Greener Routes to Non-Halogenated Flame Retardants

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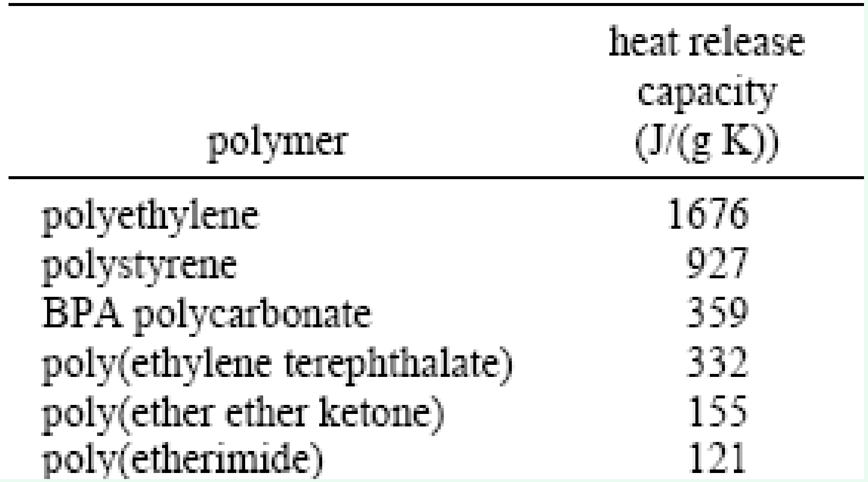
4th November 2009

Flame Retardant Materials

- Most commercial polymers are combustible and release large amounts of heat during burning

Heat Release during combustion of plastic materials

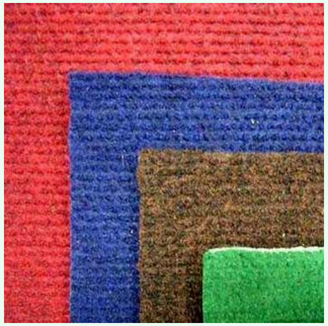


polymer	heat release capacity (J/(g K))
polyethylene	1676
polystyrene	927
BPA polycarbonate	359
poly(ethylene terephthalate)	332
poly(ether ether ketone)	155
poly(etherimide)	121

- Flame retardant (FR) materials control/reduce the risk of fire and have a direct impact on safety
- Polymer industry is one of the biggest consumers of FRs
- > 900,000 tons/year of additives used for making commercial polymers flame resistant

Flame Retardant Materials

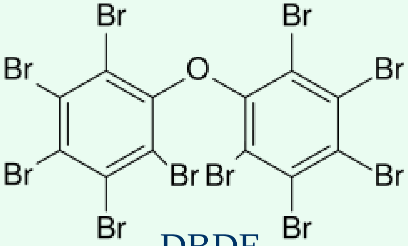
Every commonly used plastics product contain FRs

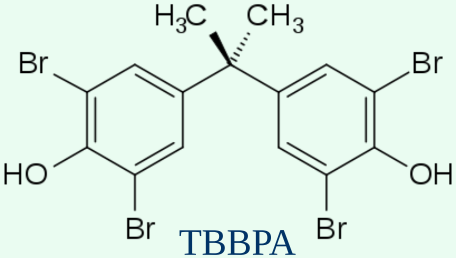


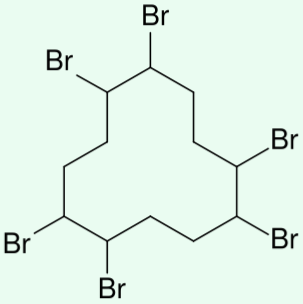
Most commonly used FR's and their problems!

FR materials are based on either

- ✓ Halogens – [(Bromine (BFRs), Chlorine]
- ✓ Phosphorous, Antimony
- ✓ Metal salts and hydroxides


DBDE


TBBPA


HBCD

Problems with Halogenated FR's

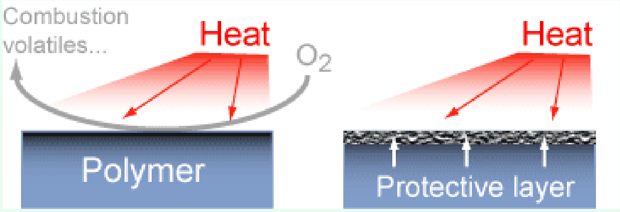
- ✧ Toxicity concerns - Endocrine disruption, Carcinogenicity and immune suppression.
- ✧ Environmental persistence of the halogenated FR's - Traces of DBDE seen in whales, dolphins and humans!

The European Union has banned the use of halogenated FR additives

'**Brominated Flame Retardants:** Rising Levels of Concern' - Sarah Janssen, *Health Care without Harm*

Mechanism of FR

FR materials can act chemically and/or physically in the either gas, liquid phase and/or solid phase.



Physical action

Thermal insulation barrier (e.g. Phosphorous/Boron compounds)

Cooling by endothermal processes (e.g. metal hydroxides)

Chemical action

Inhibition by stopping radical propagation (e.g. Halogenated FR)

1. Thermal degradation and release the respective acids
2. Acids react with the highly reactive H• and OH• radicals in the flame
3. Resulting halogen radicals have a lower potential to propagate

Our Hypothesis

If *radical scavenging* and *char formation* are key attributes to good FR, other efficient, non-toxic radical quenchers can serve as effective FR

Desired Properties of an FR

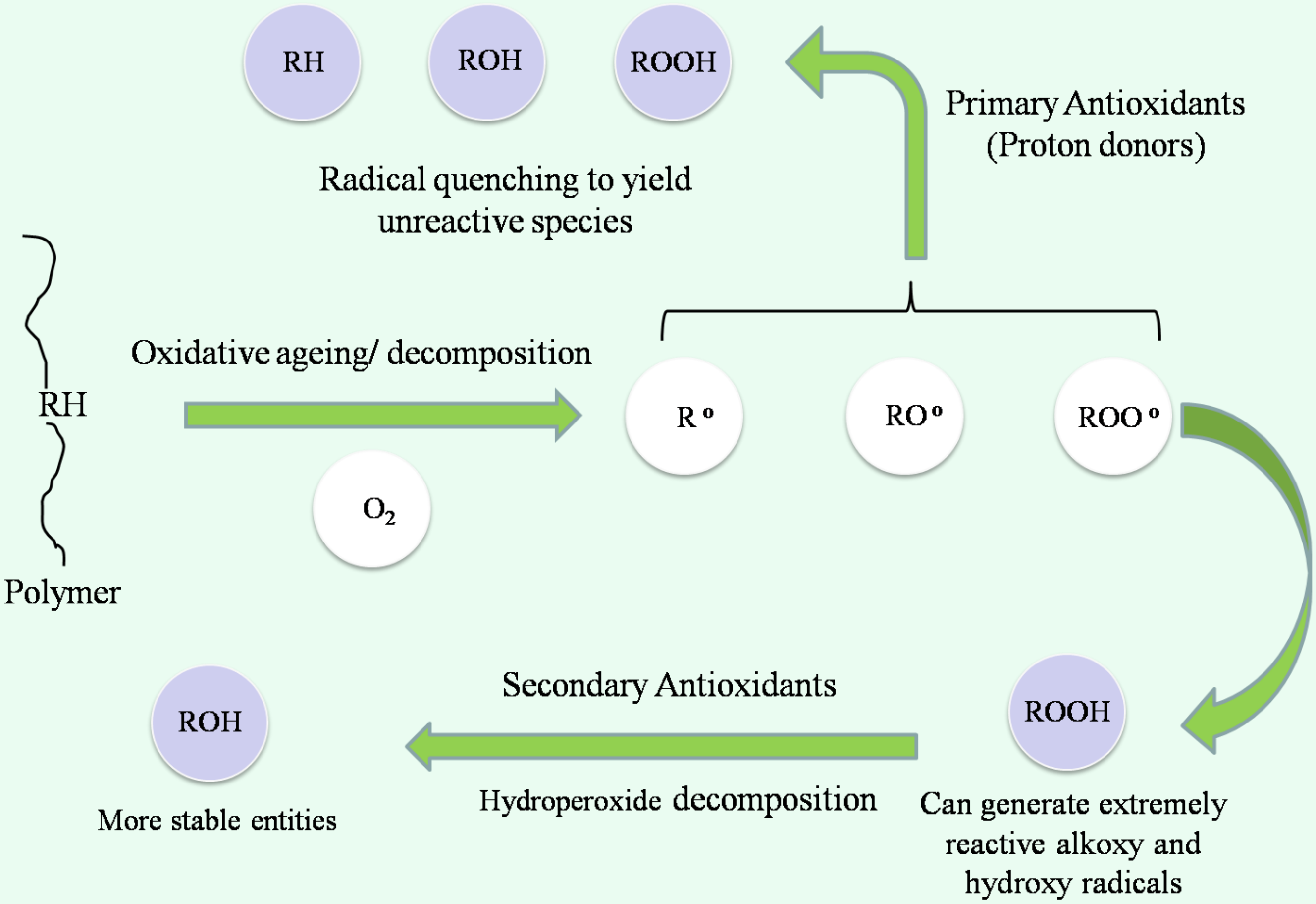
- Char formation – Through physical action or Intumescences

- Radical Quenching

  - ✓ Abstraction of reactive groups from the system under fire
  - ✓ **The presence of an easily abstractable radical which can be released over a narrow range of temperature**
  - ✓ Similar or lower decomposition temperatures as compared to the polymer matrix

- Solubility and dispersion properties to facilitate ease of incorporation and processing

Phenolics as Radical Scavengers



RH

ROH

ROOH

Primary Antioxidants
(Proton donors)

Radical quenching to yield
unreactive species

RH

Polymer

Oxidative ageing/ decomposition

O_2

R°

RO°

ROO°

Secondary Antioxidants

ROH

ROOH

More stable entities

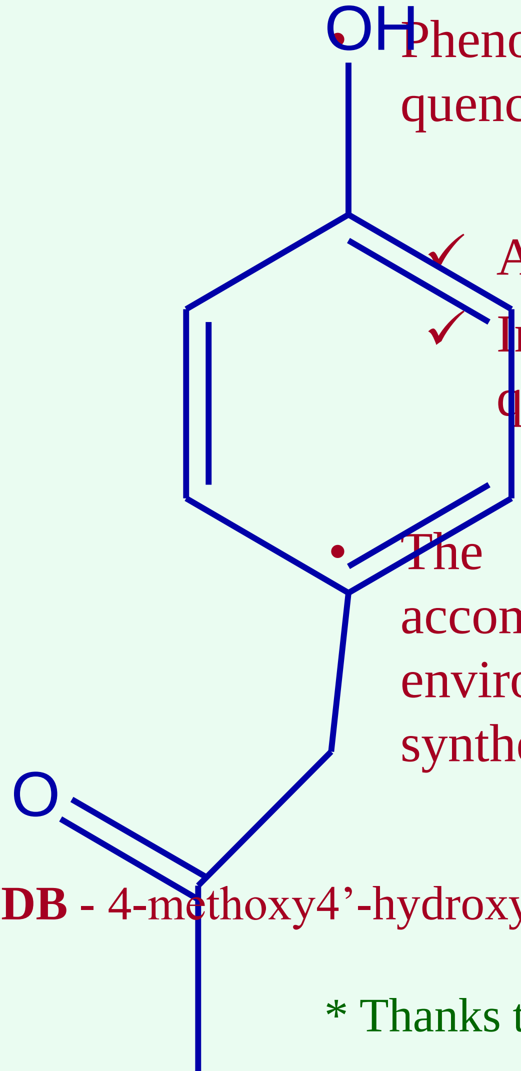
Hydroperoxide decomposition

Can generate extremely
reactive alkoxy and
hydroxy radicals

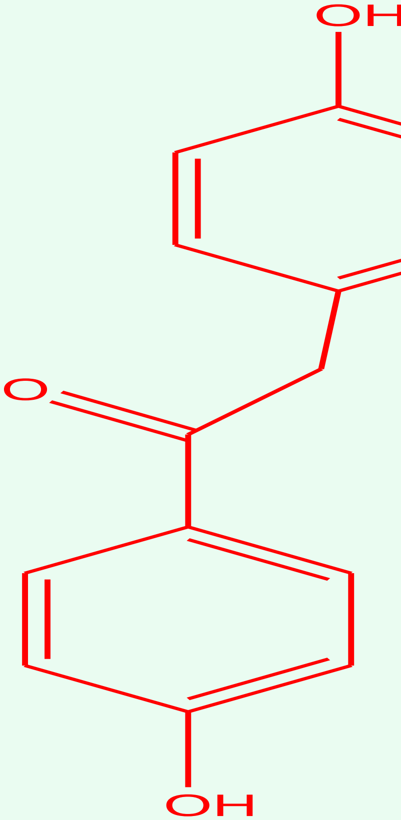
Polyphenolic materials could serve as potential FR’s because of their char and radical quenching ability

Poly(phenol) based materials as FR's

TURI Funded Project 07-08



- Phenolic monomers* with radical quenching potential can be oligomerized
  - ✓ Avoid leaching of monomers
  - ✓ Increase concentration of radical quenchers
- The process of polymerization was accomplished by the use of benign environmentally friendly enzymatic synthesis

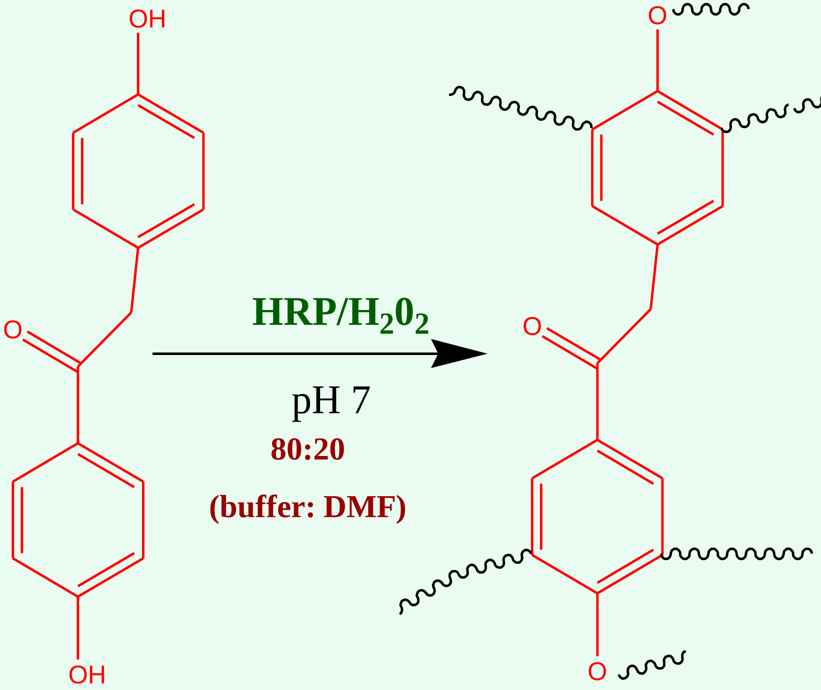


MHDB - 4-methoxy4'-hydroxydeoxybenzoin

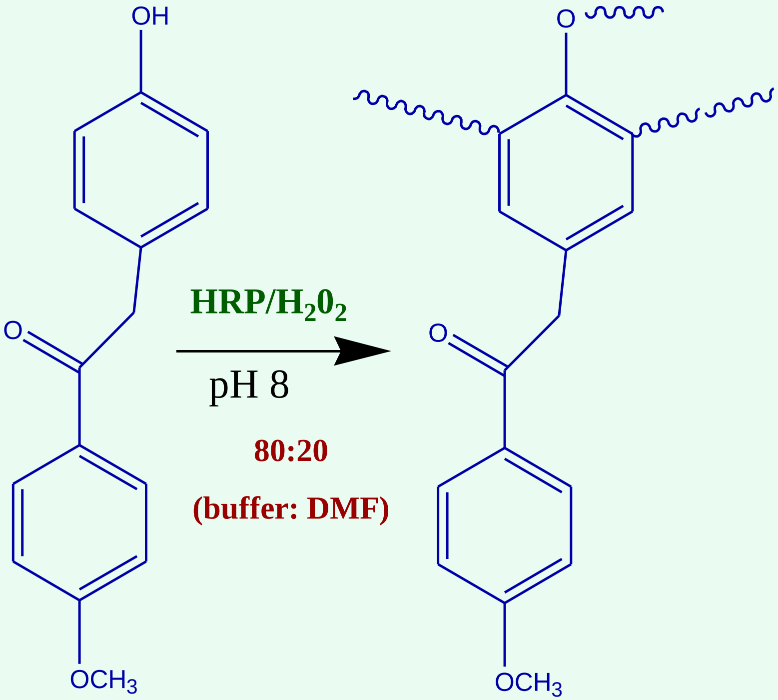
BHDB – 4,4'-Bishydroxydeoxybenzoin

* Thanks to UMASS Amherst for supplying monomers

Enzymatic polymerization of Benzoins



BHDB



MHDB

Enzyme Catalyzed polymerization:

✓Horseradish Peroxidase (HRP) – naturally occurring eco-friendly catalyst

✓Reaction carried out in environmentally-friendly solvents

Characterization of FR materials

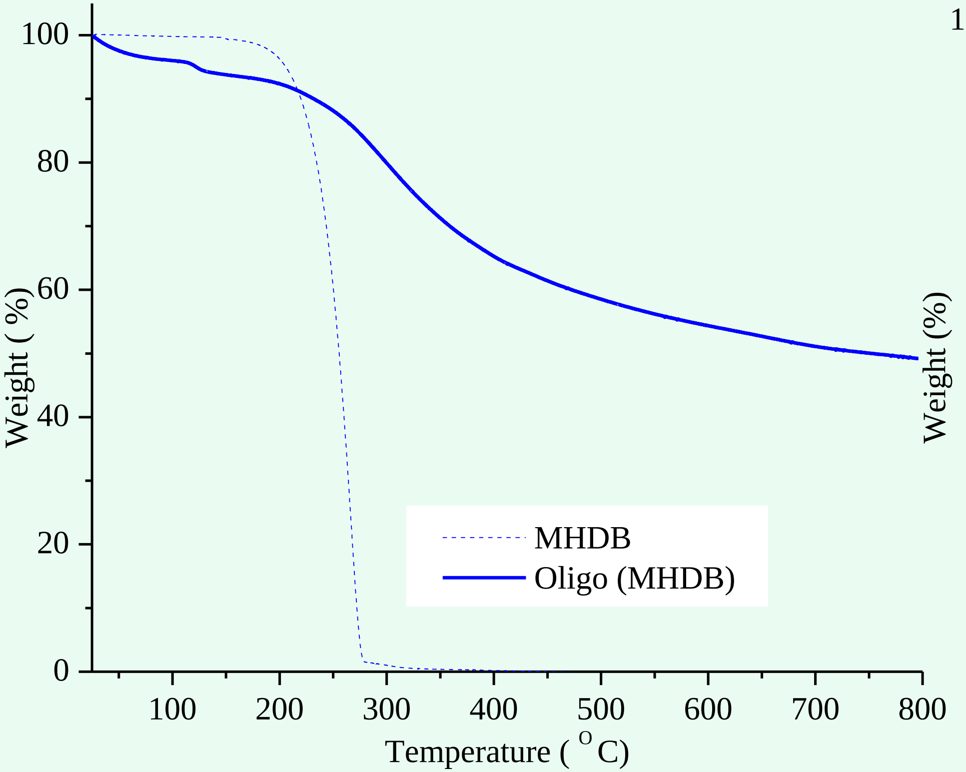
- Thermogravimetric Analysis (TGA)

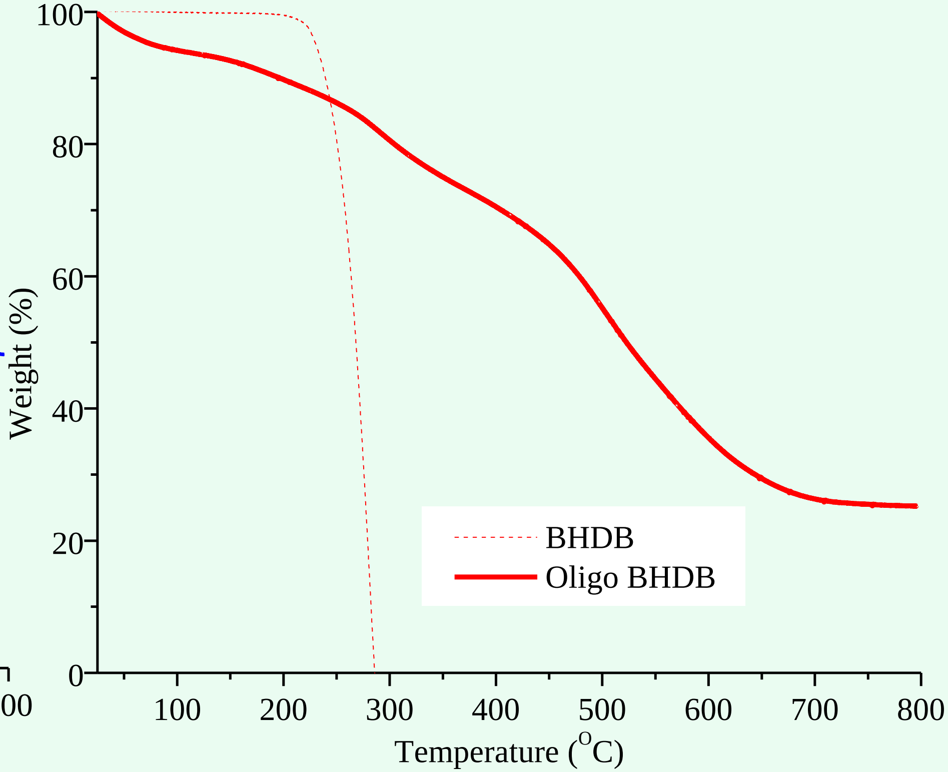
  Technique that measures the thermal stability of a polymer with respect to the % material remaining at various temperatures.

- Pyrolysis Combustion Flow Calorimetry (PCFC)

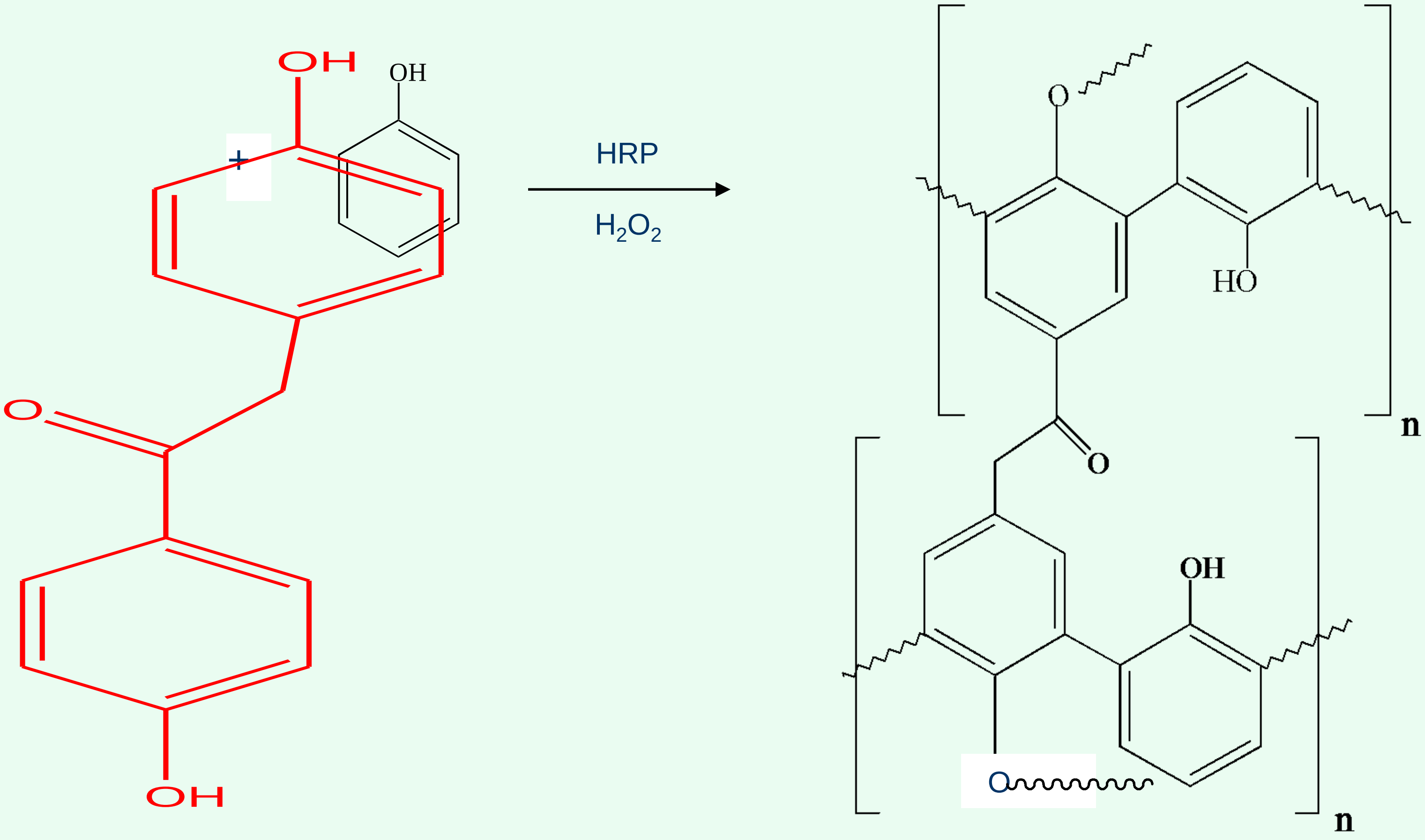
  - ✓ Technique that measures the heat release capacity of the material and gives % char yield in a nitrogen atmosphere.
  - ✓ Federal Aviation Authority (FAA) approved test for FR materials.

Thermal Stability of BHDB, MHDB polymers





Copolymerization with Phenols



Phenol was used as a spacer with the BHDB units to increase solubility of the reaction mixture

TGA data for the BHDB copolymers

Polymer	**% At 200^{o}C**	**% At 500^{o}C**	**% At 700^{o}C**
Poly(BHDB)	97	14	9
Poly(phenol)	93.2	17	11.4
BHDB:Phenol (1:1)	94	25	19
BHDB:Phenol (1:5)	95.7	26.5	21
BHDB:Phenol (1:10)	93.5	34	29

TGA analysis was carried out under air purge with a heating rate of 20^{o}C/min

TGA data for the MHDB copolymers

Polymer	**% At 200^{o}C**	**% At 500^{o}C**	**% At 700^{o}C**
Poly(MHDB)	92.5	58	52.3
Poly(phenol)	93.2	17	11.4
MHDB:Phenol (1:1)	94.8	63.8	34
MHDB:Phenol (1:5)	93	48	39.5
MHDB:Phenol (1:10)	95.4	73	68.7

TGA analysis was carried out under air purge with a heating rate of 20^{o}C/min

Pyrolysis Combustion Flow Calorimetry

BHDB and Co-polymers

#	**Polymer**	**Heat Release Capacity (HRC) (J/gK)**	**Total Heat Release (THR) (kJ/g)**	**Char yield (%) PCFC** [a)]
1	Poly(BHDB)	15 ± 0.6	3.3 ± 0.4	51.9
2	Poly(phenol)	42.0 ± 3.6	3.1 ± 0.7	47.7
4	BHDB:Phenol (1:1)	30	4.5	58.7
5	BHDB:Phenol (1:1)	37	3.9	53.8
6	BHDB:Phenol (1:1)	55	7.2	56

a) Measured at 900 ˚C

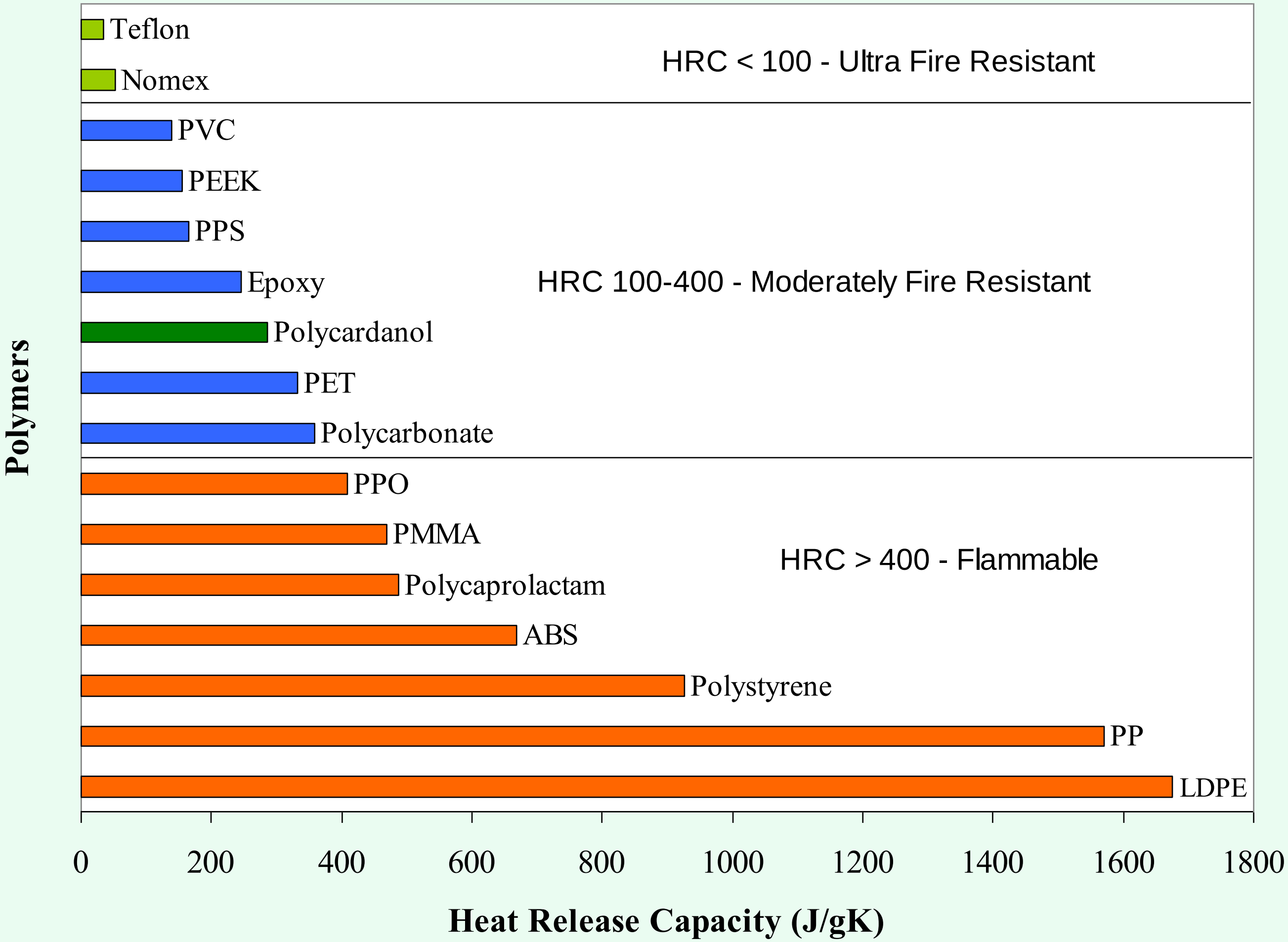
Pyrolysis Combustion Flow Calorimetry

MHDB and Co-polymers

#	**Polymer**	**Heat Release Capacity (HRC) (J/gK)**	**Total Heat Release (THR) (kJ/g)**	**Char yield (%) PCFC** [a)]
1	Poly(MHDB)	19 ± 1.7	2.8 ± 0.5	40.0
2	Poly(phenol)	42.0 ± 3.6	3.1 ± 0.7	47.7
3	MHDB:Phenol (1:1)	46	6.8	55.1
4	MHDB:Phenol (1:1)	46	7.4	54.7
5	MHDB:Phenol (1:1)	53	7.6	59.1

a) Measured at 900 ˚C

Comparison of Heat Release Capacities



All Polymers HRC in Ultra Fire Resistant

BHDB and MHDB copolymers ~ 40-50

Poly(BHDB) ~ 19

Poly(MHDB) ~ 12

Comparison with Halogenated FR

S. No	**Compound**	**Percentage remaining at 420^{O}C**
1	**Halogenated FRs**	< 10%
2	**Poly(BHDB)**	62
3	**Poly (BHDB -co- Phenol)**	> 60%
4	**Poly (MHDB)**	58
5	**Poly (MHDB-co- Phenol)**	> 60%

Pillai, V.S.; Prasad, A.R.R.; Menon, J.D.; Sudha, V.G.; Jayakumari, M.B.; Kumar, C.; Pavithran, V.K.; Tikku & Pradhan, N.K *J. Appl. Polym. Sci.*, 66, 2157**, 1997 .** Barontini, F.; Cozzani, V.; Petarca, L.; *Ind. Eng. Chem. Res.* **2001**, 40, 3270.

Molecular Weight for Oligomers

S. No	Compound	Approximate Mn (Number average mol. weight)
1	Oligo MHDB	3400
2	Oligo BHDB	3800
3	Oligo(BHDB-co-phenol)	8000-14,000
4	Oligo(MHDB-co-phenol)	7700-12200

Polymers were dissolved in DMF. A calibration curve with PS standards was used.

Phenolic FRs – A real possibility!

- Very good FR properties of polymers from phenolic based BHDB and MHDB monomers substantiate our hypothesis.

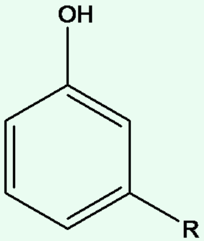
- Poly BHDB and MHDB exhibit good FR property
  - monomers are toxic and prepared by harsh synthetic routes.

- Can we explore the possibility of polymerizing phenolic compounds from natural sources.

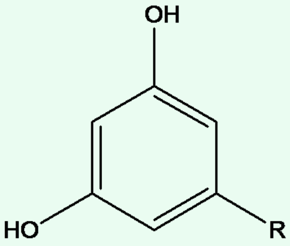
Cardanol – A renewable source

From Cashew Nut Shell

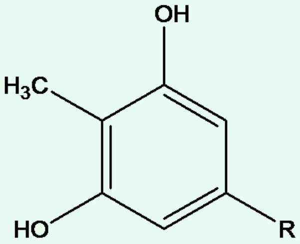
CNSL



Cardanol



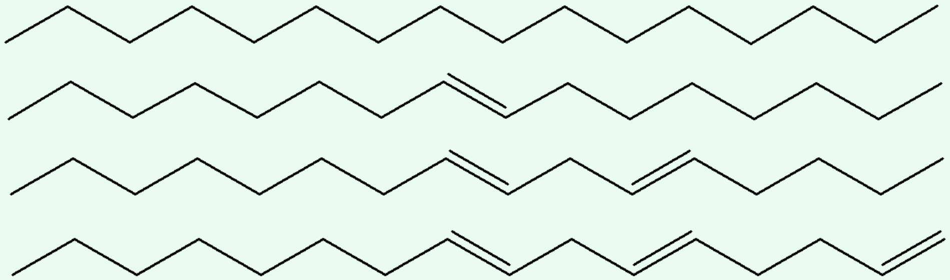
Cardol



2-methylcardol

Days	% Degradation
7	46
14	72
21	86
28	96

R =



Evaluation report on CNSL by Toxic Use Reduction Institute

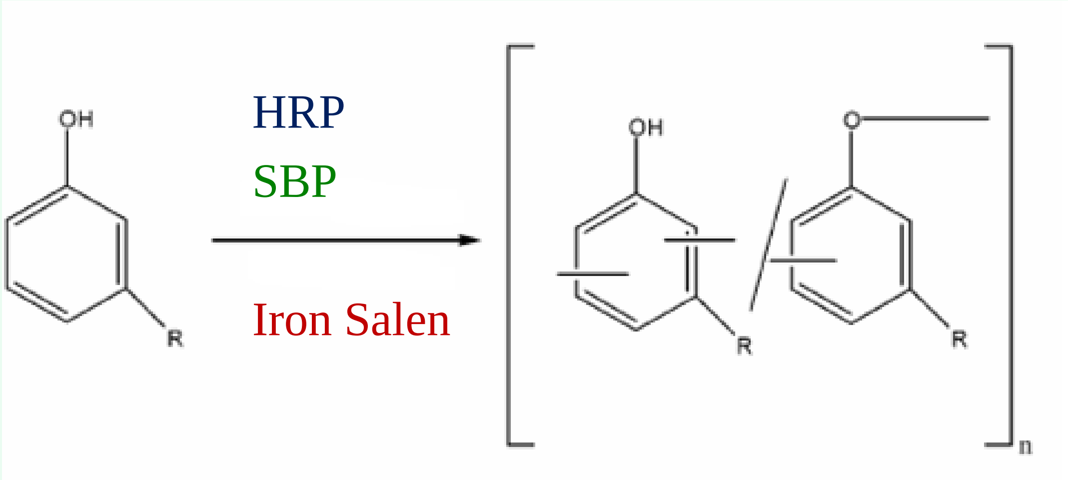
Current use of CNSL

- Cardanol based resins used as a environment friendly replacement for phenol based resins in various applications.
  - ***Cardolite*** **-** protective coatings to friction lining products.
  - ***Palmer International*** **-** coatings, paints, curing agents, friction materials based on CNSL based materials

- Brazil and India are the two largest suppliers of CNSL in the world.

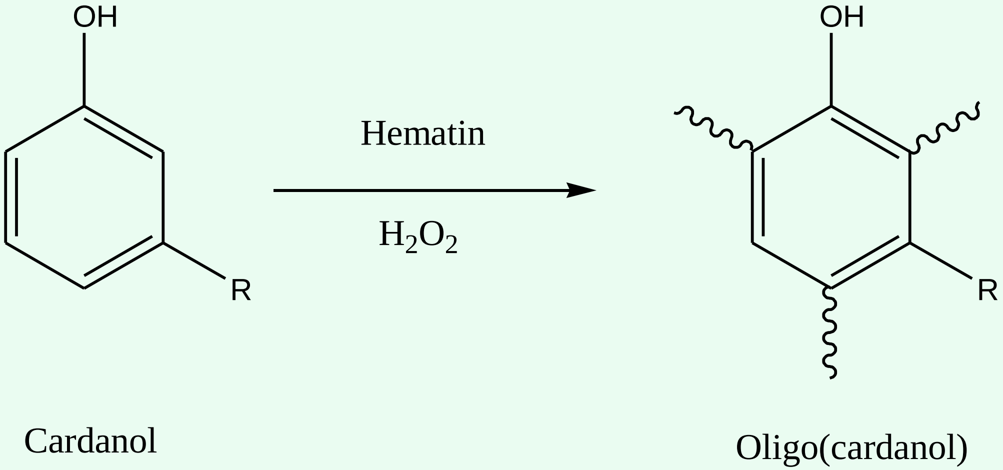
FRs based on polymers of cardanol?!

- Can cardanol be polymerized using benign solvents to obtain a FR material?
- If the polymer exhibits Flame Retardant properties, we would have the several advantages of using,
  - A renewable non-toxic material as an FR
  - Developing a benign method for synthesis of such FR’s
  - Possible use as Antioxidant
- Previous attempts on polymerizing cardanol



K. Shridhara Alva, Padma L. Nayak, Jayant Kumar, Sukant K. Tripathy, *Journal of Macromolecular Science*, **1997**, 34, 665

Solvent-less Polymerization of Cardanol



Material	% remaining at 250ºC	% remaining at 420ºC
Oligo (cardanol) with Hematin	98	71
Oligo (cardanol) with Fe salen	96	80

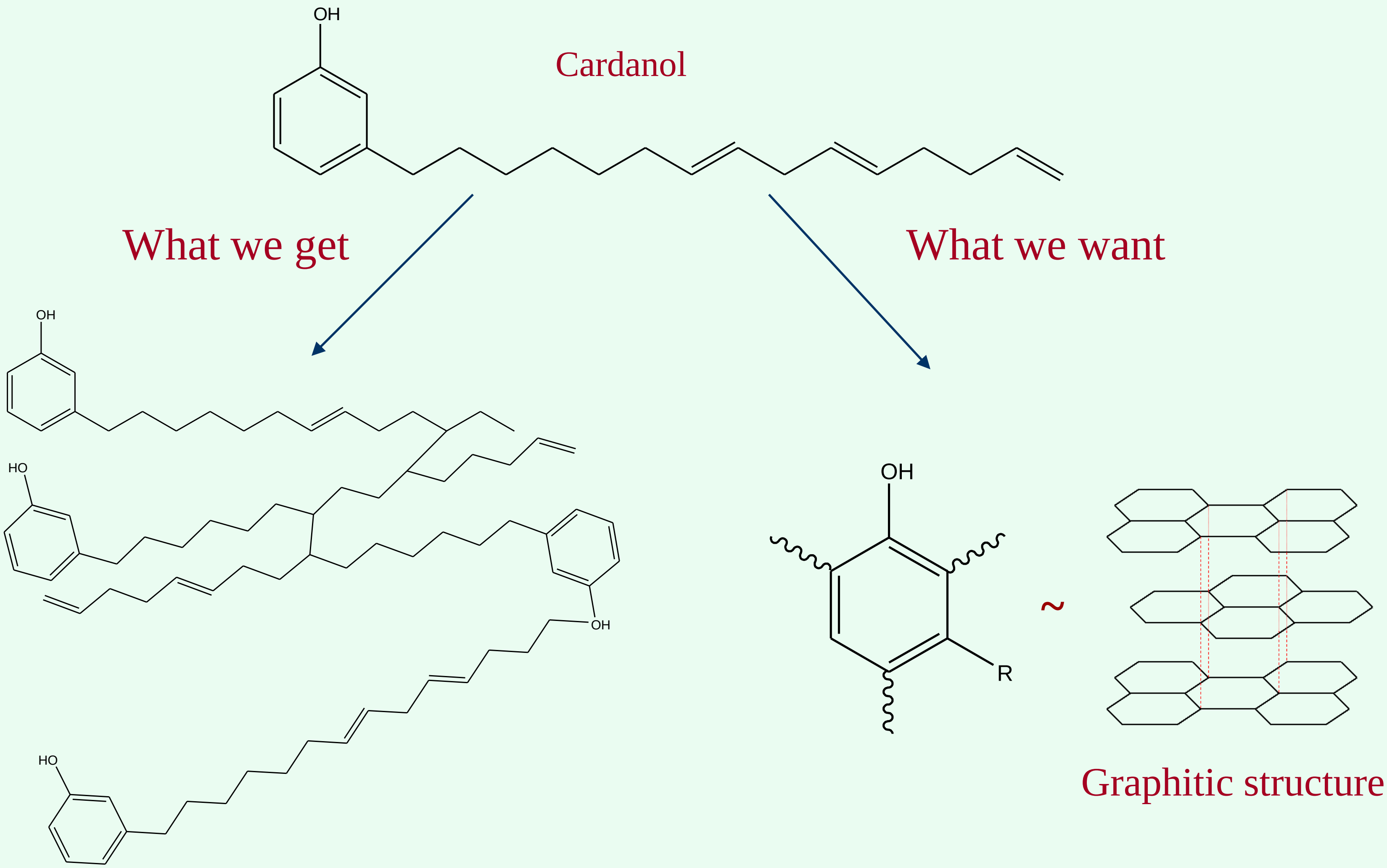
Cardanol Polymerization - Hematin

1. The resulting material was totally insoluble and infusible.

2. This material had a high value for heat release in spite of excellent char forming capabilities.

3. FTIR spectroscopy indicated extensive cross-linking and not polymerization.

Cardanol polymerization for FR's with hematin – Mechanism exploration



Cardanol

What we get

What we want

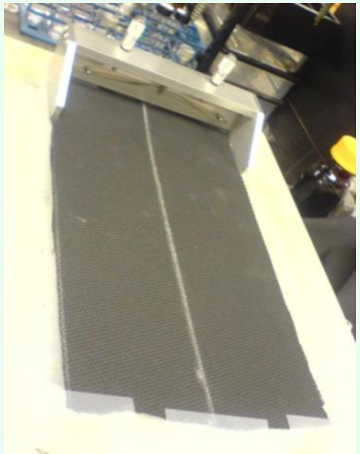
~

Highly cross-linked material

Graphitic structure

FR materials in ‘real world applications’ – practical issues

- FR materials are typically incorporated as 70% solids dispersion into a standard latex (30% solids) and coated on fabric.

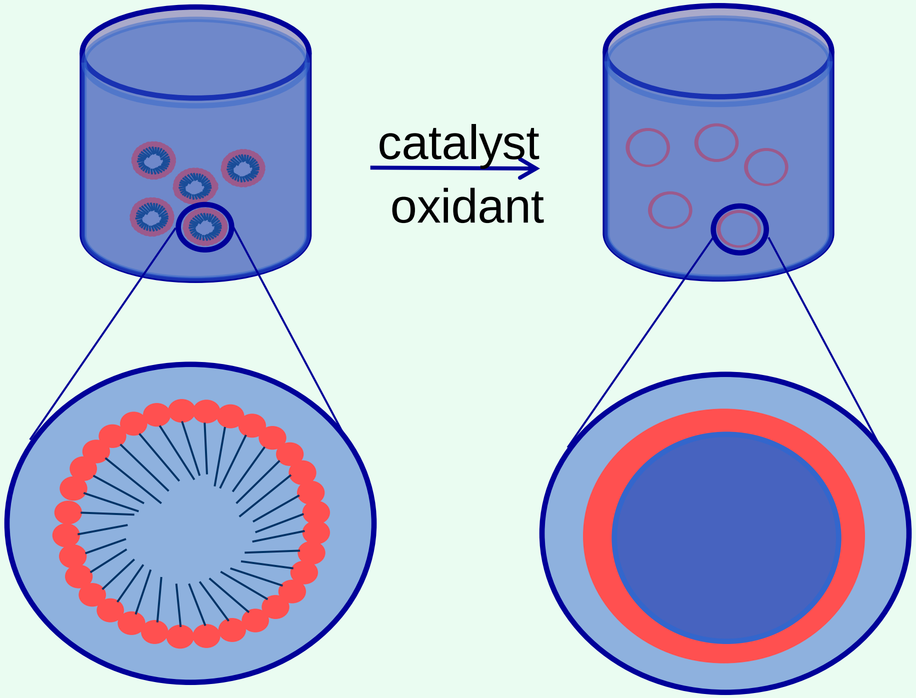


Test of FR properties carried out in collaboration with

True Textile Inc. (formerly Interface Fabric)

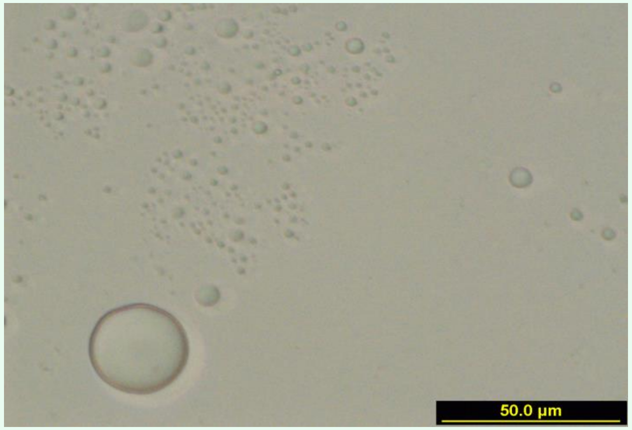
- Dispersion of FR – an important prerequisite
- Hydrophobicity of cardanol – a problem
- Amphiphilic nature of cardanol can be used to our benefit!

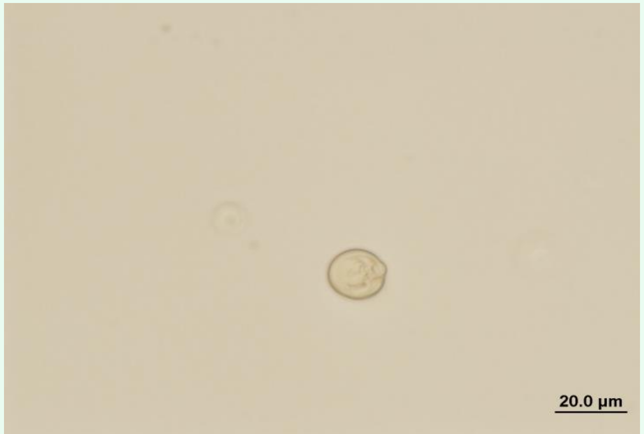
Micellar Reactions – Oil in Water



catalyst

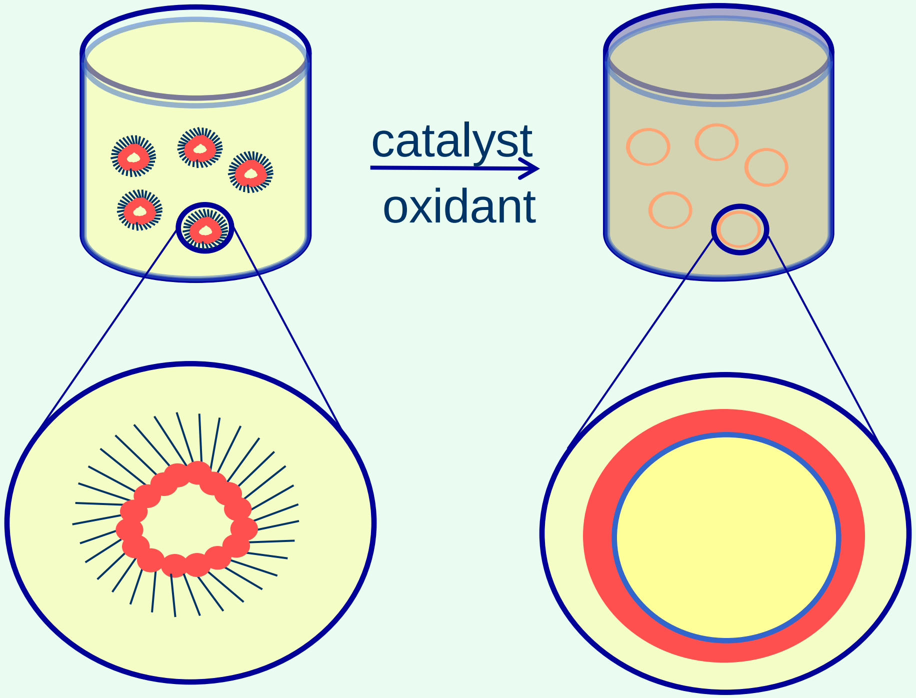
oxidant





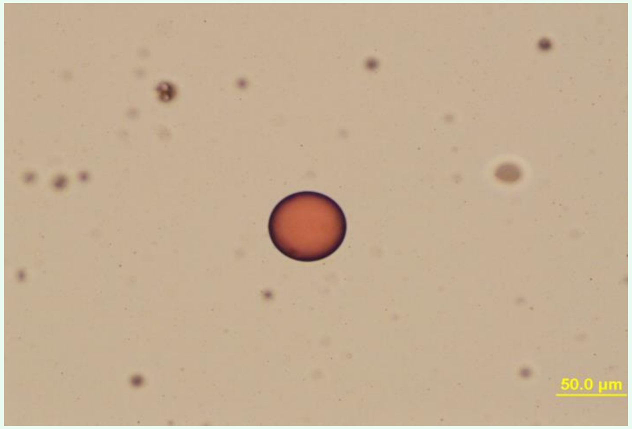
Particle Size Distribution – 100-300µm

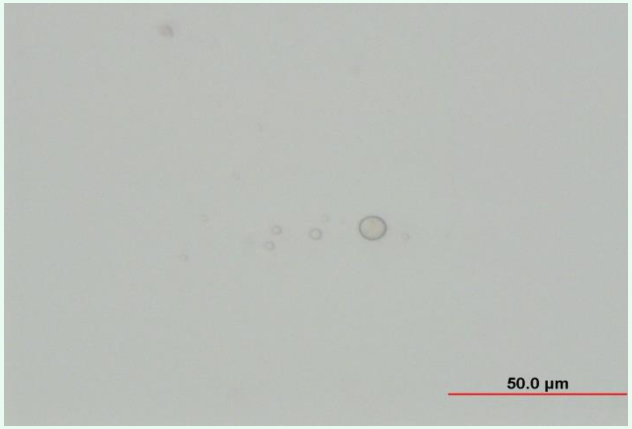
Micellar Reactions – Water in Oil



catalyst

oxidant





Particle Size Distribution – 50-250µm

Advantages of Micellar Reactions

- Polymerization of cardanol is possible under ambient conditions without interference of hydrophobic tails

- The capsules could be potentially loaded with other FRs

- The ‘oil’ phase could be potentially naturally occurring oils

- Micellar reactions gives us the possibility of facilitating better disperability into a aqueous based latex

Conclusions

- A new class of FRs based on phenolic monomers have been developed using environmentally benign synthetic methods
- FRs based on copolymers of BHDB/MHDB exhibit
  - Very good thermal stability
  - Very low heat release (comparable to nomex)
  - Good char yield
- Efforts to develop FRs based on naturally occurring phenols such as cardanol are underway
- A single step synthesis for cardanol in water has been accomplished to yield a thermally stable material
- Performance of these Non-Halogenated FRs was investigated
- Dispersability poly(cardanol) in the coating latex is currently being addressed

Acknowledgements

- The financial support from Toxic Use Reduction Institute is gratefully acknowledged.
- Ms. Pam Eliason, TURI
- Dr. Bon Cheol-Ku (UMASS Amherst) for monomers and PCFC analysis.
- Dr. Patrick Hawks and Mr. Mike Rose, True Textile Inc.,
- Dr. Ferdinando Bruno, Dr. Ravi Mosurkal and Dr. Akshay Kokil, Centre for Advanced Materials, UML.
- Palmer International, for providing cardanol and hydrogenated cardanol.

Thank you

Accomplishments

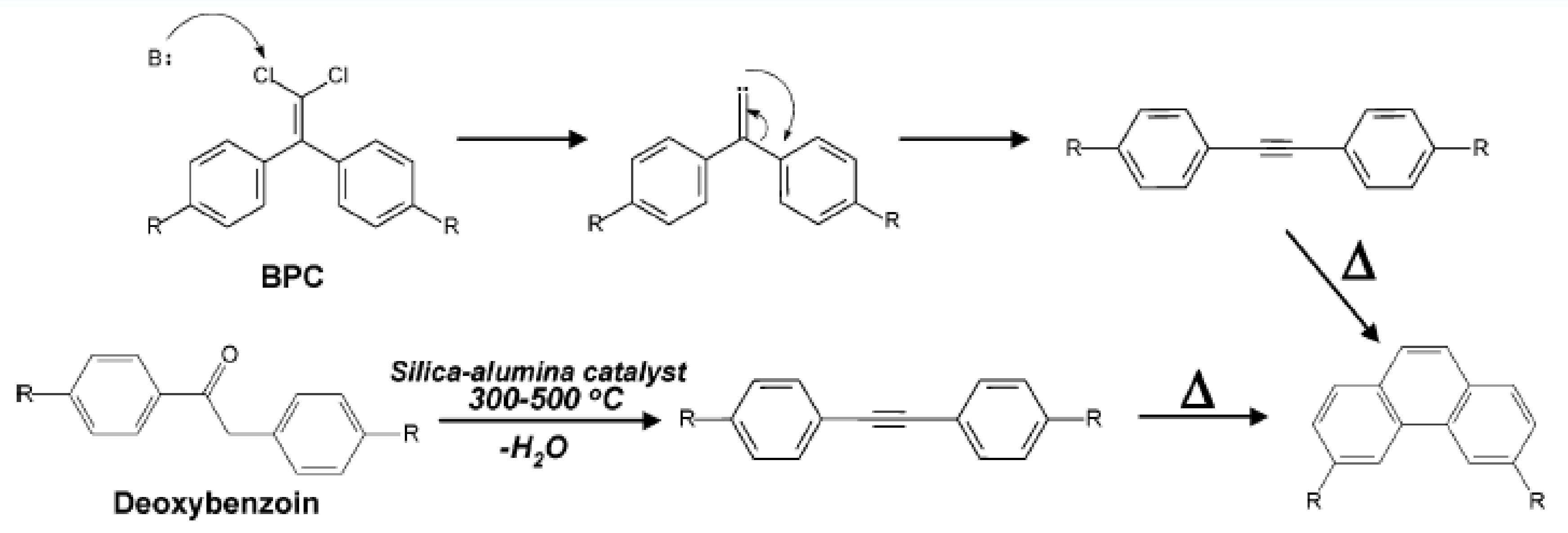
- S. Ravichandran, S. Nagarajan, R. Bouldin, J. Kumar and R. Nagarajan “Title of Sukant memorial symposium poster” poster presented at Sukant Memorial Symposium, December 2008.

- S. Ravichandran, S. Nagarajan, R. Bouldin, J. Kumar and R. Nagarajan “title of the abstract submitted to ACS PMSE” abstract submitted to 238th ACS National Meeting, PMSE division, Washington, DC.

- “Biocatalytically synthesized polyphenol-based Flame Retardant Materials” Patent disclosure under preparation

- 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.

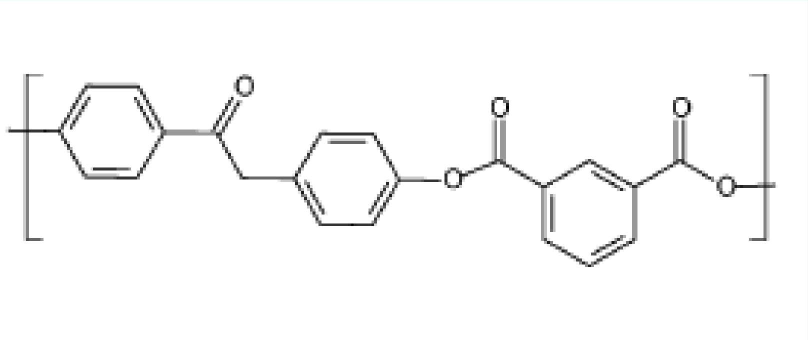
From the Literature..



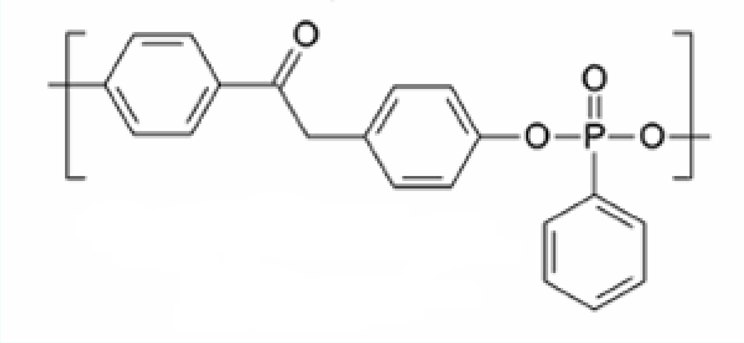
Investigations into decomposition pathways of BPC-containing polymers suggest that char formation may proceed through diphenylacetylene derivatives

van der Waals, A. C. L. M.; Klunder, A. J. H.; van Buren, F. R., Zwanenburg, B. *J. Mol Catal. A* **1998**, *134*, 179
K.A.Ellzey, T.Ranganathan, J.Zilberman, E.B.Coughlin**,** *Macromolecules* **2006,** *39*, 3553-3558.

From the Literature..



Benzoin-co-arylate

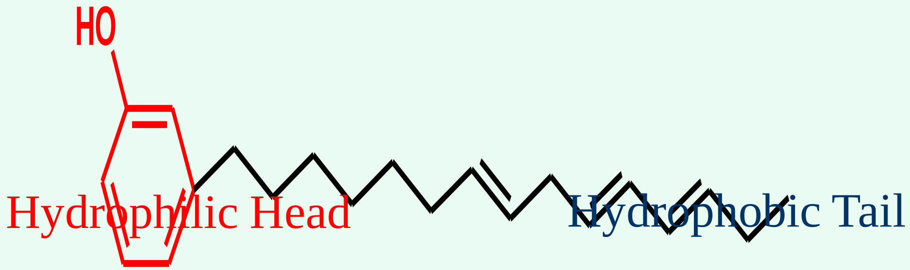


Benzoin-co-phosphonate

- Copolymers of BHDB with arylates and phosphonates gave rise to polymers with very low heat release properties.
- However involved the use of toxic starting materials and reagents

K.A.Ellzey, T.Ranganathan, J.Zilberman, E.B.Coughlin**,** *Macromolecules* **2006,** *39*, 3553-3558
T. Ranganathan, Joseph Zilberman, Richard J. Farris, E.B.Coughlin, T Emrick *Macromolecules* **2006,** *39*, 5974-5975

Cardanol – An amphiphilic molecule



Particle size analysis of cardanol dispersion in water utilizing Dynamic Light Scattering

Cardanol concentration (µg/ml)	**Particle size (nm)**
0.7	-
0.9	133.66
1	184.46
5	201.56
10	310.16

The CMC of cardanol determined by DLS was 3 x 10^{-6} mol/L