Designing Polymeric Hydrocarbons for Low Flammability Materials

10th Triennial International Aircraft Fire and Cabin Safety Research Conference
October 18, 2022

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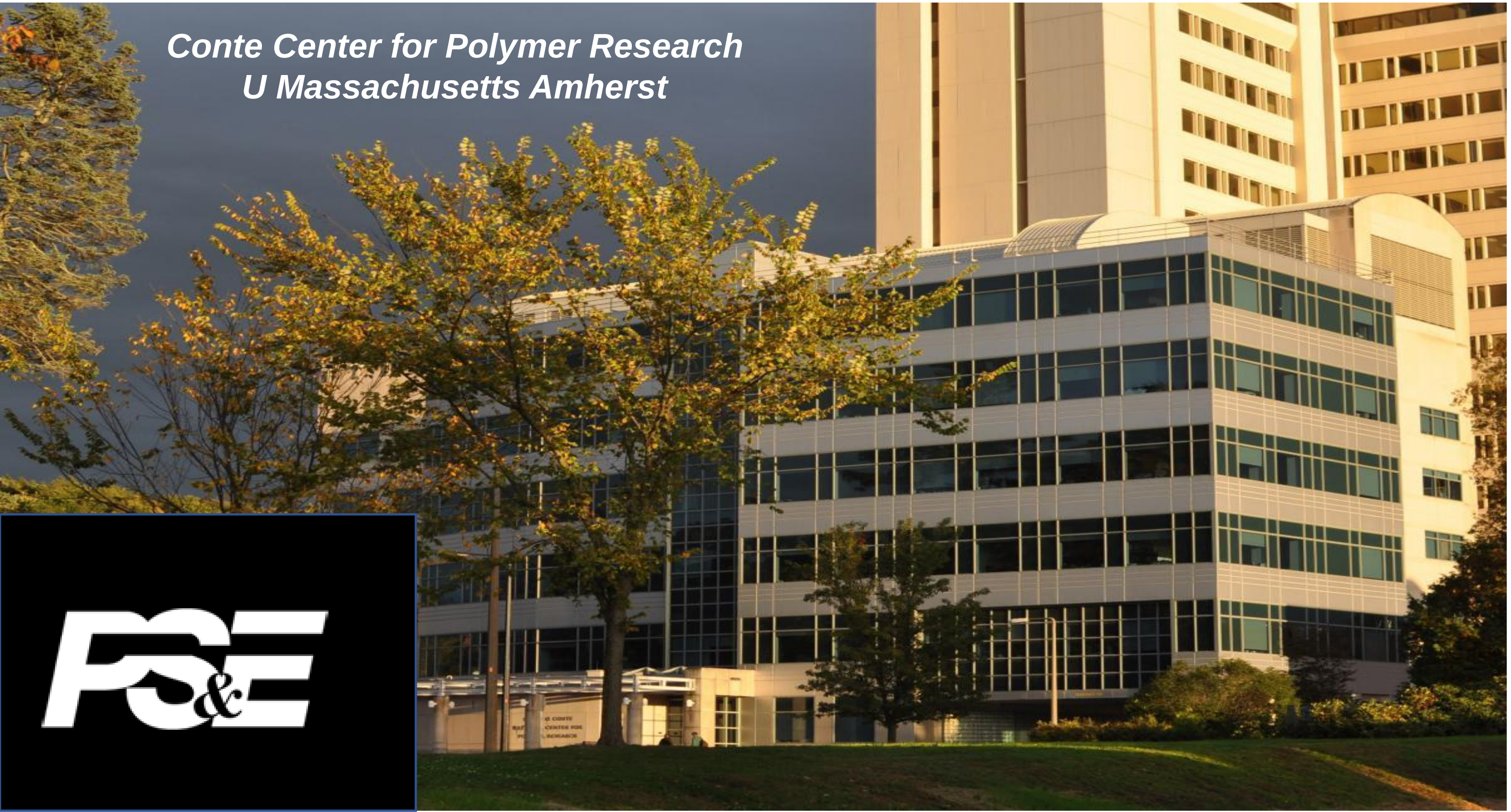


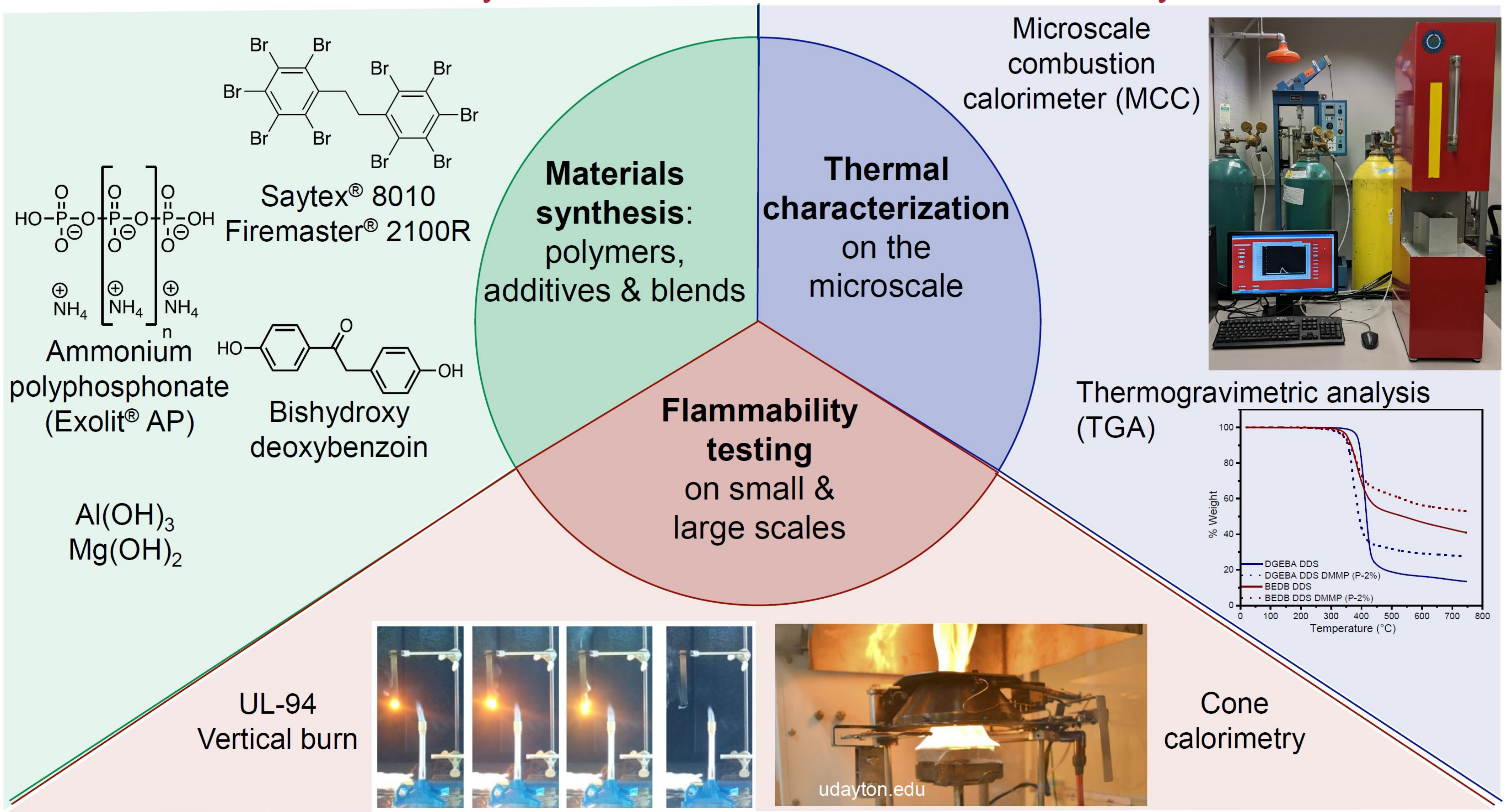
Ascend Performance Materials

LANXESS
Energizing Chemistry

Federal Aviation Administration

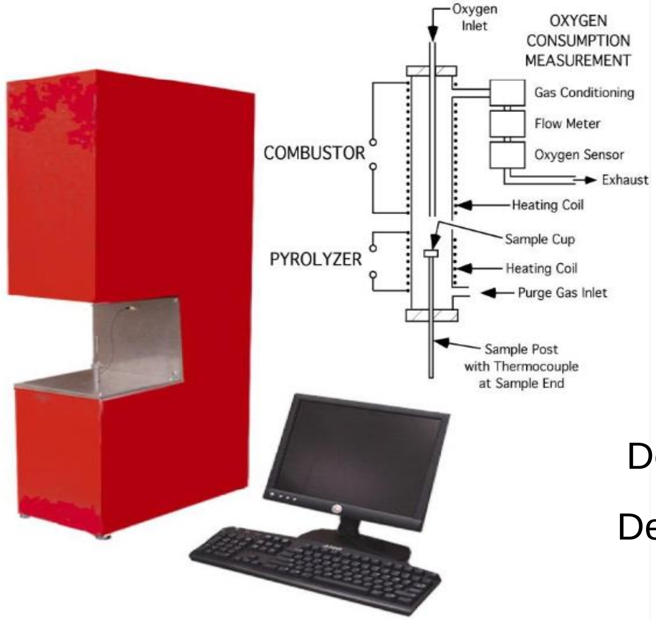
Cluster F of the Center for UMass-Industry Research on Polymers (CUMIRP)

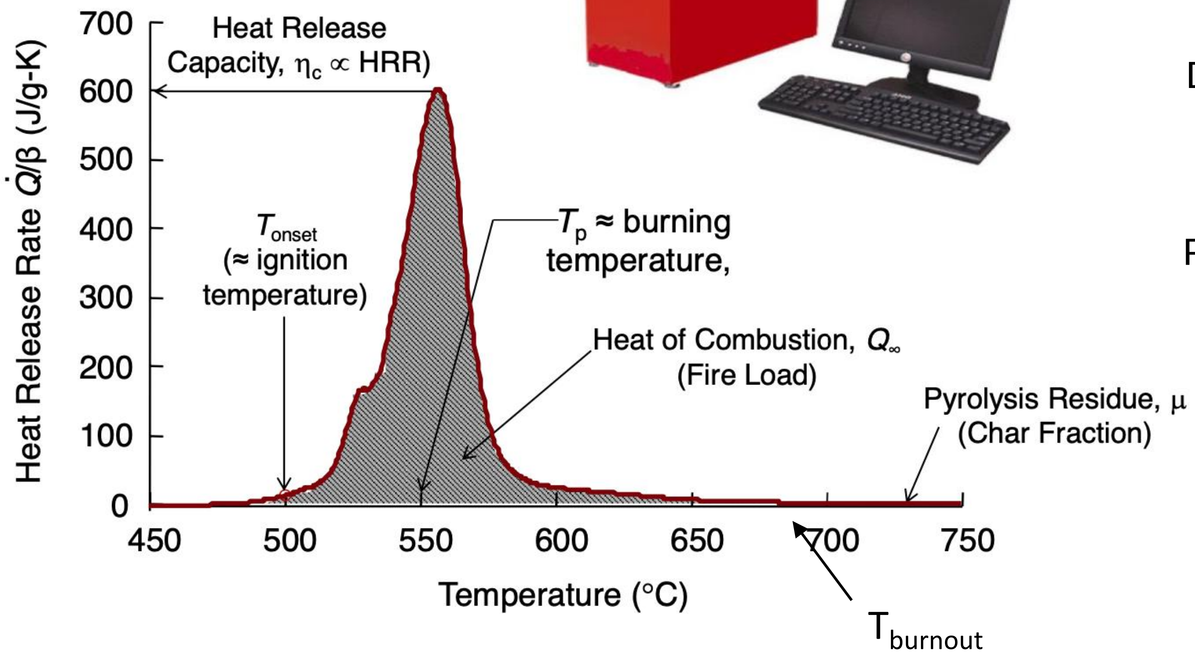
Flammability considerations: from materials to analysis



Heat Release Capacity (HRC) Measurements on Synthetic Polymers

Microscale combustion calorimetry (MCC)
milligram-scale testing



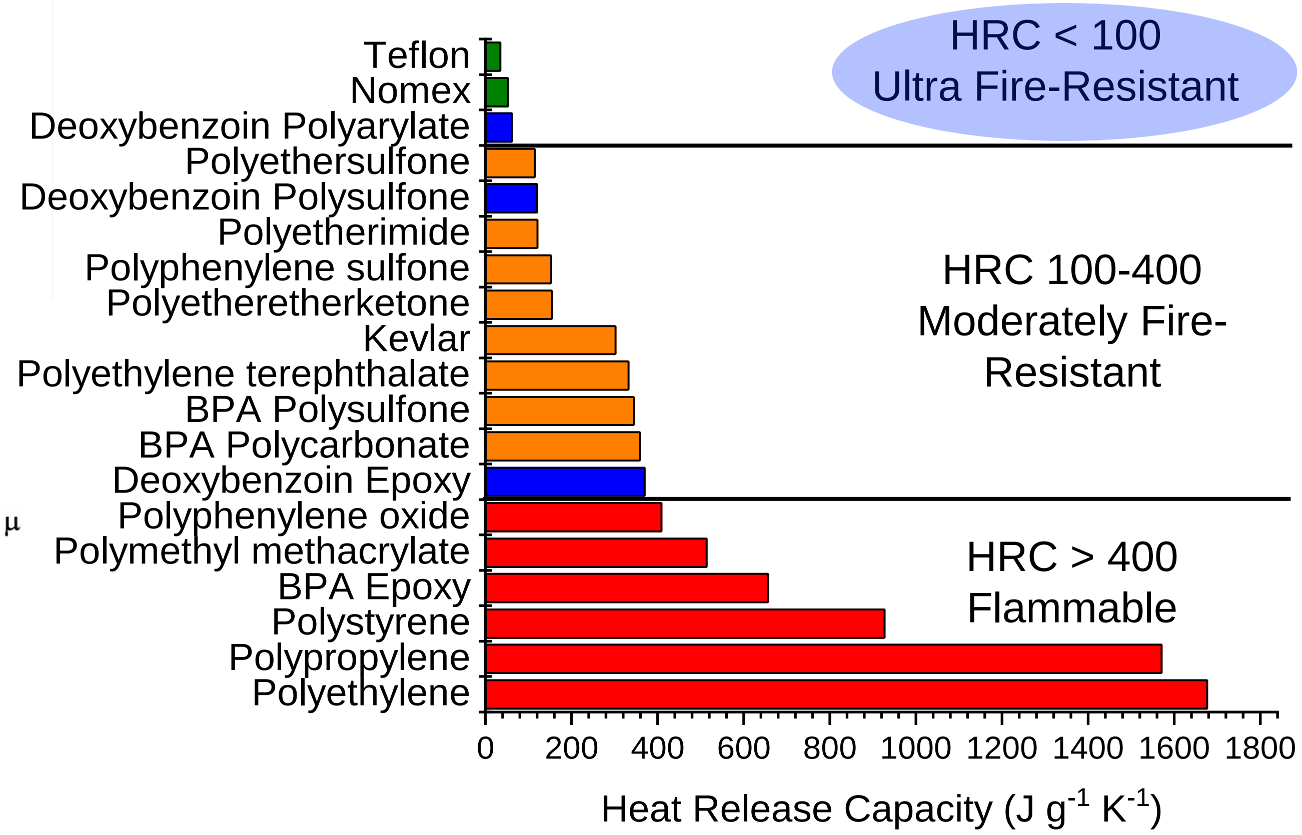


Lyon, R. *J. App. Poly. Sci.* 2004; Safronava *30th BCC* 2019

Heat release capacity (HRC):
material property that is a good predictor for fire behavior

$$HRC = \frac{\dot{q}^{max}}{\beta}$$

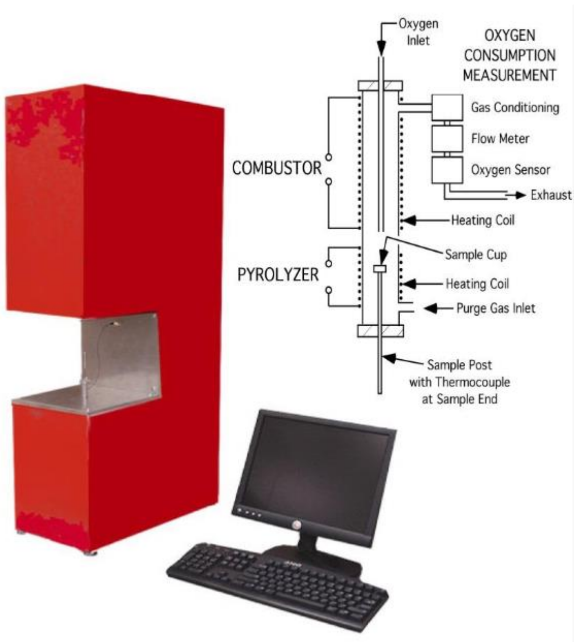
HRC values for important polymers

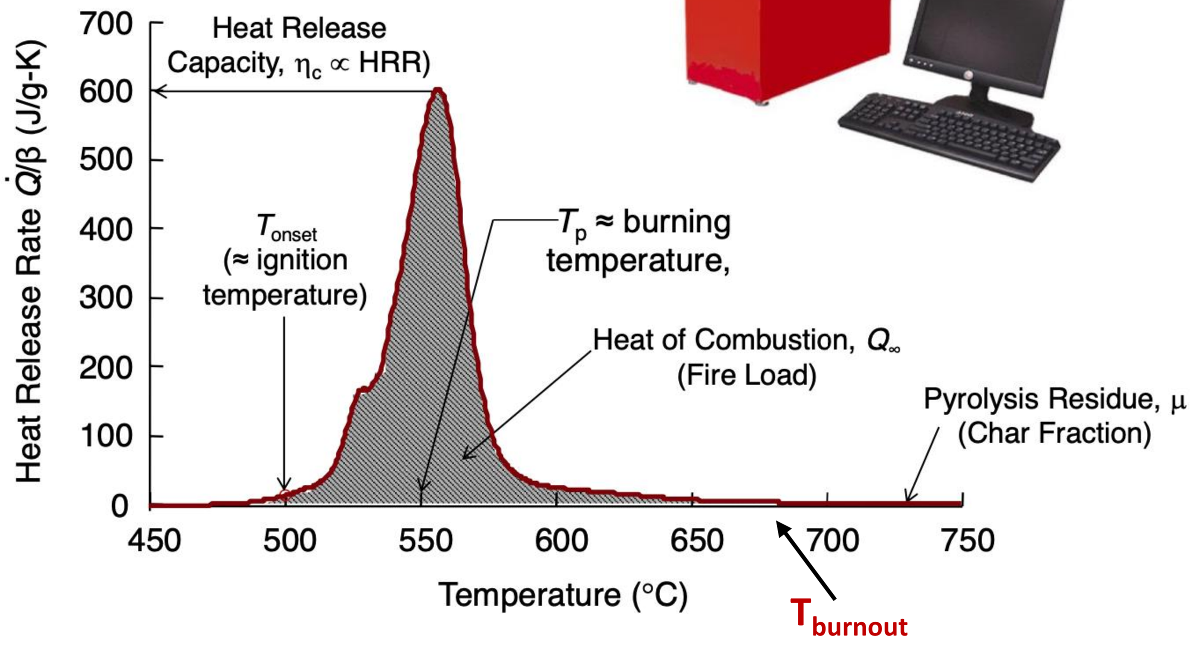


Lyon, Walters, Safronava and co-workers   Federal Aviation Administration

Fire Growth Capacity (FGC) Measurements on Synthetic Polymers

Microscale combustion calorimetry (MCC)
milligram-scale testing

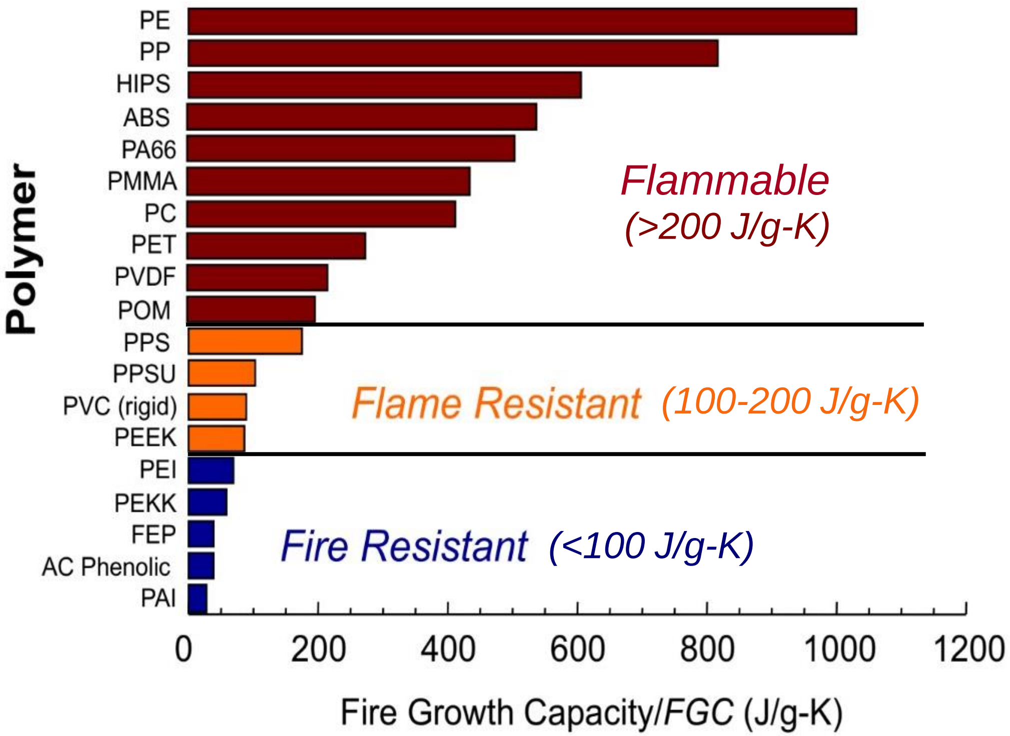




Fire growth capacity (FGC):
HRC + Ignition capacity

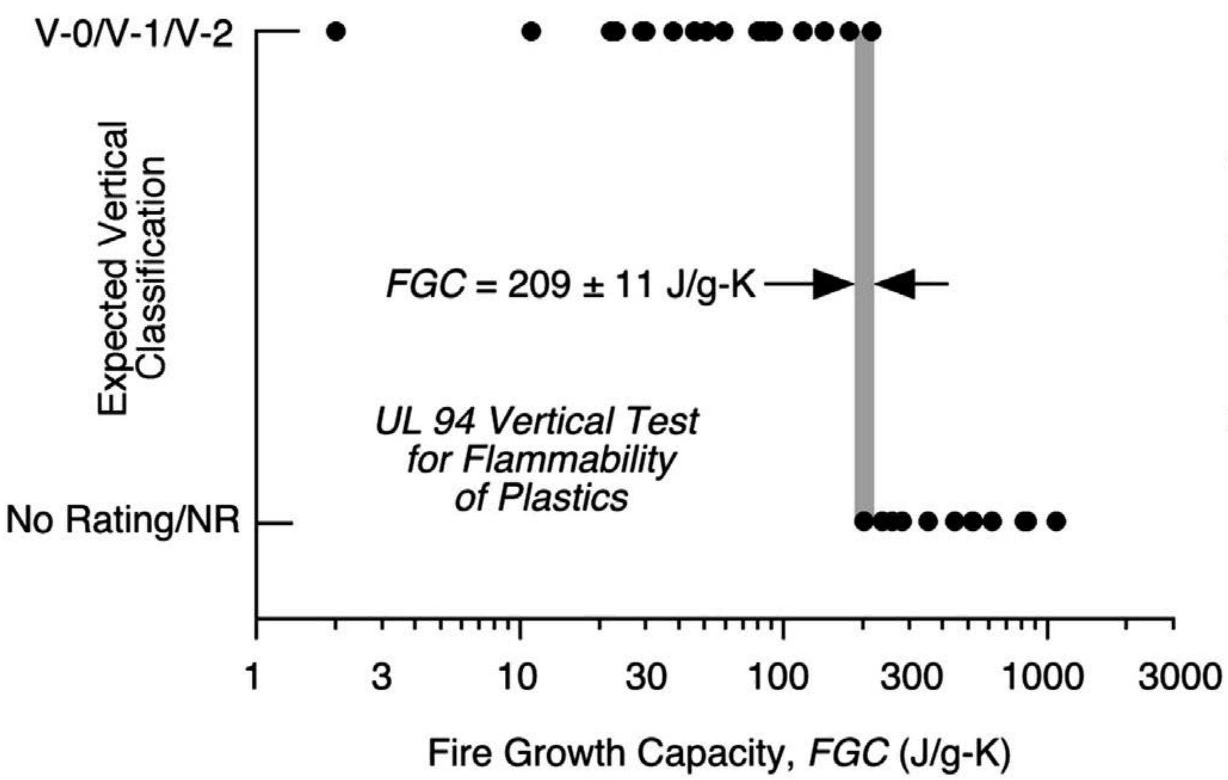
$$FGC = \left(\frac{Q_\infty}{T_{burnout} - T_{ign}}\right)\left(\frac{T_{burnout} - T_0}{T_{ign} - T_0}\right)$$

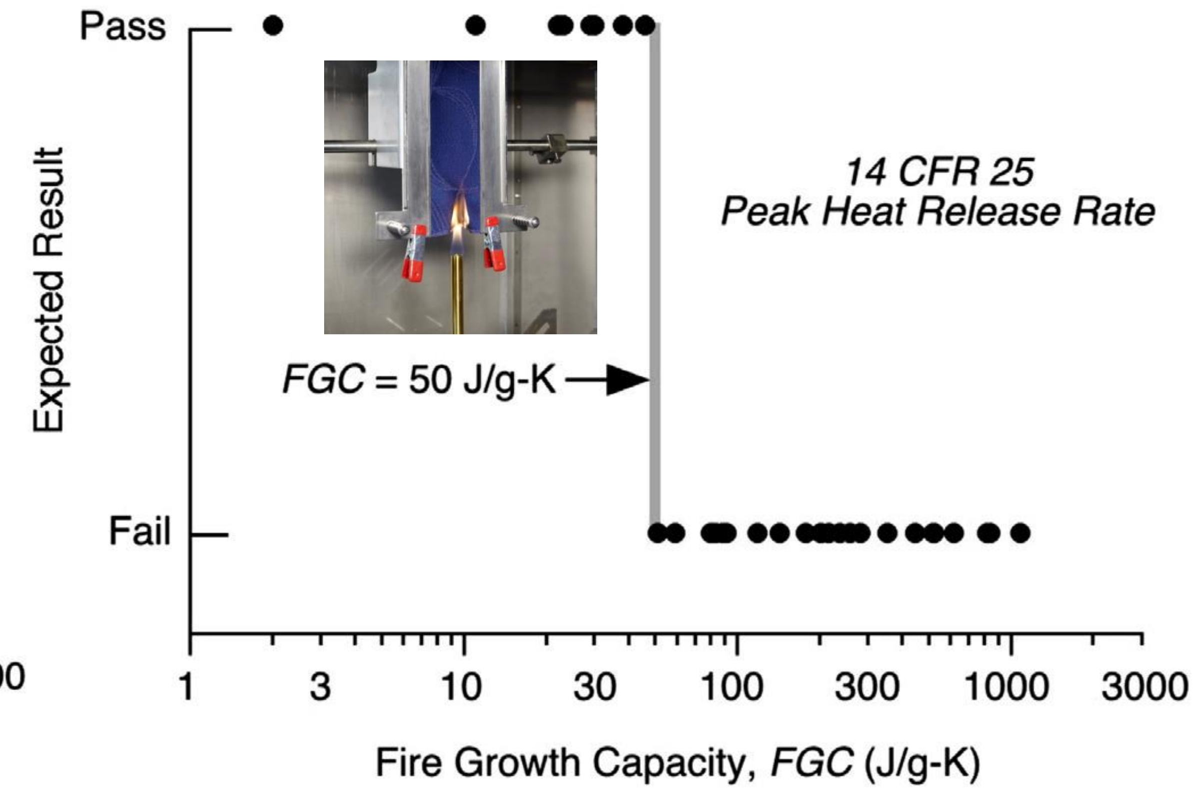
FGC for common polymers



Lyon *J. App. Poly. Sci.* 2004; Safronava *30th BCC* 2019

FGC and Bench Scale Tests (UL 94 Vertical and 14 CFR 25)



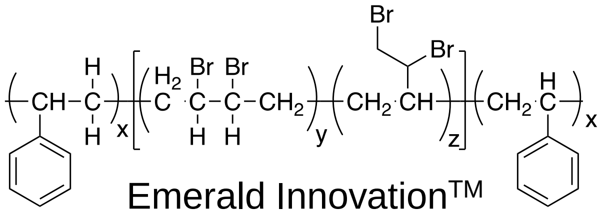


POLYMER	HDPE	PP	PS	PC	PPS	PVC	PEI	Nomex	FEP	Phenolic	PBO	PAI	PI	BPC-PC
FGC (J/g-K)	1078	836	815	237	142	88	83	51	38	46	29	30	23	11

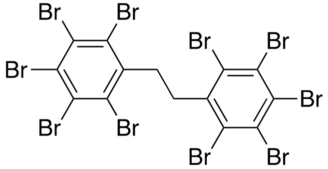
Lyon, Safronava, Crowley, and Walters, Polymer Degradation and Stability, 2021

Ongoing Progress in Organic and Polymeric Flame Retardants

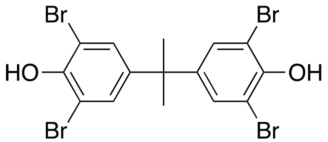
Halogenated additives



Emerald Innovation™ 3000



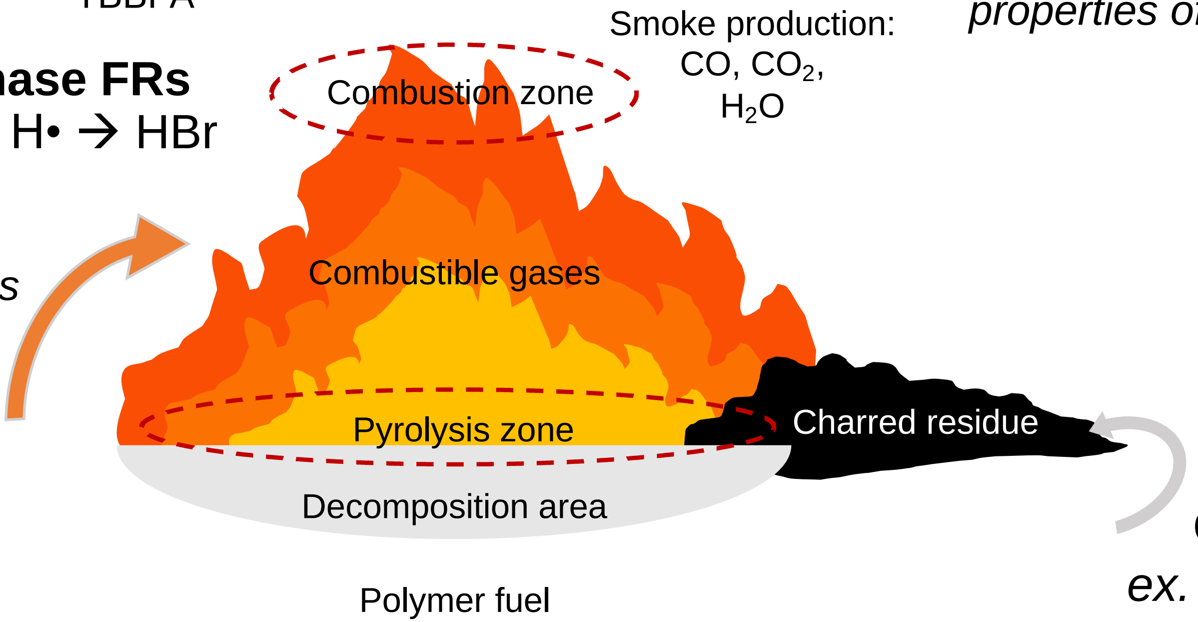
Saytex® 8010



monomer or additive TBBPA

Gas phase FRs

ex. Br• + H• → HBr



+ Effective use in commodity polymers

- Leaching from polymer
- Environmental persistence
- Toxicity, increasing legislation

Inorganic fillers: non-halogenated

Aluminum trihydrate ($Al(OH)_3$)

Magnesium hydroxide ($Mg(OH)_2$)

+ Better environmental prospects
Scalable for commodity polymers

- High loading needed for FR activity
- Negative impact on mechanical properties of host polymer materials

Condensed phase FRs

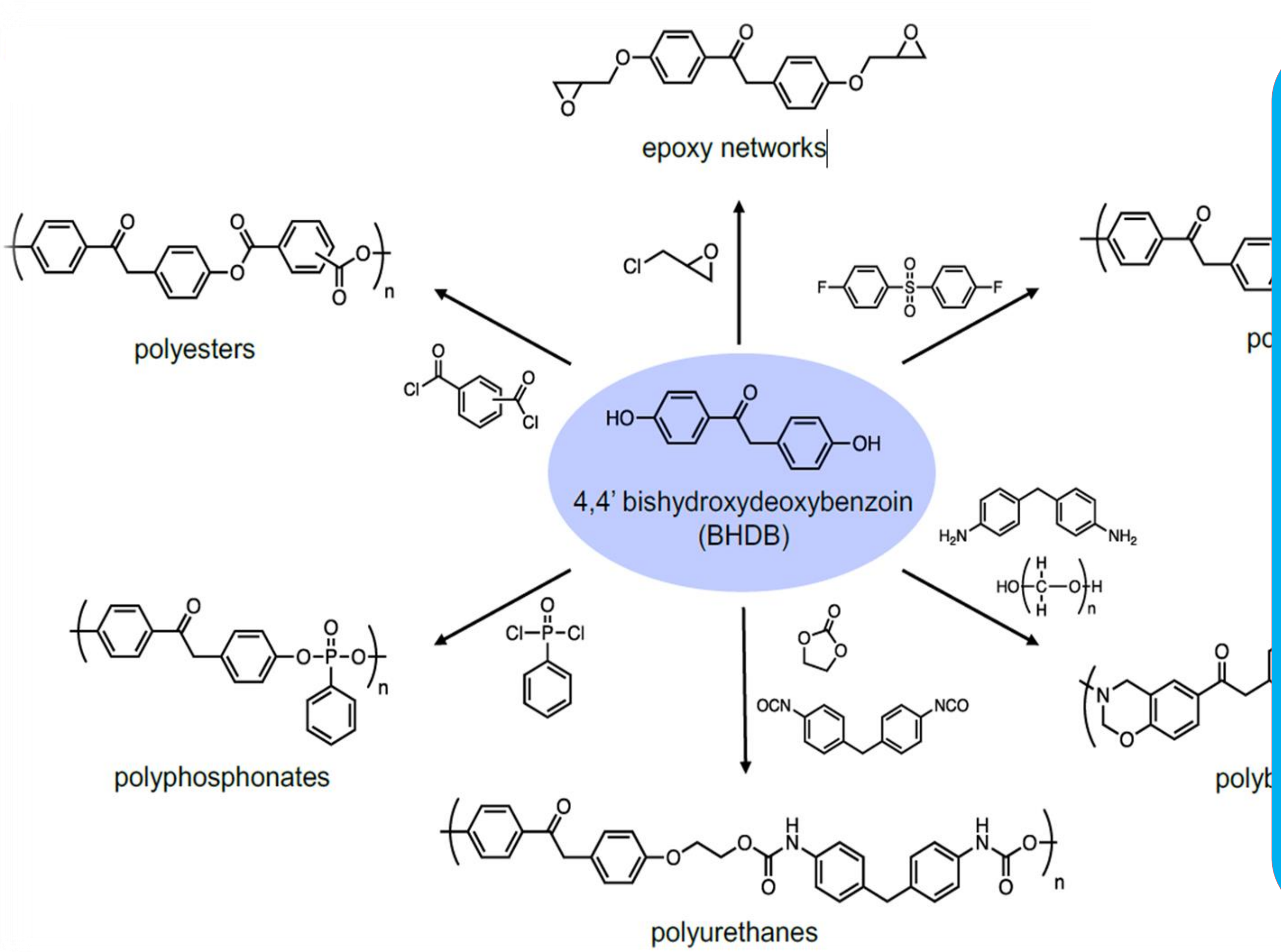
ex. $2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$

Our objective: develop inherently non-flammable polymers without halogen, phosphorous, or inorganic additives

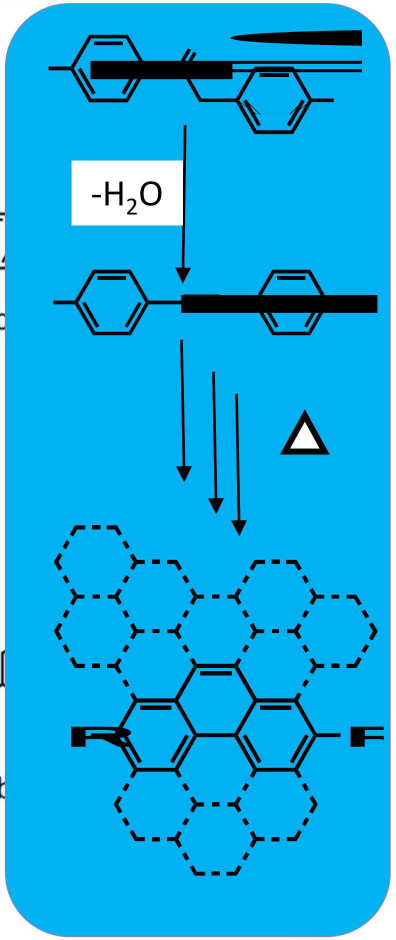
Deoxybenzoin as a Precursor to Non-flammable Polymers

Objective:

Demonstrate the Versatile Chemistry of Deoxybenzoi



Hypothesized char-forming mechanism



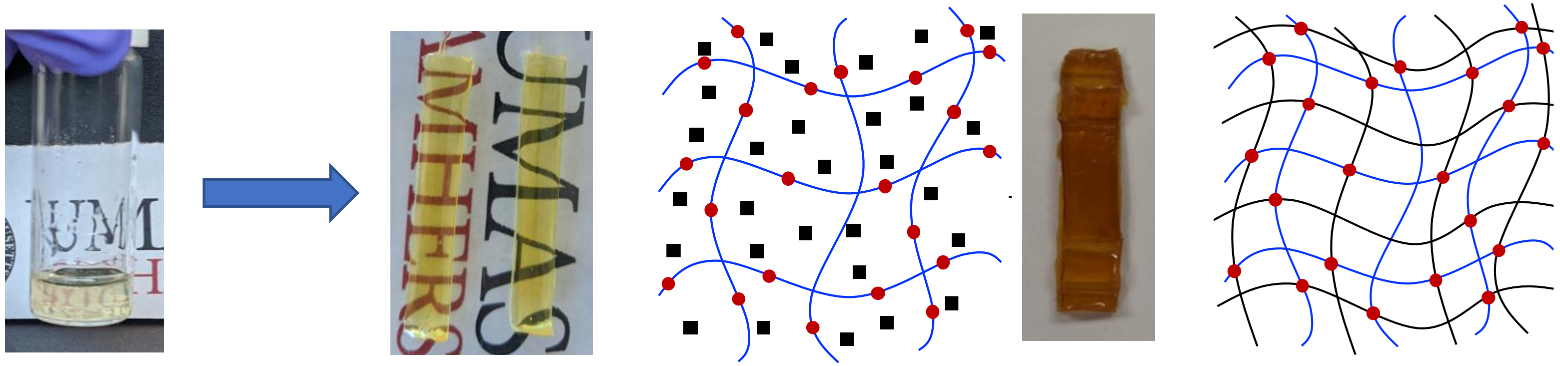
Van der Waals et al. J. Mol Catal. A 1998

*Polymer, **2016**, 84, 59e64; Macromolecules **2017**, 50, 3772−3778; Macromol. Mater. Eng. **2021**, 306, 2000567*

Presentation outline

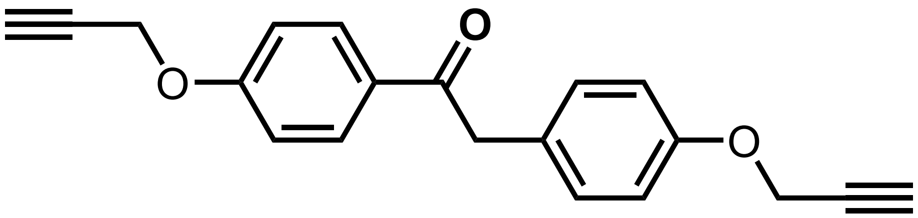
New Synthetic Routes to Deoxybenzoin
as Key Component of Non-flammable Polymers and Additives

I. High-yield syntheses of deoxybenzoin monomers and cross-linked polymer networks



II. Alkynyl-functionalized deoxybenzoins: preparation and use in step-growth polymerization reactions

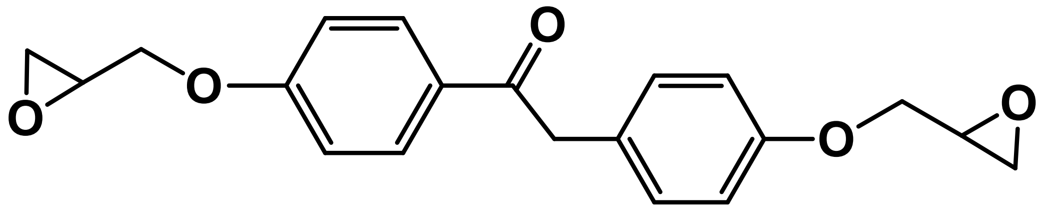
Bis-propargyl deoxybenzoin (BPD)



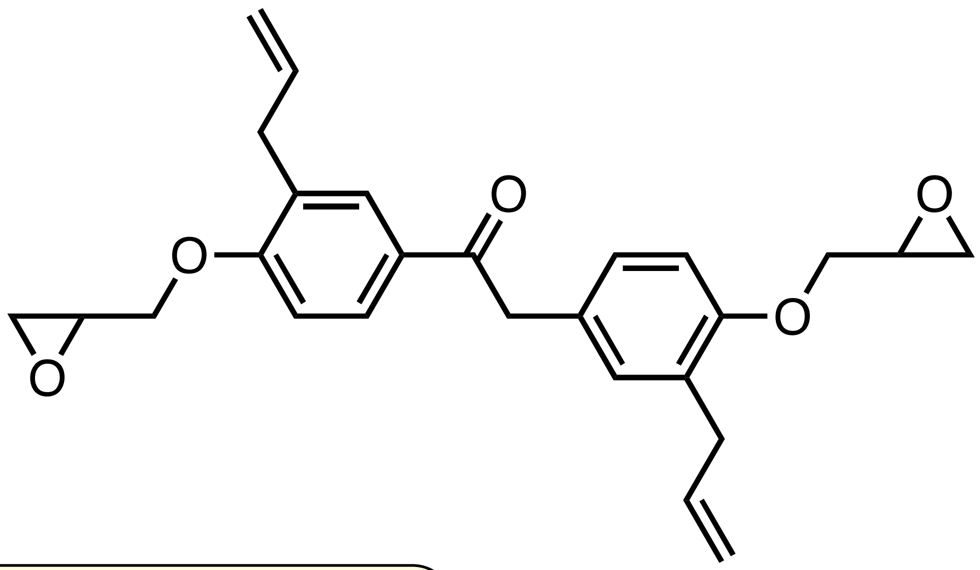
Precursor to low heat-release oligomers and polymers

I. Deoxybenzoins for Integration into Epoxy Networks

Bis-epoxy deoxybenzoin (BEDB)



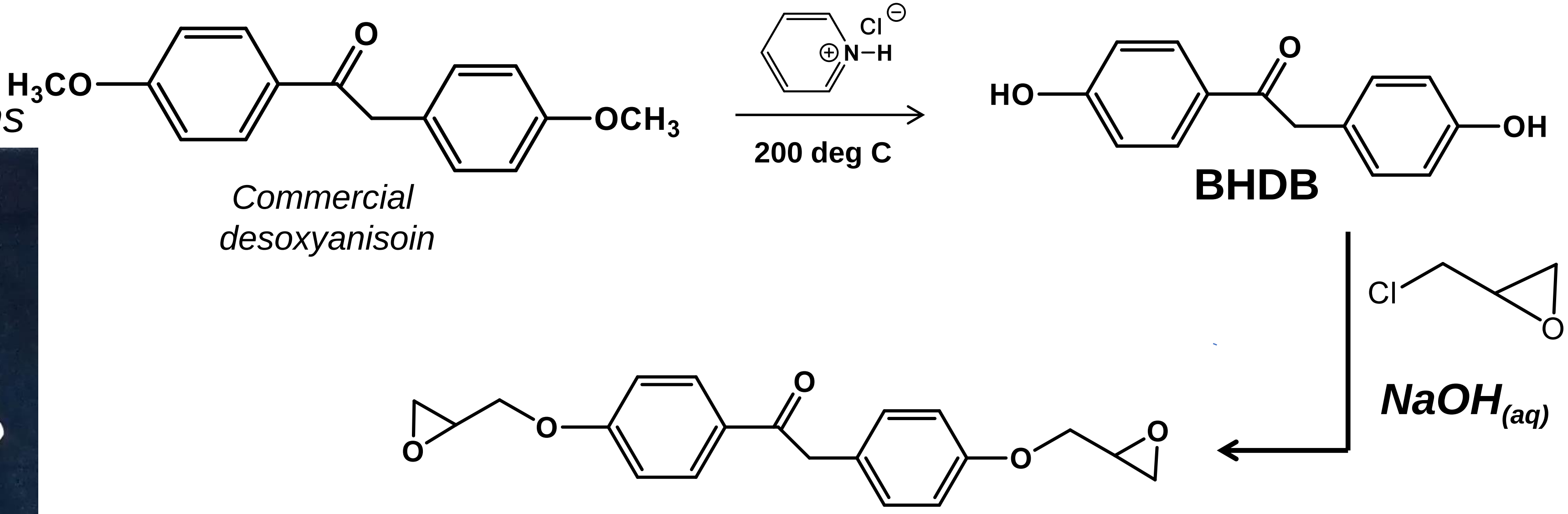
Bis-allyl BEDB (BA-BEDB)



- Monomer syntheses
- Network formation
- Heat release and flammability evaluations

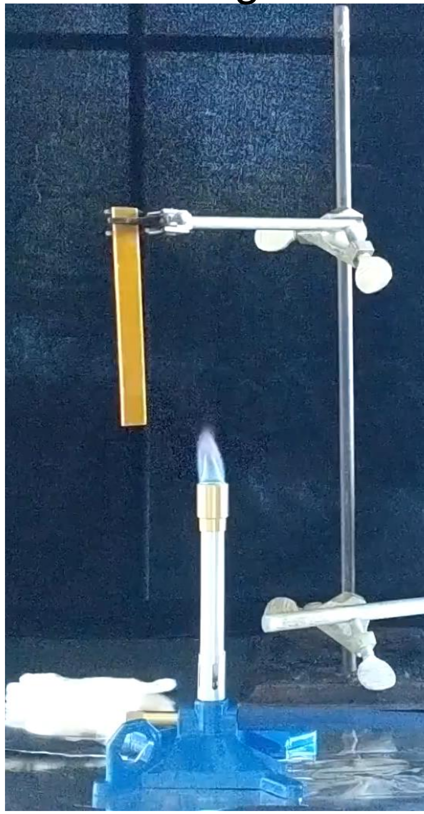
Bis-epoxy deoxybenzoin (BEDB)
simple synthesis → excellent properties

BPA-epoxy:
Ignites and burns



BEDB

BEDB-epoxy:
self-extinguishes



Easy to scale up: 200-gram batches in UMass labs

Networks from BEDB:
Heat release is ~1/2 that of BPA-epoxies;
mechanical properties (lap shear evaluation) similar/better than BPA.

Macromolecular Materials and Engineering, 2020

Deoxybenzoin Doubles Char Yield and Halves Heat Release

Heat release capacity (HRC) and total heat release (THR) from pyrolysis combustion flow calorimetry

Thermal properties and flammability of the resins cured with mixed amines.

	Formulation[a]	Thermal property		Flammability	
		T_g (°C)[b]	Residue[c] (%)	HRC (J/(g K))	THR (kJ/g)
Bis-phenol A resins	EBPA/4,4′-DDS	198	12	513 ± 10	25.3 ± 0.2
	EBPA/4,4′-DDS$_{0.8}$ 4,4′-DDM$_{0.2}$	196	14	454 ± 30	24.9 ± 0.4
	EBPA/4,4′-DDS$_{0.5}$ 4,4′-DDM$_{0.5}$	185	15	577 ± 28	25.4 ± 0.2
	EBPA/4,4′-DDS$_{0.2}$ 4,4′-DDM$_{0.8}$	178	16	693 ± 21	26.2 ± 0.4
	EBPA/4,4′-DDM	179	16	737 ± 24	26.8 ± 0.4
Deoxybenzoin resins	BEDB/4,4′-DDS	181	30	420 ± 14	17.2 ± 0.2
	BEDB/4,4′-DDS$_{0.8}$ 4,4′-DDM$_{0.2}$	180	33	342 ± 4	17.5 ± 0.5
	BEDB/4,4				
	BEDB/4,4				
	BEDB/4,4				

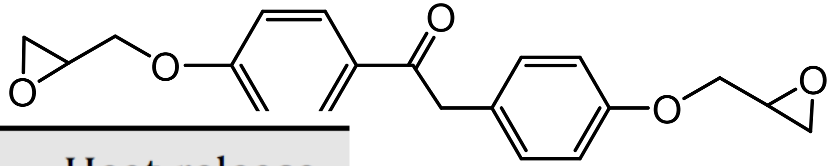
[a] Subsc
[b] T_gs w
[c] Char
min).

Lap

ASTN

THR: heat of combustion of pyrolysis gas

HRC: maximum heat release rate divided by the heating rate



EDB

Formulation	Thermal property			Heat release
	T_g (°C)[a]	T_{di} (°C)[b]	Residue[c] (%)	HRC (J/(g K))
EBPA/4,4′-DDS	198	385	12	513 ± 10
BEDB/4,4′-DDS	181	377	30	420 ± 14
ETBBA/4,4′-DDS	213	304	23	443 ± 11
EBPA/4,4′-DDM	179	372	16	737 ± 24
BEDB/4,4′-DDM	145	354	35	439 ± 7
ETBBA/4,4′-DDM	192	274	24	308 ± 14
EBPA/*m*-PDA	176	367	14	761 ± 23
BEDB/*m*-PDA	144	340	29	391 ± 40
ETBBA/*m*-PDA	177	263	23	238 ± 3

Polymer 2009

Impact of Small Weight Percent Additives on Deoxybenzoin Networks

FULL PAPER

Macromolecular
Materials and Engineerin
www.mme-journal.d

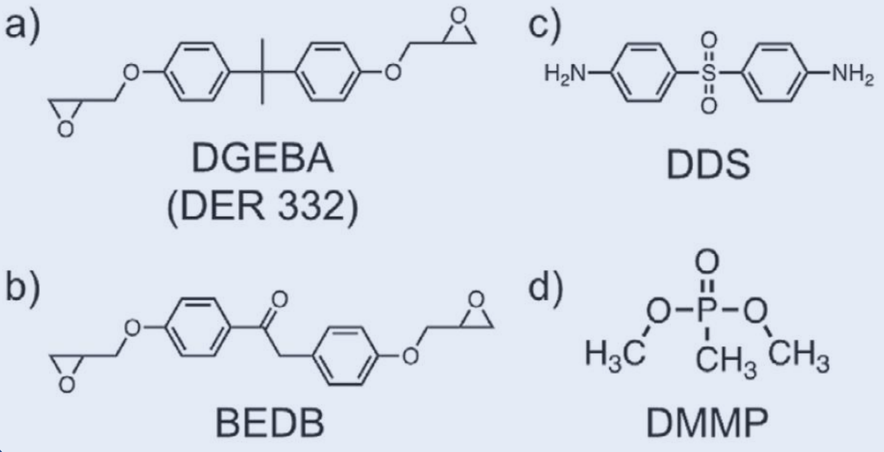
Combining Mechanical Fortification and Ultralow Flammability in Epoxy Networks

Chinmay Saraf, Elizabeth Stubbs, Weiguo Hu, Todd Emrick,* and Alan J. Lesser**

Multifunctional organophosphorus additives present opportunities to engineer epoxy networks with both enhanced mechanical properties and ultralow flammability. This paper describes a systematic investigation of the effect of dimethyl methylphosphonate (DMMP) on the mechanical and heat release properties of both conventional and inherently low flammability epoxy resins. The findings demonstrate that integration of DMMP into epoxy networks produces materials with outstanding flame retardance and increased stiffness. Thermogravimetric analysis of DMMI

matrix. While halogens, especially aromatic bromides, effectively reduce the heat release of epoxies by acting as gas phase flame retardants,[6] the resultant release of corrosive and toxic gas introduces health and safety concerns.[7] In addition, environmental legislation concerning the manufacture of halogenated molecules complicates their continued

Epoxies, crosslinker, and phosphonate additive



MCC measurer

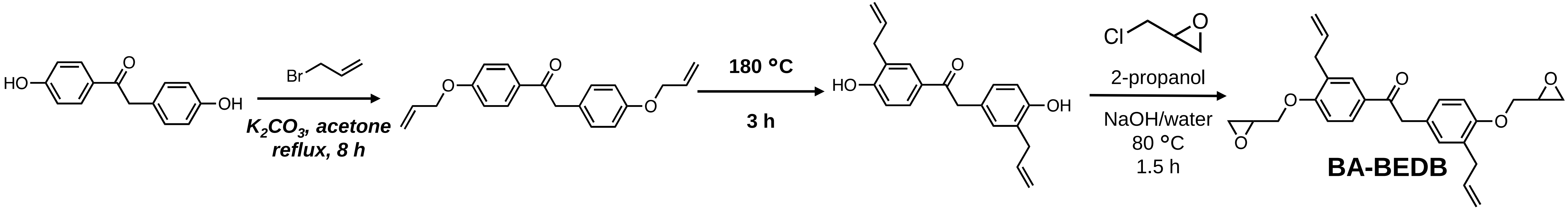
BPA-based net

measurements

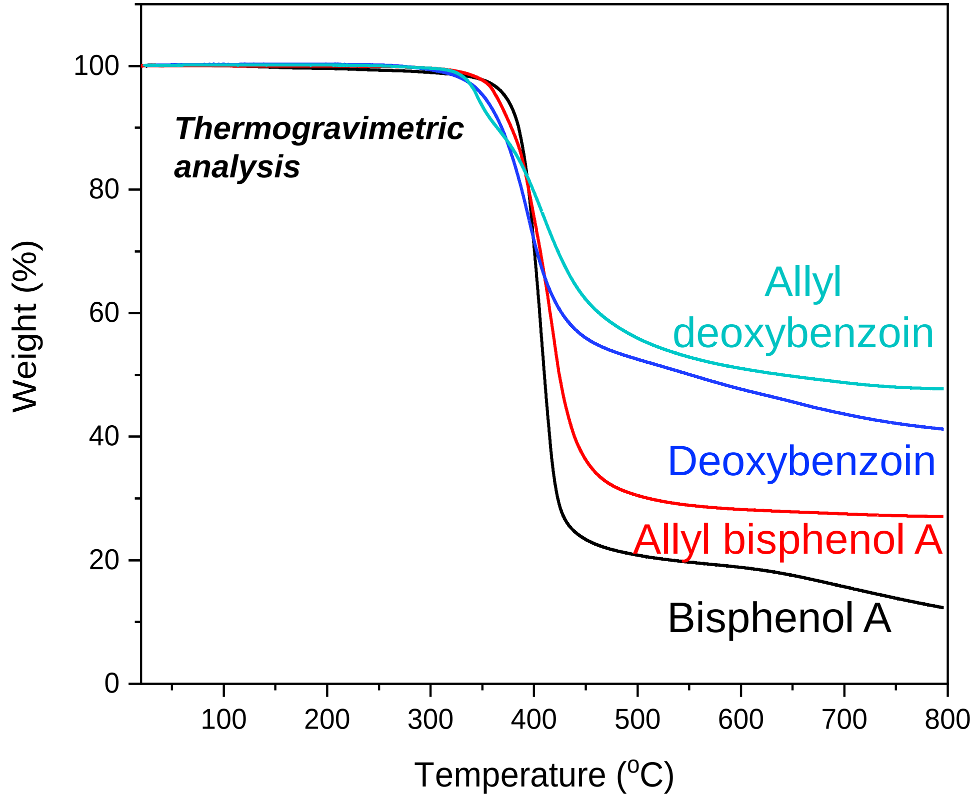
-based networks

Phosphorus concentration [wt%]	DGEBA-based formulations [J g^{-1} K^{-1}]	BEDB-based formulations [J g^{-1} K^{-1}]
0	384	194
0.5	351	76
1.0	311	65
1.5	286	56
2.0	273	56

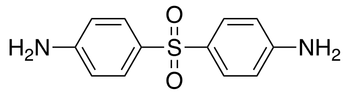
BA-BEDB:
Multifunctional and Orthogonal Crosslinking Mechanisms



Allyl group contribution to char

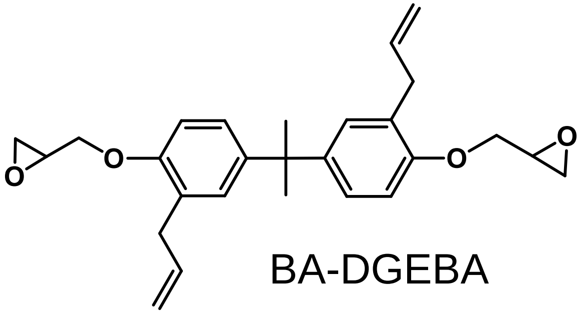


Curing conditions



diphenyldiamino sulfone

190 °C
8 h

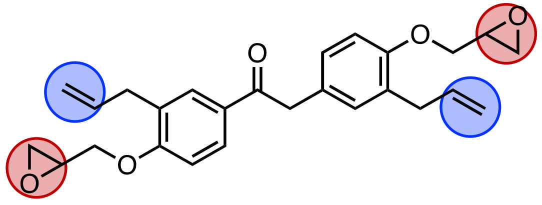


BA-DGEBA

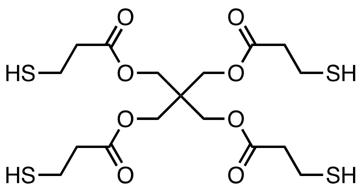
Epoxide	T_g (°C)	HRC (J/g-K)	peak HRR (W/g)
DGEBA	215	602 ± 79	373 ± 25
BA-DGEBA	**119**	**240 ± 40**	**220 ± 16**
BEDB	177	232 ± 8	217 ± 2
BA-BEDB	**152**	**185 ± 6**	**146 ± 5**

Multistage Curing: Thiol-ene and Epoxy-amine

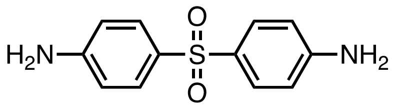
Network components



bisallyl deoxybenzoin

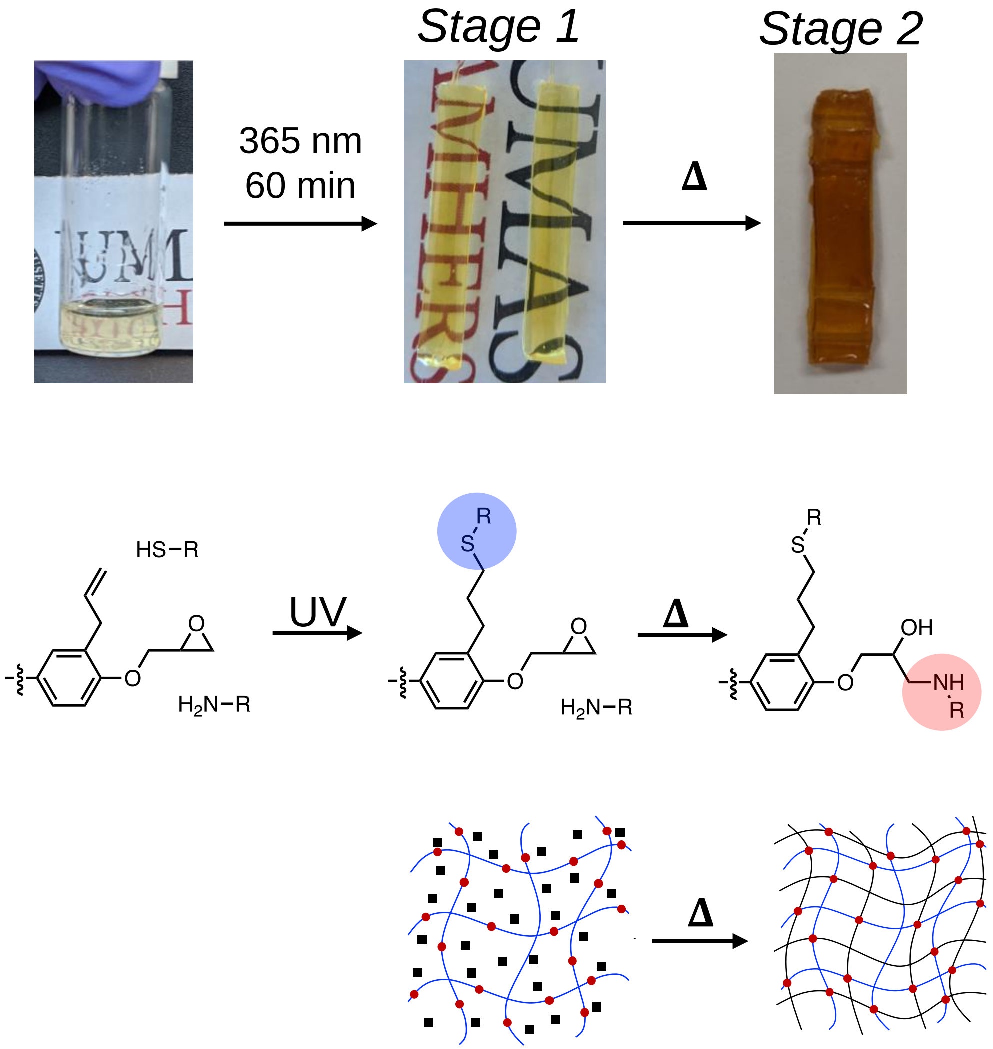


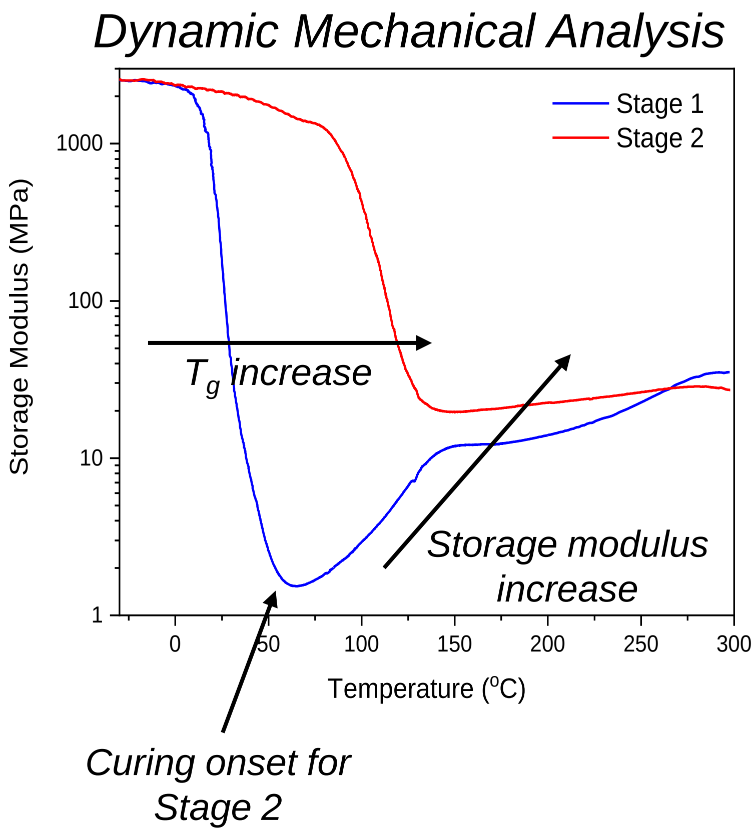
Tetrathiol-substituted pentaerythritol



diphenyl diamino sulfone

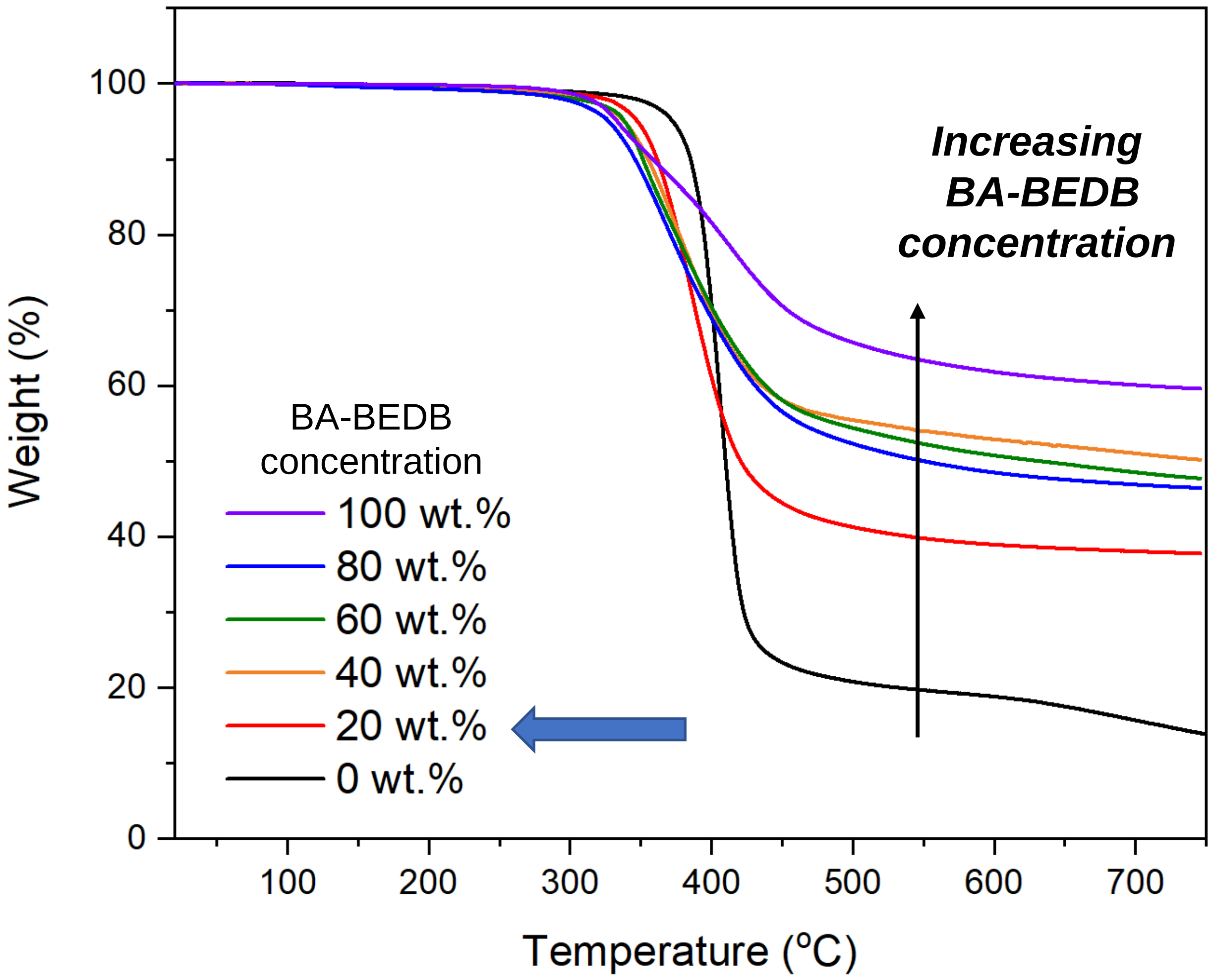
Network fabrication



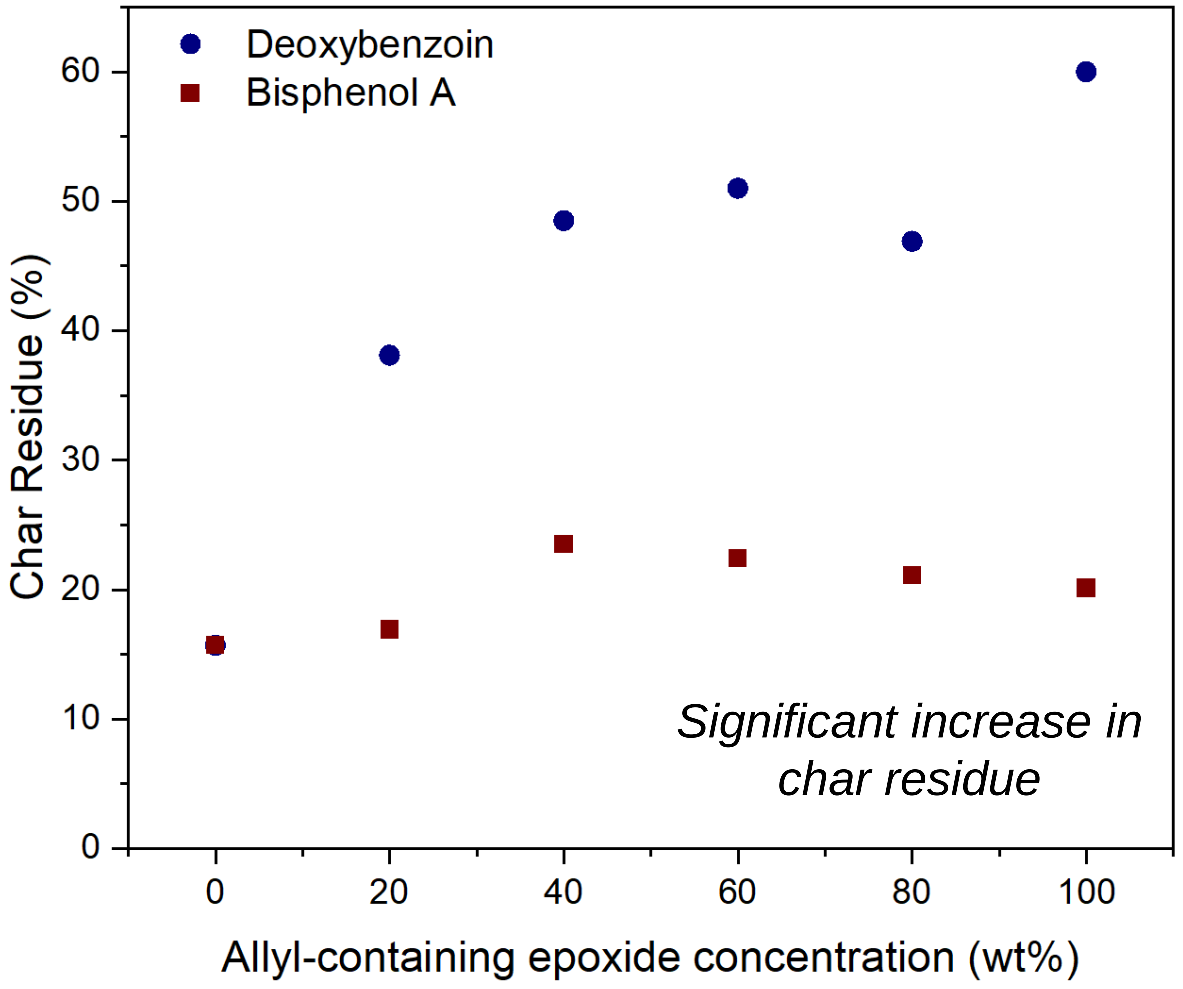


High-char Network and Impact of Deoxybenzoin Weight Percent

Thermogravimetric analysis

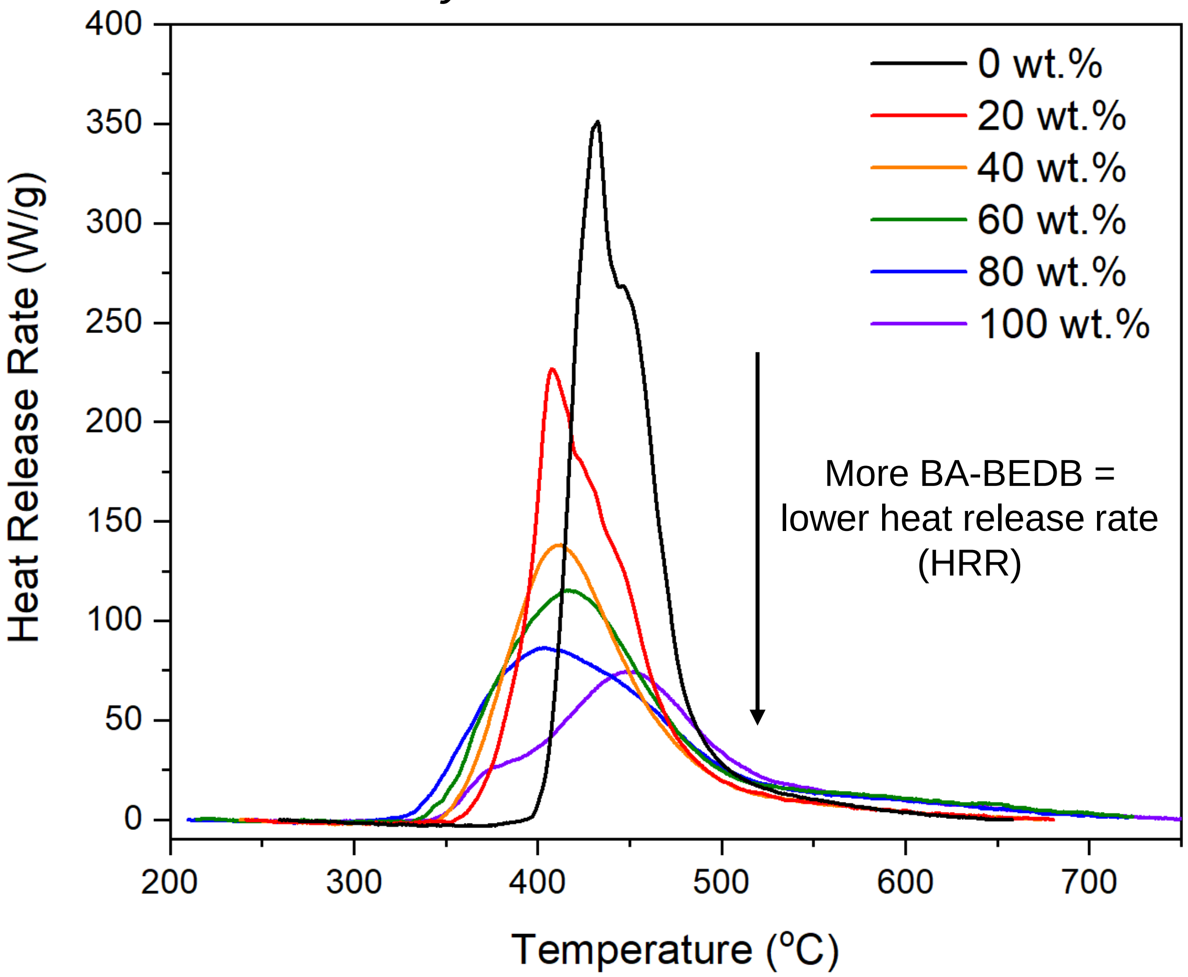


Char residue determined by TGA at 700 °C

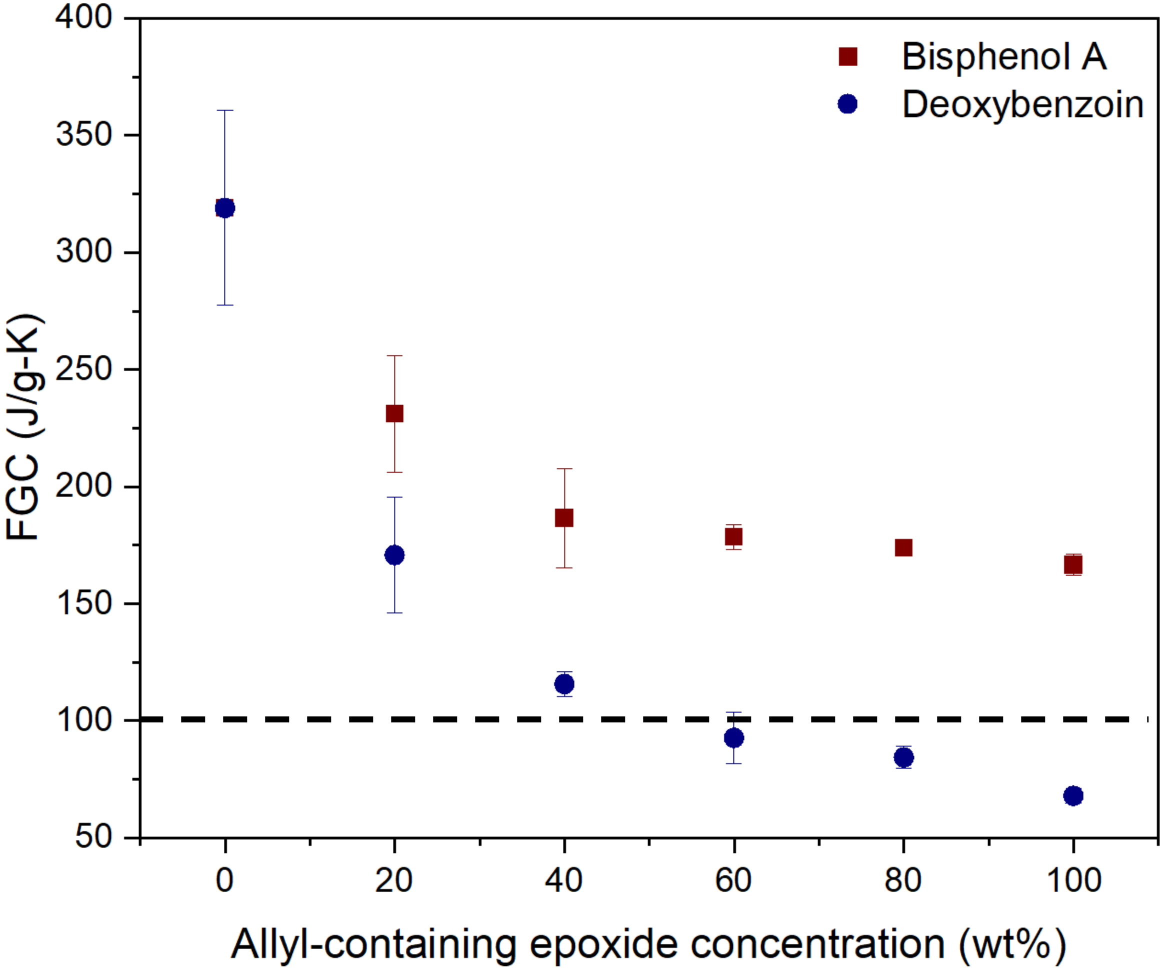


Low Heat Release Polymer Networks

Deoxybenzoin-based networks



Fire growth capacity



Large heat release decline with increasing BA-BEDB content

Indications of BHDB as a Bio-friendly Alternative to BPA

When exposed to estrogen or BPA, male Japanese Medaka fish express the egg yolk precursor protein vitellogenin II (vtg II) in the liver.
(normally expressed only in female fish)

N = 7/sample

→

72h exposure to 1nM E2,
2-17µM monomer samples

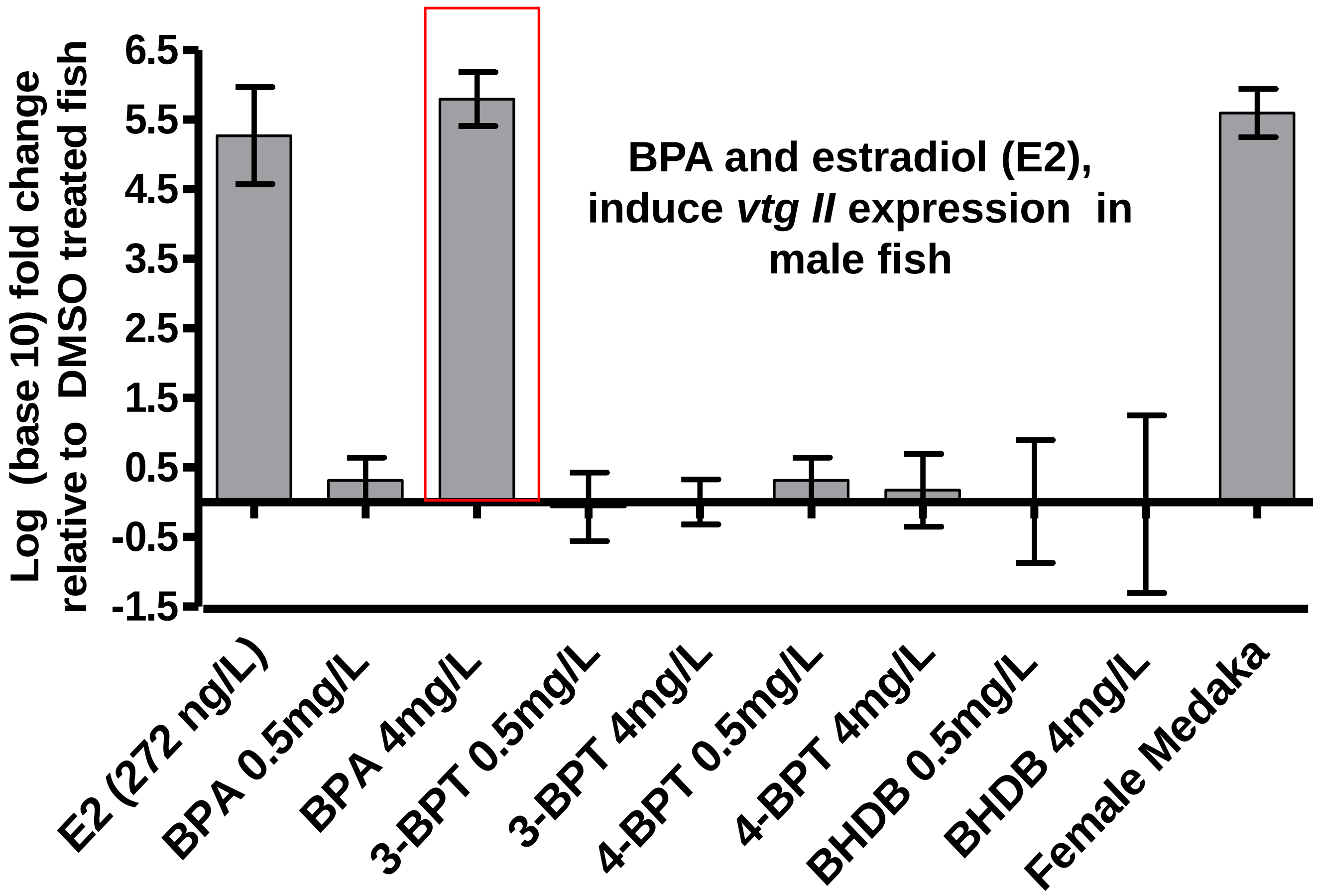
↓

Sacrifice fish; Isolate liver → Isolate DNA and mRNA → qPCR of individual samples

→ *Estrogenic bio-activity confirmed by measuring Vtg II gene expression*

In vivo estrogenic bio-activity assay

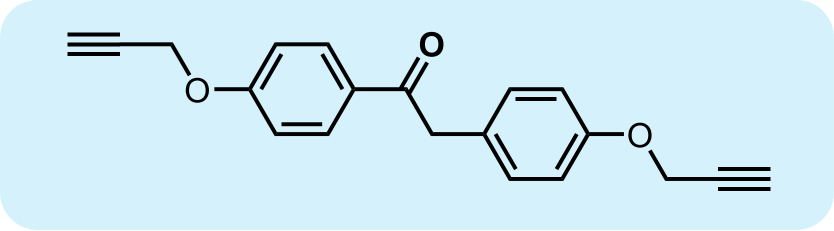
- Male Medaka fish exposed to monomers at 2 µM or 17 µM for 72 hours
- Using quantitative PCR, fish liver probed for expression of vtg II



BHDB, and the bis-phenol triazoles (BPTs), appear to be non-estrogenic

Bis-propargyl Deoxybenzoin (BPD)

BPD



Multigram synthesis in high yield and purity

Opportunities for azide-alkyne & thiol-yne click reactions

US 20170101361A1

(19) **United States**

(12) **Patent Application Publication**

Mir et al.

(10) **Pub. No.: US 2017/0101361 A1**

(43) **Pub. Date: Apr. 13, 2017**

(54) UNSATURATED DEOXYBENZOIN COMPOUNDS AND POLYMERS PREPARED THEREFROM

(71) Applicant: **The University of Massachusetts**, Boston, MA (US)

(72) Inventors: **Aabid A. Mir**, Amherst, MA (US); **Todd Emrick**, South Deerfield, MA (US); **Umesh Choudhary**, Shrewsbury, MA (US)

(21) Appl. No.: **15/286,768**

(22) Filed: **Oct. 6, 2016**

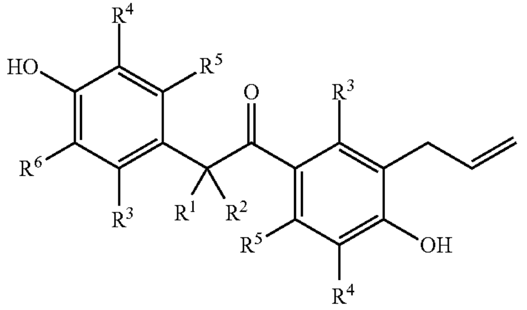
Related U.S. Application Data

(60) Provisional application No. 62/238,186, filed on Oct. 7, 2015.

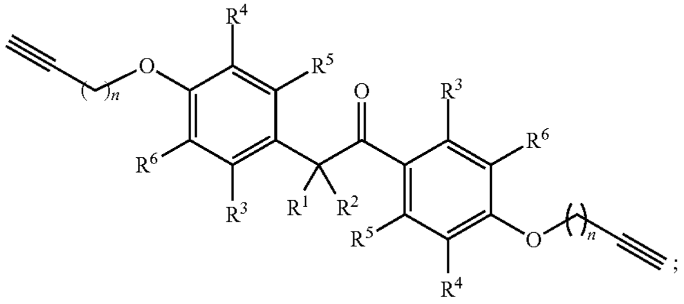
Publication Classification

-continued

(II)



(III)



wherein R^1, R^2, R^3, R^4, R^5, R^6, and n are defined herein. Also disclosed are polyesters including repeating units having the structure (IV), (V), or a combination thereof

Polymers Built from Bisphenol Triazole (BPT)

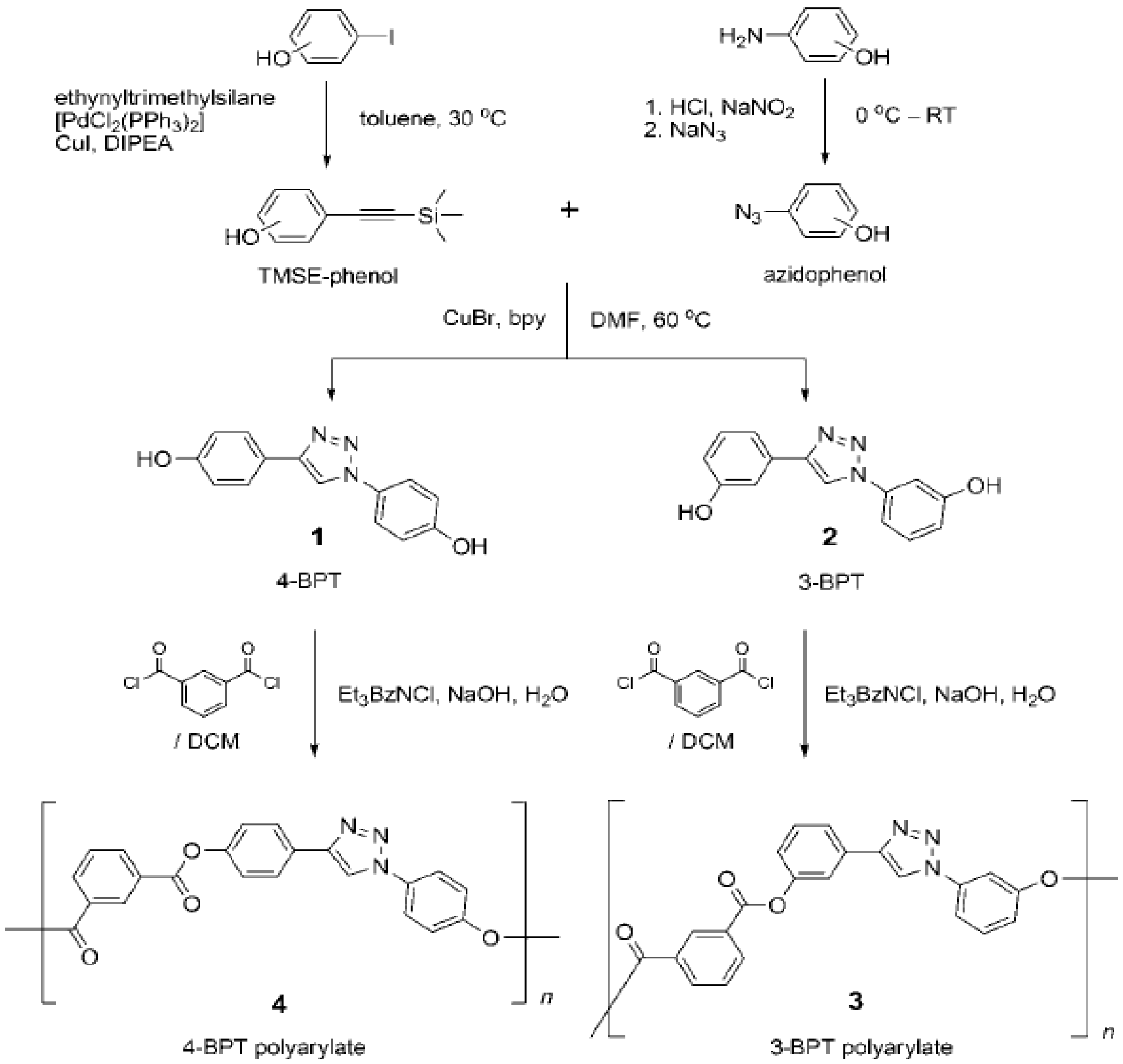
Thermally Induced Structural Transformation of Bisphenol-1,2,3-triazole Polymers: Smart, Self-Extinguishing Materials**

*Beom-Young Ryu and Todd Emrick**

Table 1: Heat release capacity (HRC), total heat release (THR), and charring properties of BPT-containing polymers and commercial high-performance materials.

Entry	Polymer	HRC [$J\,g^{-1}\,K^{-1}$]	THR [$kJ\,g^{-1}$]	Char [%][b]
1	BPA polyarylate	456 ± 13	17.7 ± 0.5	26
2	4-BPT/BPA (50/50)	95 ± 4	12.0 ± 0.5	38
3	4-BPT	46 ± 5	6.8 ± 0.3	47
4	3-BPT/BPA (50/50)	102 ± 5	11.3 ± 0.4	44
5	3-BPT	23 ± 3	4.6 ± 0.2	56
6	Kevlar[a]	363 ± 2	8.8 ± 0.5	38
7	Nomex[a]	99 ± 0.5	6.6 ± 0.2	43
8	Kapton[a]	14	4.0	66

[a] Data taken from the references.[11] [b] Data obtained from TGA at 850 °C in nitrogen (heating rate 10 °C min^{-1}).

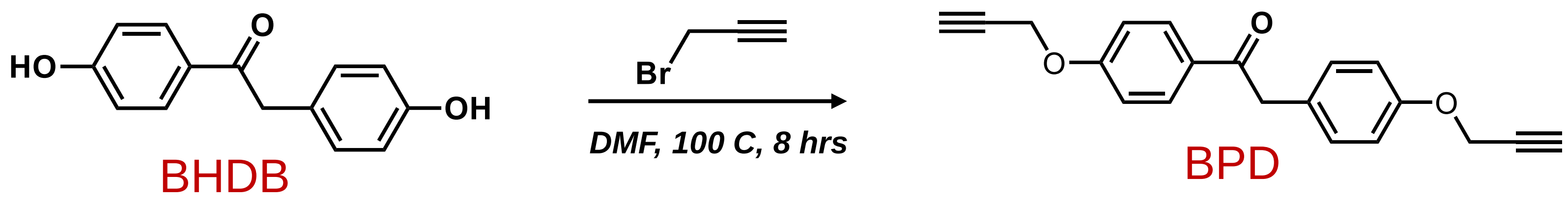


Scheme 2. Synthetic procedures for BPT polymers. bpy = bipyridine, Bz = benzoyl, DCM = dichloromethane, 4-BPT = 1,4-bis(4-hydroxyphenyl)-1,2,3-triazole, 3-BPT = 1,4-bis(3-hydroxyphenyl)-1,2,3-triazole.

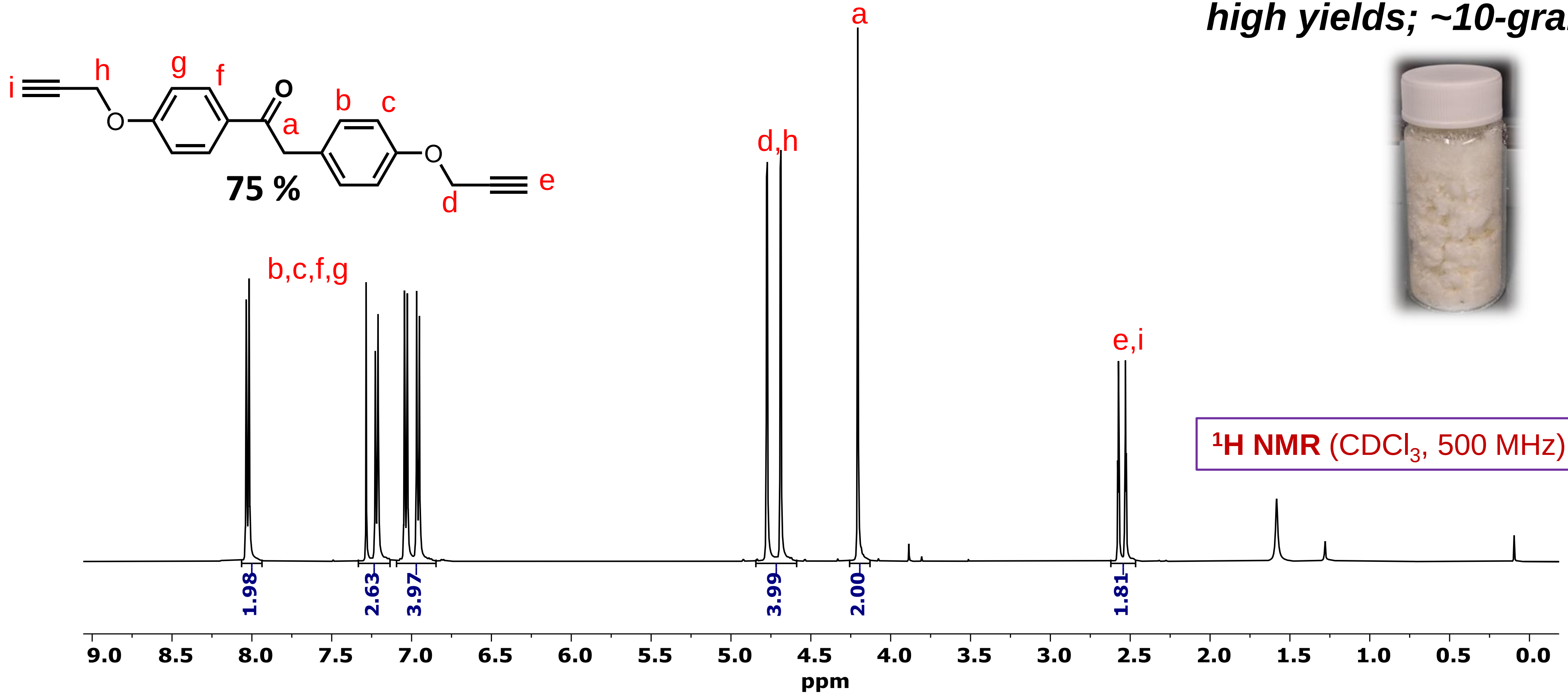
Beom-Young Ryu and Todd Emrick, Angew. Chem. Int. Ed. ***2010****, 49, 9644 –9647*

Bis-propargyl Deoxybenzoin (BPD)

Dr. Krishnamurthy Munusamy



Initial synthetic attempts: high yields; ~10-gram scale

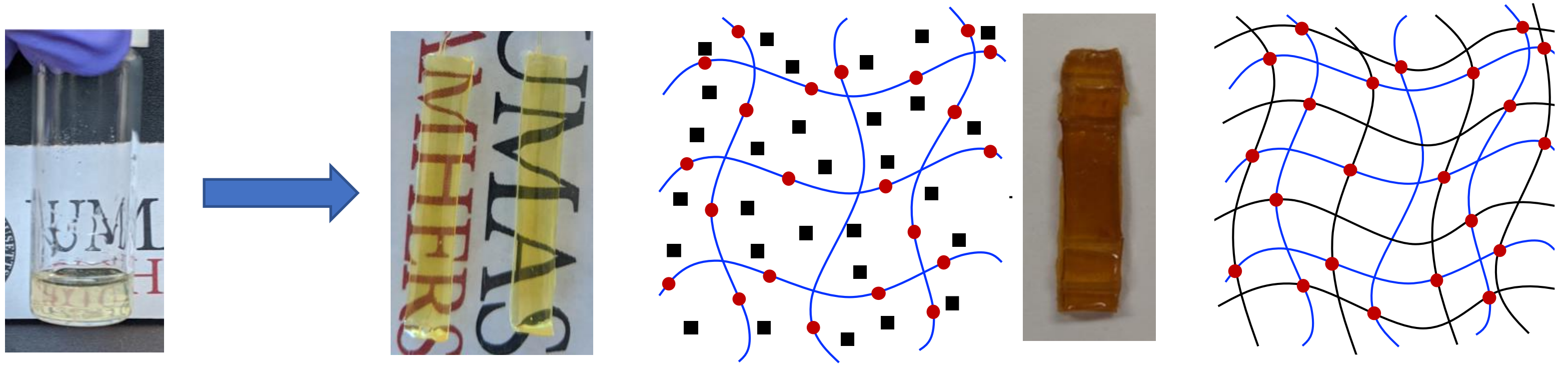


^{1}H NMR ($CDCl_3$, 500 MHz)

Presentation outline

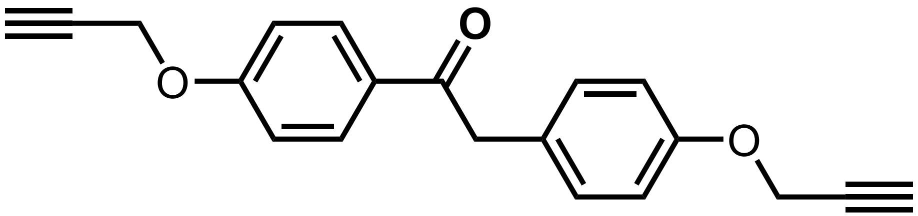
New Synthetic Routes to Deoxybenzoin
as Key Component of Non-flammable Polymers and Additives

I. High-yield syntheses of deoxybenzoin monomers and cross-linked polymer networks



II. Alkynyl-functionalized deoxybenzoins: preparation and use in step-growth polymerization reactions

Bis-propargyl deoxybenzoin (BPD)

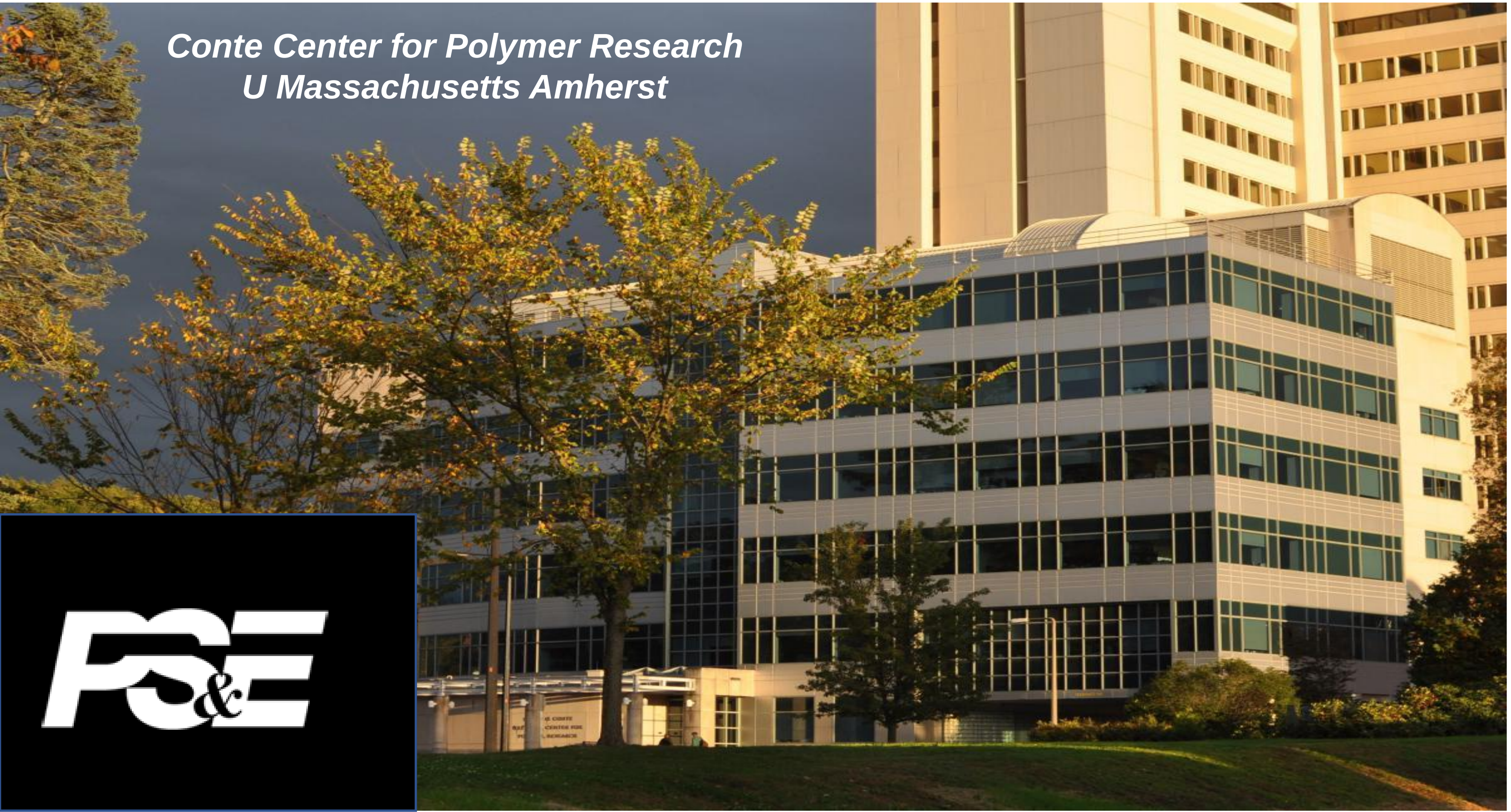


Precursor to low heat-release oligomers and polymers

Designing Polymeric Hydrocarbons for Low Flammability Materials

10th Triennial International Aircraft Fire and Cabin Safety Research Conference
October 18, 2022

*Todd Emrick, **Elizabeth Stubbs**, Chien-Han Chen, and **Krishnamurthy Munusamy***
Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA 01003



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