, seals, dolphins and even in the humans, poses enormous environmental and health issues throughout the world. In addition to their inherent toxicity, their persistence is a worrying factor for environmentalists around the world.

The ongoing industrial production of these compounds should be reevaluated and preferably replaced by more environmentally friendly methods of production that minimize the overall impact on human health and our environment. It should be noted that the European Union has banned the use of many halogenated FR additives in specific applications, and it is possible that the US EPA may do the same. Thus, the development of safer alternatives to the halogenated FR materials is important both from environmental and commercial point of view.

This research focuses on solving important problems related to toxicity and persistence of additives that are commonly used for imparting flame retardancy to polymers. With increasing awareness of toxicity of halogenated FR there is a growing demand for development of new less toxic, high performance FR additives. One aspect of our proposed solution deals with the use of a sustainable hydrocarbon source (Cardanol from CNSL) processed using naturally occurring catalysts (enzymes/enzyme analogues) to yield polymers with improved FR properties. The reaction will be carried out at room temperature in predominantly aqueous media making the process clearly sustainable.

5. Materials and Methodology

5a. Materials

1. FRs based on synthetic phenols

   4,4'-bishydroxydeoxybenzoin (BHDB), monohydroxydeoxybenzoin (MHDB) were obtained from academic colleagues at UMass Amherst.

2. FRs based on natural materials

   Technical grade cardanol (MW 300) was obtained from Palmer International. It is an extract from Cashew Nut Shell Liquid (CNSL) containing more than 95% of cardanol. It was used without further purification. Hydrogenated cardanol was also obtained from Palmer international.

3. Catalysts and oxidants

   Horseradish peroxidase (HRP), type II, (200 U s/mg) used for the oligomerization process was purchased from Sigma Chemical Co., St. Louis, MO with RZ (Reinheitszahl value) > 2.2. Reinheitszahl is measured by the ratio of A_{403}/ A_{275}. It is a measure of hemin content of the enzyme. Soybean peroxidase (SBP) was obtained from Bioresearch Products, Inc. One unit of the enzyme (SBP) is defined as the amount of enzyme that catalyzes the conversion of 1 µmole of Guaiacol to its oxidized state per min at pH 6.0, 30 °C. Hydrogen peroxide (30 wt %) was obtained from Aldrich and was diluted to 0.3% (in deionized water), and this solution was used for oligomerization. Spectra-pore™ dialysis membrane was purchased from VWR Scientific. Potassium ferricyanide was purchased from Sigma Chemicals Co. (St. Louis, MO). All other chemicals were of reagent grade or better.

4. Coating materials

   A proprietary water based emulsion (70% solids) was provided by True Textiles Inc. for incorporation of FR materials and coating on fabric to impart flame retardancy.

5b. Characterization

1. Oligomer molecular weight: GPC analyses for the oligomers were carried out on an Agilent GPC with RI detector using DMF as a solvent and 0.05% Lithium Bromide. Poly (styrene) standards were used for calibrating the column. The sample solutions were filtered through 0.4 μm filters, and 20μL of solution was loaded into the column.

Structural characterization of oligomers: FTIR measurements were taken on a Thermo Scientific Nicolet 4700 with a Smart Orbit ATR accessory.

2. Thermal Characterization of FR oligomers:

a. Thermogravimetric analysis (TGA) was done using a TGA Q50 from TA Instruments, Inc. The sample was heated from ambient temperature to 700°C at a rate of 20°C/min under constant air flow at the rate of 10mL/min.

b. Pyrolysis Flow Combustion Calorimetry

There have been numerous methods developed for testing flammability and for the measurement of heat release rate during combustion of materials[7,8]. But most of the test results are heavily dependent on sample thickness[9], sample orientation[10], ventilation[11] and edge conditions. The sample size required for these flammability tests are usually high (on the order of 100g).

Thermogravimetric analyses of flammability have focused on the decomposition temperature or char yield and typically relate the chemical composition of the material to its flame test performance. Individually, these thermal stability parameters have not been true indicators of the flammability of a material.

Pyrolysis-combustion flow calorimetry (PCFC) is a test of flammability originally designed by the Federal Aviation Administration (FAA). In a PCFC experiment, the sample is heated using a linear temperature program. The volatile thermal degradation products are swept from the pyrolysis chamber by an inert gas and combined with excess oxygen in a furnace at flame temperatures to force complete combustion (oxidation) of the fuel as shown in Figure 6. Time-integration of the PCFC heat release rate gives the heat of complete combustion/oxidation. The char yield is measured by weighing the sample before and after the test. The maximum amount of heat released per unit mass per degree of temperature (J g^{-1} K^{-1}) is a material property which is a good predictor of flammability[12]. If the pyrolysis is conducted in air so that the organic char is completely oxidized during the high temperature hold period, time-integration of the oxygen consumption signal gives the net heat of complete combustion of the solid as would be determined in a high pressure oxygen bomb calorimeter.

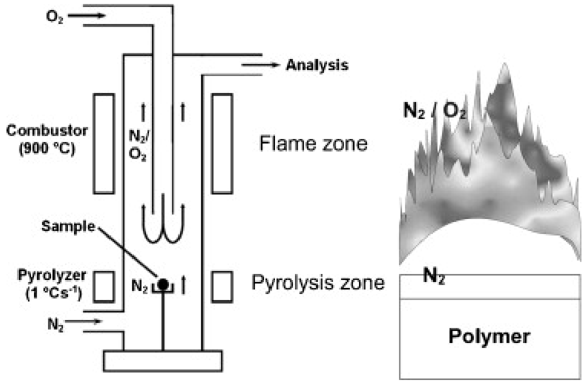


Figure 6: Schematic of a pyrolysis flow combustion calorimetry setup

In addition, PCFC possesses a significant advantage over the conventional techniques like bomb calorimetry in that only milligram size samples are required for analysis using PCFC[13].

6. Results and Discussion

6a. Co-oligomerization of BHDB and MHDB with phenol

Our previous research indicated that co-polymerization of phenol with BHDB and MHDB monomers would provide the following advantages::

- To increase the solubility of reactants before the start of the reaction
- To increase the yields of the reaction

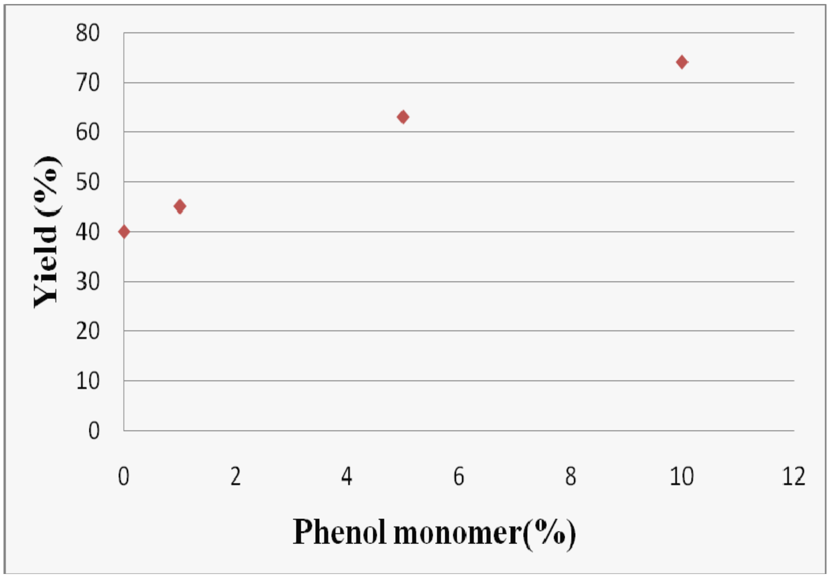


Figure 7: Effect of phenol incorporation in the reaction yield

Co-oligomerization of MHDB and BHDB with phenol was carried out in mixtures of pH 7 phosphate buffer and DMF (80:20) as shown in Figure 8. The insolubility of MHDB and BHDB in water necessitated the use of an organic solvent dimethyl formamide (DMF) in small amounts. The presence of phenol also assisted in the reaction mixture solubility. The reaction is a one–step process carried out in ambient conditions. The starting materials can be readily removed from the final products by simple purification methods such as dialysis. After the reaction was completed, the reaction mixture was dialyzed in 1000 molecular weight dialysis bags against water. The solvent in the mixture was then rotary evaporated under low pressure to yield the product.

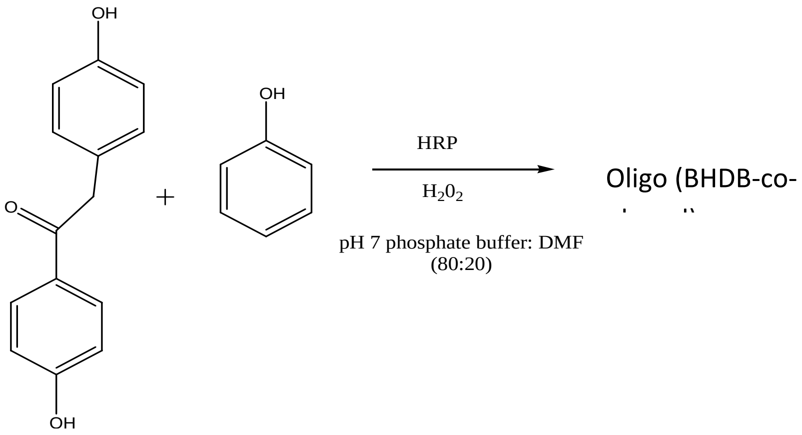


Figure 8: Scheme for the co-oligomerization of BHDB with phenol

6b. Oligomer molecular weight:

Gel Permeation Chromatography (GPC) was used to confirm the formation of oligomers and in determining the molecular weight of the oligomeric species. The resulting data are summarized in Table 2. Co-oligomerization not only serves to improve reaction yields, but it also increases the molecular weight of the products as shown in table.

#	Compound	Average Number Average Molecular weight (Mn)
1	**Oligo MHDB**	**3400**
2	**Oligo BHDB**	**3800**
3	**Oligo(BHDB-co-phenol)**	**8000-13000**
4	**Oligo(MHDB-co-phenol)**	**7700-1200**

Table 2: GPC results on molecular weight for the BHDB, MHDB based oligomers

6.c. Thermal properties:

Our initial tests with the TGA indicated that the products had very good thermal stability, quantified in terms of the char remaining beyond 700^{o}C. PCFC analysis was carried out to measure the heat release capacity of these materials as shown in Table 3.

#	Compound	Heat Release Capacity (HRC) (J/gK)	Char yield (%) PCFC
1	**Poly(BHDB)**	**15**	**51.9**
2	**Poly(MHDB)**	**19**	**40**
3	**Poly(phenol)**	**42**	**47.7**
4	**BHDB:Phenol (1:1)**	**30**	**58.7**
5	**BHDB:Phenol (1:5)**	**37**	**53.8**
6	**BHDB:Phenol (1:10)**	**55**	**56**
7	**MHDB:Phenol (1:1)**	**46**	**55.1**
8	**MHDB:Phenol (1:5)**	**46**	**54.7**
9	**MHDB:Phenol (1:10)**	**53**	**59.1**

Table 3: PCFC results for BHDB and MHDB copolymers with phenol

Oligomerization imparts thermal stability and renders them non-flammable with heat release values lower than even Nomex® (a well known fire-resistant polymer). It can be seen that there is a slight increase in the HRC values with increasing phenol content in the polymer. However, there is a significant increase in the yield of these reactions from 40% to almost 80%. The percent char remains more or less constant, due to the formation of similar decomposition products from the deoxybenzoin units. Moreover, the total heat release for all these samples was also quite low (typically around 5 kJ/g) as compared to all commodity plastics (typically around 30 kJ/g). Both BHDB and MHDB copolymers follow a similar trend in terms of the copolymer yield and HRC values.

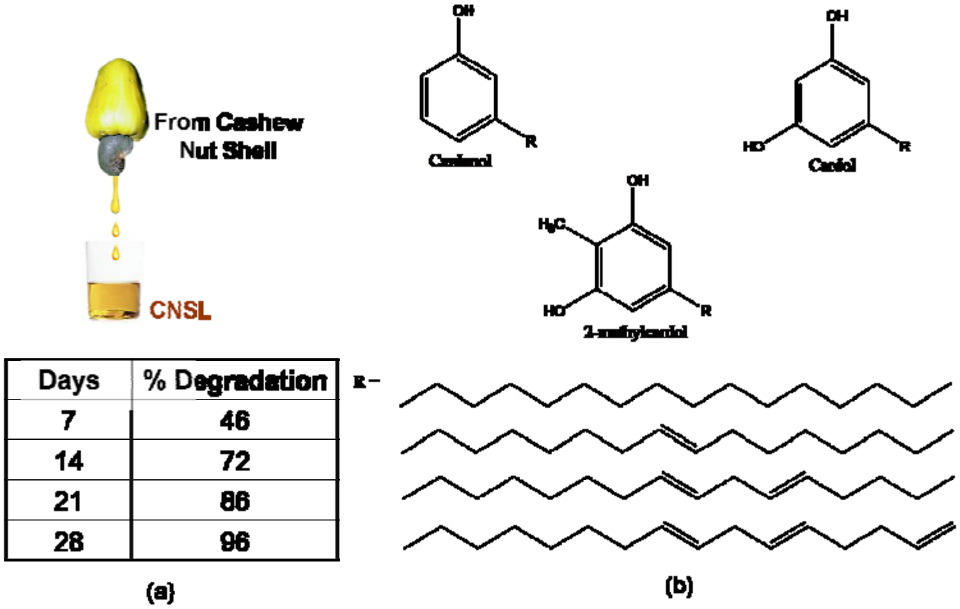
Summary:

- An enzymatic route for the synthesis of oligomers of BHDB and MHDB was carried out in benign solvent conditions.
- Co-oligomerization significantly improves the reaction yields.
- Both the homo and co-oligomers of BHDB and MHDB based compounds are extremely fire resistant with heat release values less than 50 J/gK and can be classified as ultra-fire resistant materials.

7. Polymerization of cardanol derived from cashew nut shell liquid

7.1 Cashew Nut Shell Liquid (CNSL):

Cashew nut shell liquid (CNSL) is a renewable resource and the by-product of cashew nut industry. CNSL is a mixture of anacardic acid, cardanol, and traces of cardol and 2-methylcardol. The alkyl side chain (R) in these compounds can be saturated, monolefinic (8-ene), diolefinic (8,11-diene) and triolefinic (8,11,14-triene). Due to the decarboxylation of anacardic acid during the distillation process, cardanol is the main component of distilled CNSL (Figure 9). Cardanol is a phenol derivative containing a C15 unsaturated hydrocarbon chain in the meta position with the number of double bonds varying from 1 to 3[14].



Days	% Degradation
7	46
14	72
21	86
28	96

Figure 9: (a) Bio-degradability data on cardanol – Evaluation report by TURI and (b) Structures of CNSL derivatives

The presence of phenolic groups and an unsaturated hydrocarbon chain in cardanol offers opportunities to functionalize and tune the structure for desired properties. This monomer is a renewable raw material with low levels of persistence in the environment. The biodegradability studies[15] conducted on this material (table in Figure 9) indicates excellent degradation properties.

Cardanol and its derivatives have been investigated for use in a variety of applications[16]. Cardanol has been used as a starting material with lignin based compounds for synthesizing polyurethanes with good thermal and mechanical properties[17]. The unsaturated chain of cardanol has been grafted with natural rubber to serve as an additive and the resulting compound had much better thermo-oxidative stability[18]. Derivatives of cardanol have also shown promise as anti-oxidants in the stabilization of gasoline[19]. However most of the synthetic protocols employed for modifying cardanols are not environmental friendly.

7.2 Cardanol polymerization with Hematin

Hematin is an iron containing porphyrin which has shown promise as an oxidative catalyst for the polymerization of anilines and phenols. It is extracted from porcine blood, making it less expensive than oxidoreductase enzymes.

In our study, we have used hematin as a catalyst for the oxidative oligomerization of cardanol as shown in Figure 10. This reaction was performed under solventless conditions. Hematin was added to a viscous solution of cardanol and the reaction was initiated by the addition of hydrogen peroxide. The reaction mixture was stirred for 24 hours at room temperature. A portion of the reaction mixture during the propagation of the reaction was dissolved in DMF for a GPC analysis which revealed a molecular weight of about 4500 Daltons.

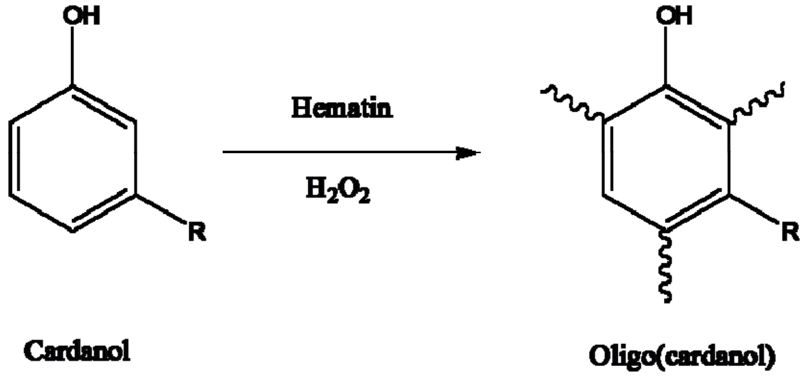


Figure 10: Scheme for polymerization of cardanol with hematin

The thermal stability of the product is shown in Table 4. The product was thermally very stable with more than 20% remaining after 600°C.

Compound	% remaining at 250°C	% remaining at 450°C	% remaining at 600°C
Oligo(cardanol)	**98**	**72**	**21**
Oligo(hydrogenated cardanol)	**21**	**3**	**0**

Table 4: TGA of material synthesized with Hematin

The product was totally insoluble in most organic solvents. Fourier transform infrared spectroscopy on these products showed that all the double bonds vanished after the completion of the reaction, suggesting the possibility of extensive cross-linking of the double bonds in the side chain of cardanol leading to an insoluble product as shown in Figure 11 (reaction scheme on the left). This cross-linking phenomenon with cardanol was confirmed by trying out a model reaction in which a hydrogenated form of cardanol (Figure 12) was reacted with hematin. The oligomerization reaction did not proceed, indicating that there is only extensive cross-linking of the double bonds with the regular non-hydrogenated form of cardanol and no real oligomerization was taking place.

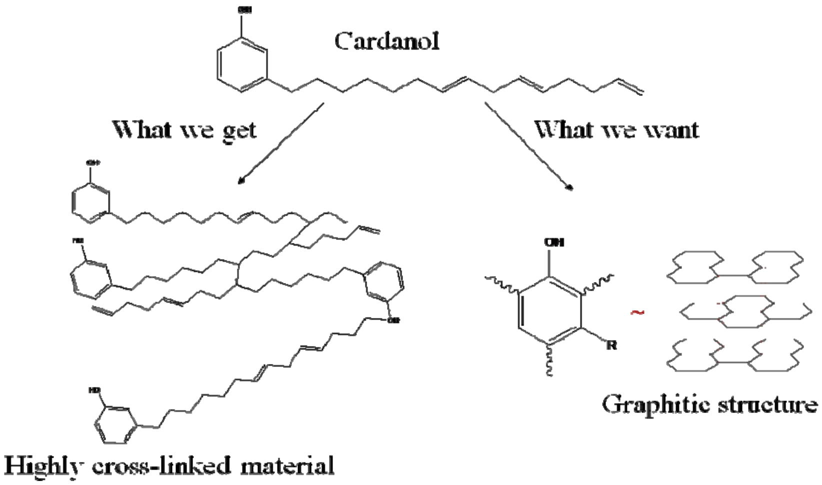


Figure 11: proposed scheme for cross-linking of cardanol with hematin

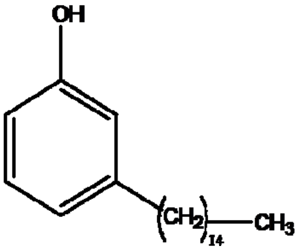


Figure 12: Structure of hydrogenated cardanol

7.3 Cardanol polymerization in aqueous media

The polymerization of 2,6-dimethylphenol in water with various oxidants with good polymer yields has been reported [20]. High pH conditions provide an ionized phenol which can be polymerized readily using a strong oxidant. The reaction scheme for our reaction modeled from the above mentioned concept is shown in Figure 13**.**

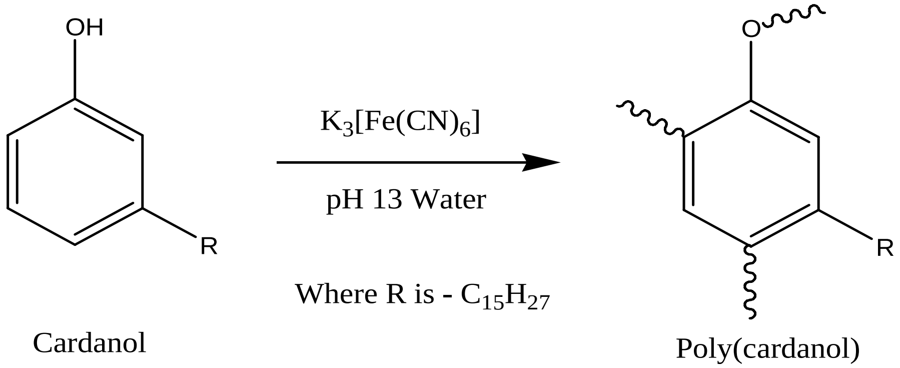


Figure 13: Scheme for cardanol polymerization in water

Cardanol when dissolved in high pH forms a dark pink colored solution which then oligomerizes to a dark brown insoluble product. Cardanol (0.3g, 1mmol) was dissolved in 100ml water containing sodium hydroxide (2g, 50 mmol) maintained at 50°C. Potassium ferricyanide (0.658g, 2 mmol) was then added to the solution and the mixture was vigorously stirred at 1100 rpm for 6 hours. The oligomer was obtained as a brown mass by filtration after salting out with sodium chloride (5.84g, 0.25 mol) and washing with water. The filtered product was then washed with hexanes in a soxhlet extractor for 24 hours. Soxhlet extraction helps remove residual monomer.

The Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectra of (a) cardanol and (b) poly (cardanol) are as shown in Figure 14. The figure shows characteristics peaks at 1240, 1190 and 1155 cm^{-1} which correspond to vibrations of C(Ar)-O-C(Ar) and C(Ar)-OH linkages. There is large decrease in the intensity of the peak at 3400 cm^{-1} which corresponds to vibrations due to O-H linkages indicating the possibility of extensive C-O-C coupling. The spectrum correlates very well with the IR spectra reported in the literature[21] for oligo (cardanol).

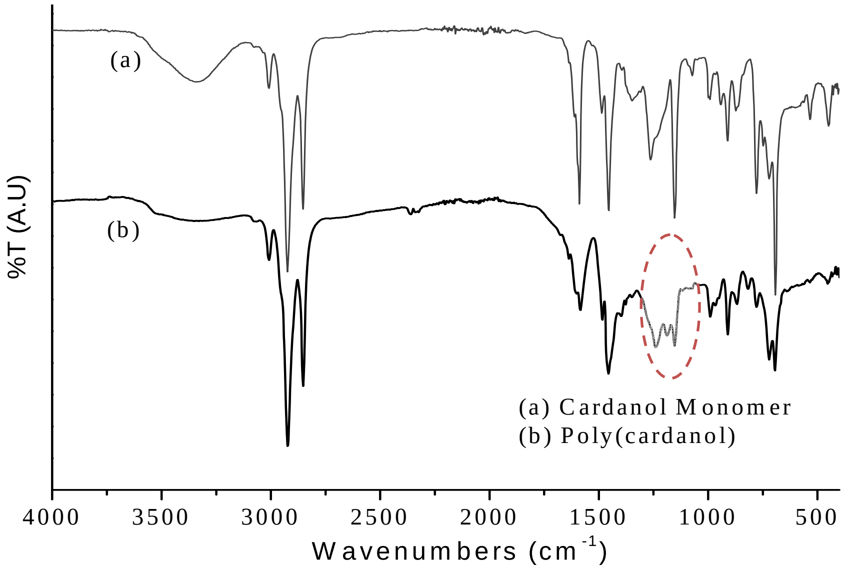


Figure 14: FTIR-ATR analysis poly(cardanol) synthesized using $K_3[Fe(CN)_6]$ in water

Compound	% remaining at 300°C	% remaining at 500°C	% remaining at 800°C
Cardanol monomer	**17**	**2**	**0**
Oligo(cardanol)	**98**	**65**	**22**

Table 5: TGA of poly(cardanol) synthesized in water using $K_3[Fe(CN)_6]$

It can be seen clearly from Table 5 that there is a marked increase in the thermal stability of the polymer with 22% remaining even at temperatures as high as 800°C. The high amount of char formed on combustion can potentially inhibit flame propagation through the substrate matrix. In spite of its very good performance in inhibiting char, the heat release values tested for these materials are close to 280 J/gK making reasonably flammable. The reason for this high HRC value is currently being investigated.

The use of potassium ferricyanide as the catalyst in the cardanol reaction increases its overall environmentalimpact, making this a less favorable alternative FR. However, if the oligomers of cardanol exhibit promising properties, it would be advantageous to investigate other synthesis routes that would eliminate this problem.

Summary:

- The oligomerization of cardanol was successfully accomplished in completely aqueous medium for the first time.
- The Oligo(cardanol) synthesized had good thermal stability with reasonably good heat release capacity (285 J/gK) and can be categorized as a moderately fire resistant material.
- Additional studies need to be conducted to find an alternate catalyst that allows this reaction to go forward.

8. Evaluation of polyphenol as an FR coating for automotive upholstery applications

As part of this research we collaborated with True Textiles Inc. to test the performance of our polyphenol based FR materials fortextile applications. The effectiveness of the FRs was tested on fabrics used in automotive upholstery application. A standard MVSS302 horizontal burn for evaluation of automotive upholstery was performed on samples coated with water based acrylic dispersion of the FR.

8.1 Dispersion of FR into acrylic latex

The particle size of the oligo(cardanol) synthesized in water was reduced by ball milling for 24 hours to facilitate dispersion in the acrylic based water emulsion. After milling, the particles were physically mixed into the emulsion.

8.2 Fabric coating and drying

The fabric was coated using a blade knife coater as shown in Figure 15. The dry add-on of FR latex is normally approx 50-60 grams per square meter of the sample to meet the requirements of the company standard. The fabric after coating was dried in an oven with constant air flow at 140^{o}C for 6 minutes.

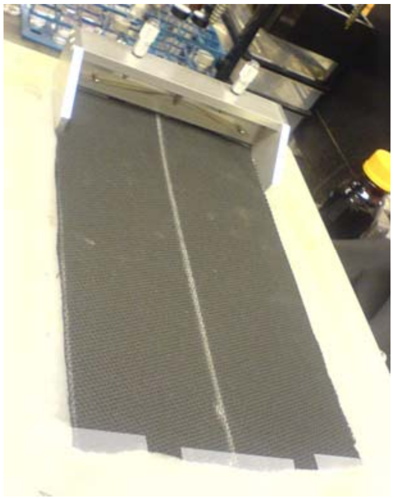


Figure 15. Blade knife coating of automotive textile

8.3 Coated fabric performance

The coated fabric was sent to True Textiles Inc for standard testing procedures. Based on their testing and evaluation, the performance of the sample was not up to the recommended industrial standards as a flame retardant coating. The reason for the lack of performance of the coated sample could be attributed to the following:

- Non-uniform dispersion of cardanol in the water based emulsion. Cardanol has a long hydrophobic aliphatic side chain. This would lead to a micro phase separation of these particles in a water based emulsion system.
- The long waxy chain might facilitate burning due to its intrinsic flammability (as shown by PCFC analysis of cardanol).
- The oligocardanol is a fairly low molecular weight product. Higher molecular weight products would possibly have better FR properties.

We are currently trying to resolve some of these problems and specifically on improving the performance of these oligomers to better cater to the industrial needs and 'real world' applications.

9. Conclusions:

- Environment friendly methods of syntheses have been employed for a new array of polyphenolic flame retardant materials.
- FRs based on copolymers of BHDB/MHDB exhibit
  - Very good thermal stability
  - Very low heat release (comparable to Nomex™)
  - Good char yield
  - Ultra fire –resistant material characteristics
- A single step synthesis for oligomers of cardanol (a naturally occurring phenol) in water has been accomplished to yield a thermally stable material. Efforts are underway to further tune the synthetic strategy, to yield FR additives that can be dispersed easily in aqueous emulsions suitable for coating applications
- Performance of the non-halogenated FRs in automobile upholstery fabric is currently being investigated

10. Future Work

- Polymers of other phenolic monomers are being investigated.
- We are investigating the possibility of tethering titania nano-particles to the synthesized polyphenols to give enhanced flame retardant properties.
- Coating parameters (preparation of dispersion) are being optimized to obtain more stable and uniform dispersions of FR that can be coated on fabric.
- Quantification of FR materials based on other standard flame retardant quantification techniques such as measurement of Limiting Oxygen Index (LOI) values is also being explored.

11. Accomplishments

- S. Ravichandran, S. Nagarajan, R. Bouldin, J. Kumar and R. Nagarajan "**Oxidative polymerization of cashew nut shell liquid derivatives in water to yield naturally derived flame retardant material**" preprint submitted to 238th ACS National Meeting, PMSE division, Washington, DC to be presented in August 2009.

- 2009 National Science Foundation (NSF) Scholar travel grant was obtained by the student Sethumadhavan Ravichandran to travel to for 13th Annual Green Chemistry & Green Engineering Conference, Washington DC in June 2009.

- S. Ravichandran, S. Nagarajan, R. Bouldin, J. Kumar and R. Nagarajan, **"Greener routes to non-halogented flame retardants"**, Abstract submitted to the Journal of Clean Production, May 2009.

- A joint proposal with U.S Army Natick on improving flame retardant properties of natural fiber-based composites has been submitted to the "Strategic Environmental Research and Development Program", Department of Defense in March 2009.

- S. Ravichandran, S. Nagarajan, R. Bouldin, J. Kumar and R. Nagarajan "**Oxidative Polymerization of Cashew Nut Oil Derivatives in Water to Yield Naturally Derived Flame Retardant Material**" poster presented at Sukant Memorial Symposium, December 2008.

- **"Biocatalytically synthesized polyphenol-based Flame Retardant Materials"** Patent disclosure under preparation

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