Deoxybenzoin-containing Polymers: Combining Tailored Polymer Architectures with Non-halogenated Materials

The Ninth Triennial International Fire & Cabin Safety Research Conference
Atlantic City, NJ October 29 2019

Todd Emrick
Polymer Science and Engineering Department
University of Massachusetts Amherst

Research Support

Federal Aviation Administration

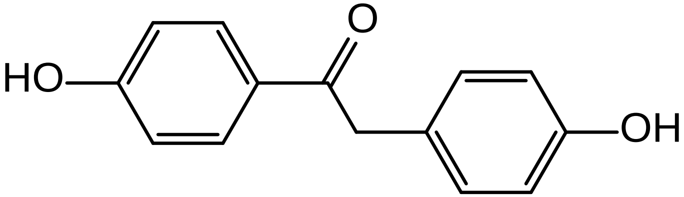
Industrial support through the Center for UMass-Industry Research on Polymers (CUMIRP)

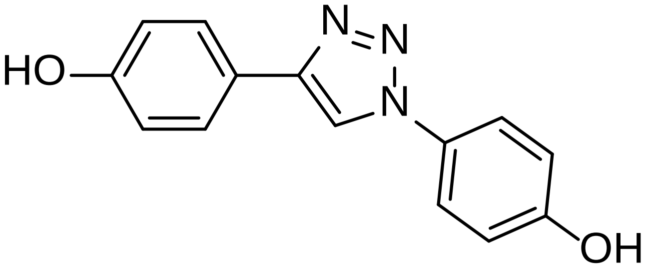
@Emrickgroup

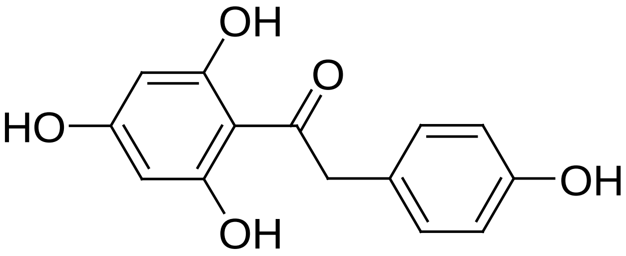
Synthetic Progress on Low-flammability Materials Enabled by FAA Support

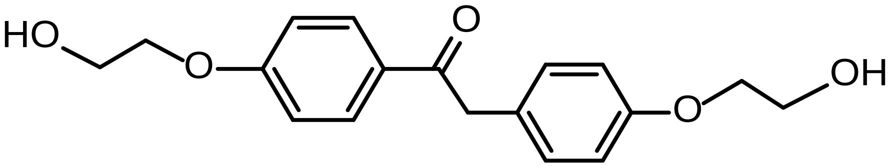
Objective: New materials discovery to produce scalable, non-flammable materials

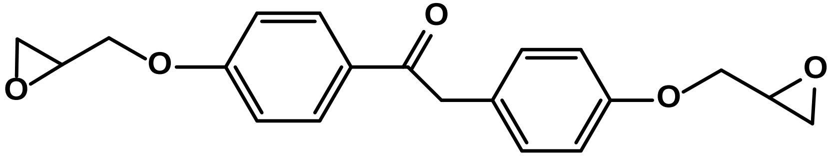
*Non-halogenated precursors to polymers with **high char yield** and **low flammability***

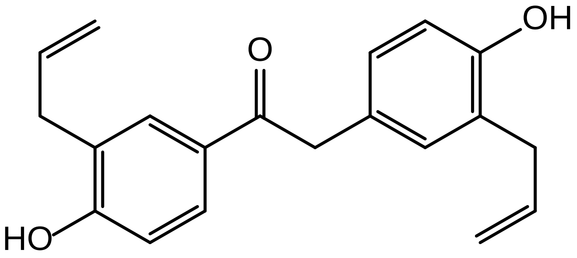


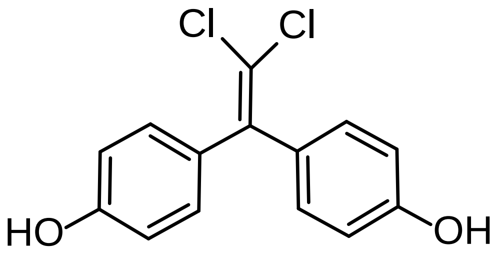








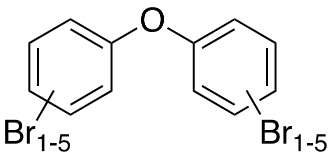


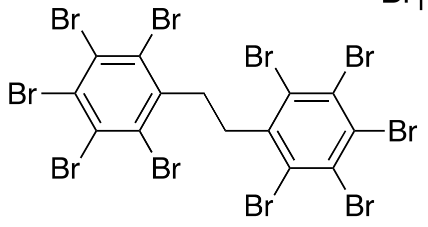


Precursors to polymeric epoxies, sulfones, esters, urethanes, carbonates, and others

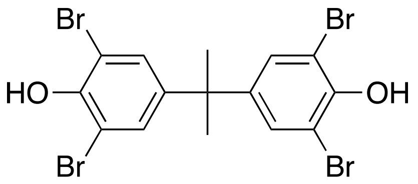
Progress in Organic and Polymeric Flame Retardants

Halogenated small molecule additives



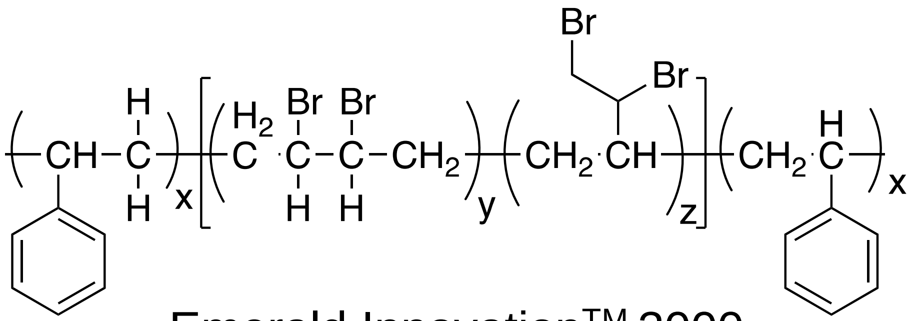


Saytex® 8010
Firemaster® 2100R



monomer or additive

Halogenated polymeric additives



Emerald Innovation™ 3000

+ *Effective use in commodity polymers (polycarbonate, polyurethanes, epoxy, polystyrene etc.)*

- *Leaching from polymer material*
Environmental persistence
Toxicity
Restrictions and legislation

Inorganic fillers: non-halogenated

Aluminum trihydrate

Magnesium hydroxide

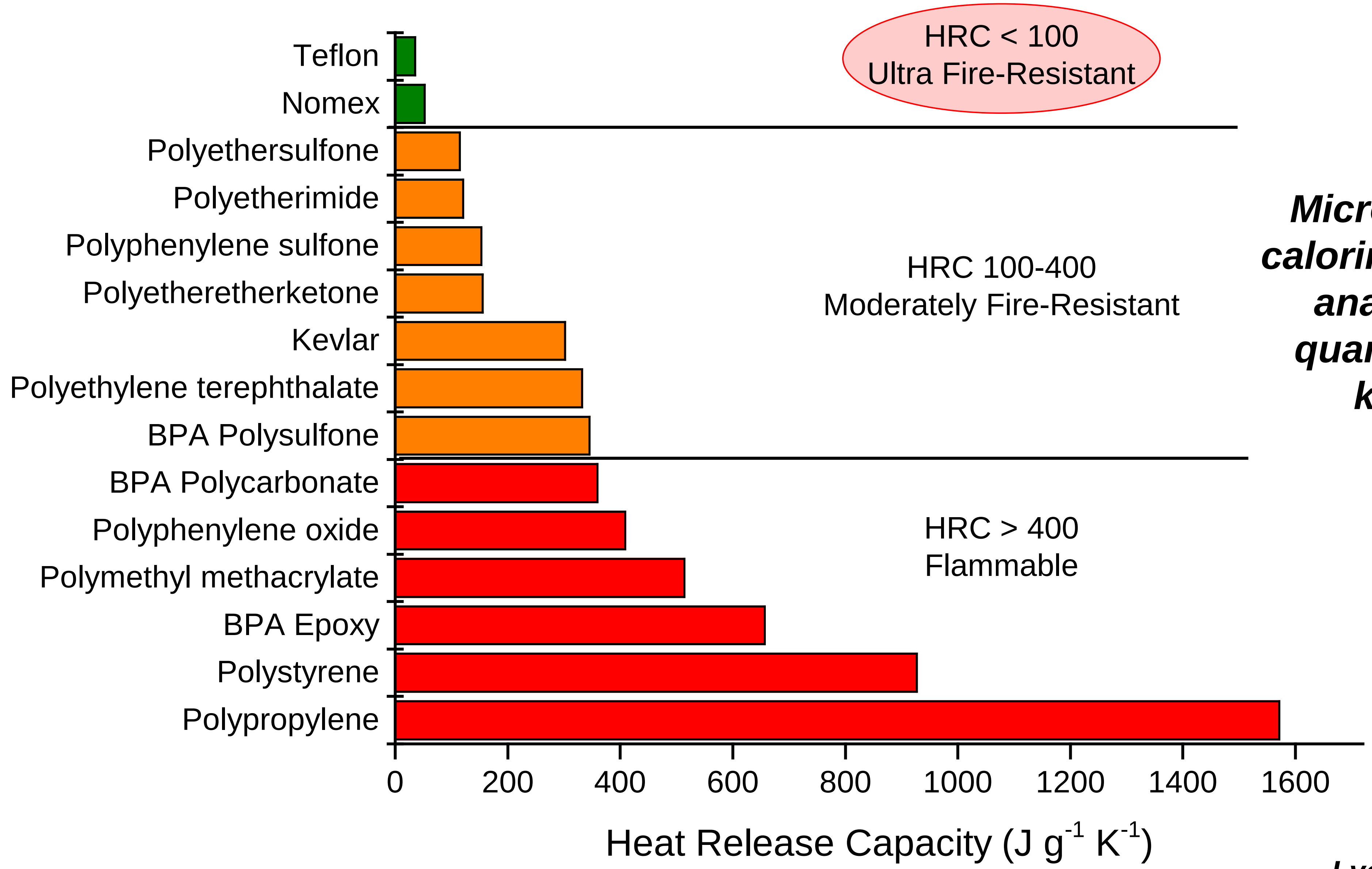
Phosphorus, nitrogen, and silicon-based inorganics

+ *Environmentally-friendly*
Used in commodity polymers

- *High loading needed for FR activity*
- *Negative impact on mechanical properties of host polymer materials*
- *Limitations in high-temperature applications*

Our objective: develop *inherently* non-flammable polymers: no halogen, no P, no Al, etc…..

Heat Release Capacity (HRC) Measurements on Synthetic Polymers



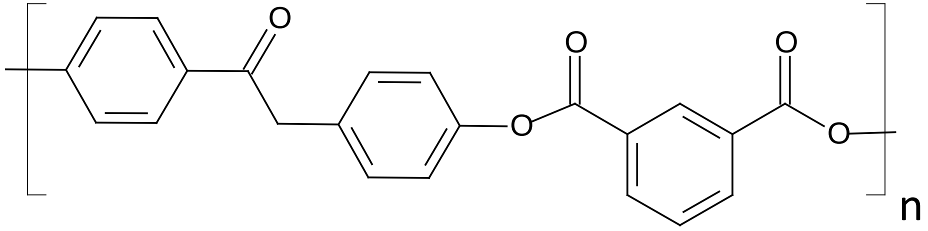
Microscale combustion calorimetry (MCC) enables analysis of milligram quantities of novel and known materials

Lyon, Walters, and co-workers
Federal Aviation Administration

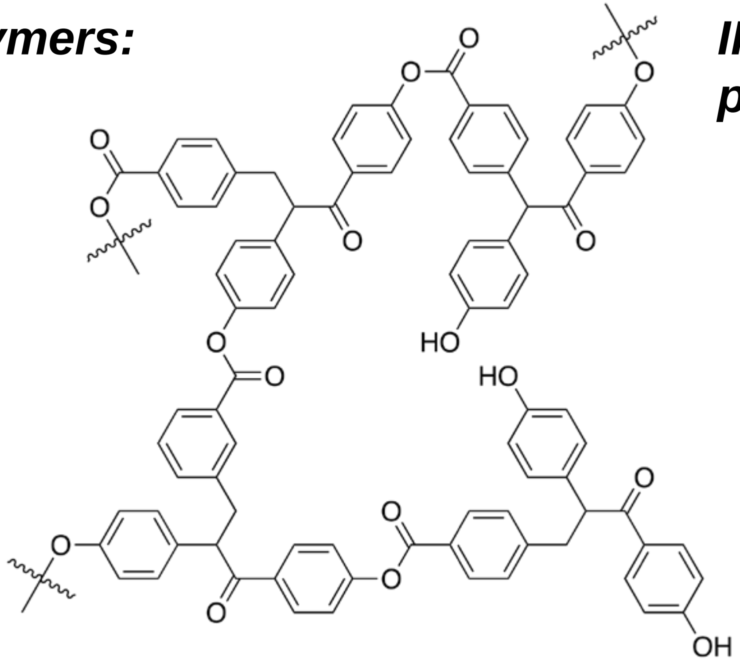
Presentation Outline

Deoxybenzoin as a component of aromatic hydrocarbon flame-retardants

I. Brief background on polymers derived from deoxybenzoin



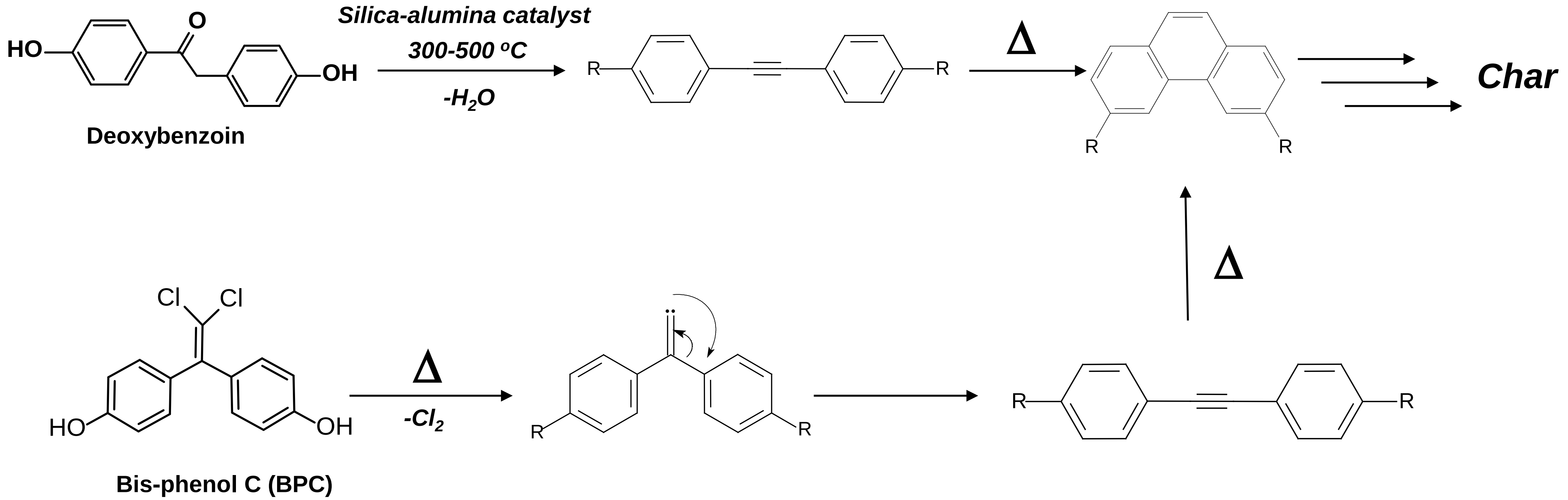
II. Branched deoxybenzoin polymers: new, polymeric additives



III. Deoxybenzoin polymers + phosphorus derivatives

Deoxybenzoin: Pathway to Char Formation

Deoxybenzoin converts to diphenylacetylene at high temperatures

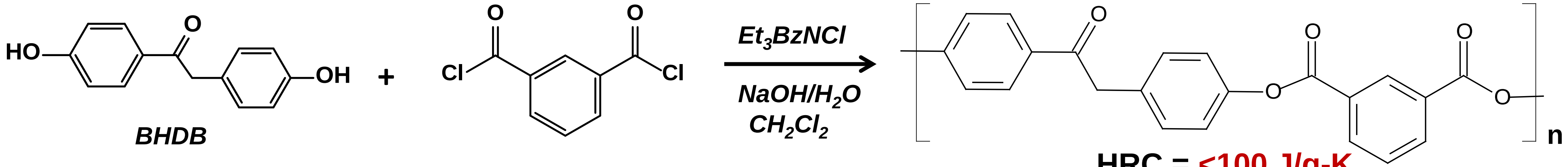


Polyesters, polyurethanes, epoxy polymers, polysulfones, polyester/triazoles, polyamides, vinyl polymers

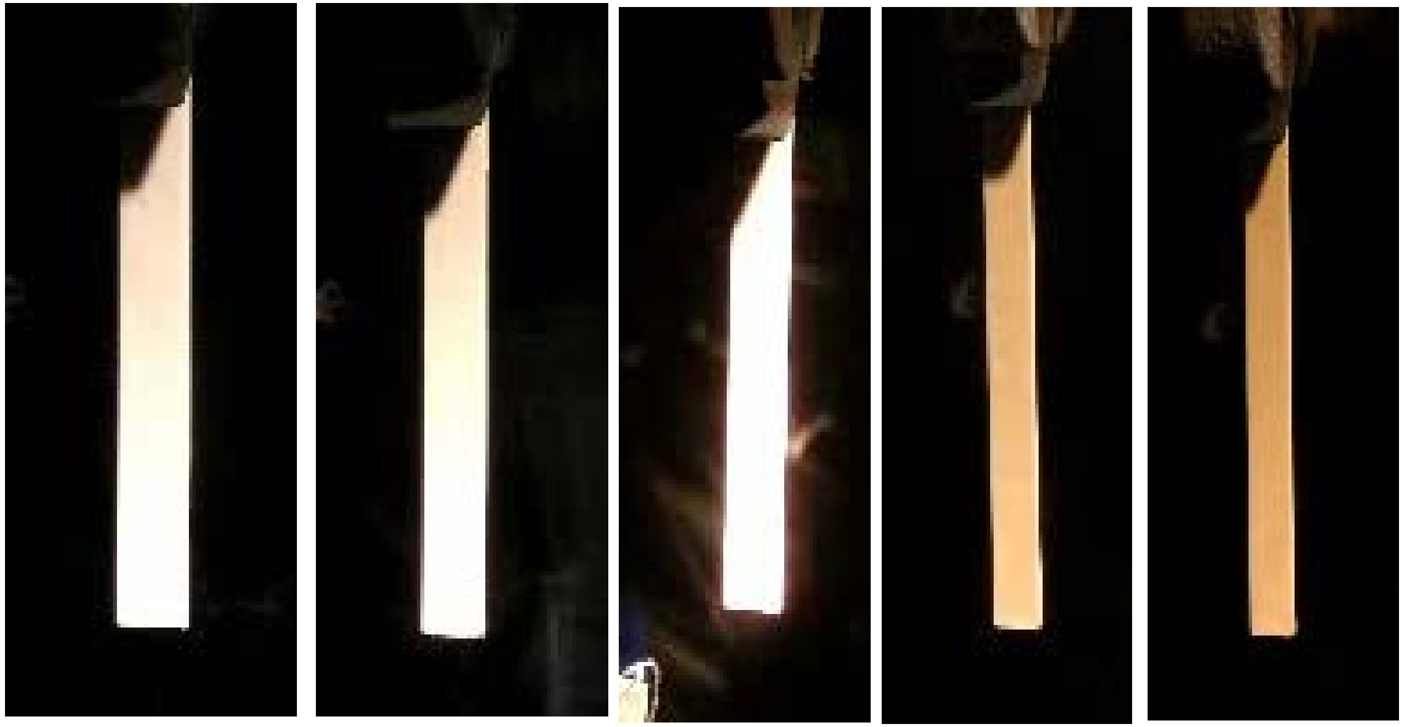
Ramirez, M. L. *Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers. DOT/FAA/AR-00/42.*; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001; Stoliorav, S.I.; Westmoreland, P.R. *Polymer* **2003**, *44*, 5469; van der Waals et al. *J. Mol. Cat. A* **1998**, *134*, 179

Examples: Deoxybenzoin Incorporation into Aromatic Polyesters

BHDB Polyarylate

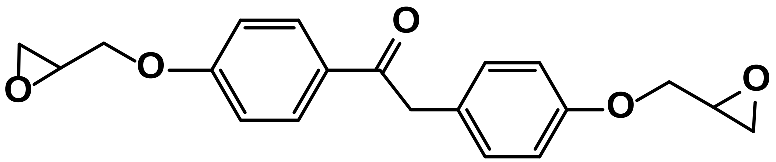


HRC = <100 J/g-K
Char yield = 45%

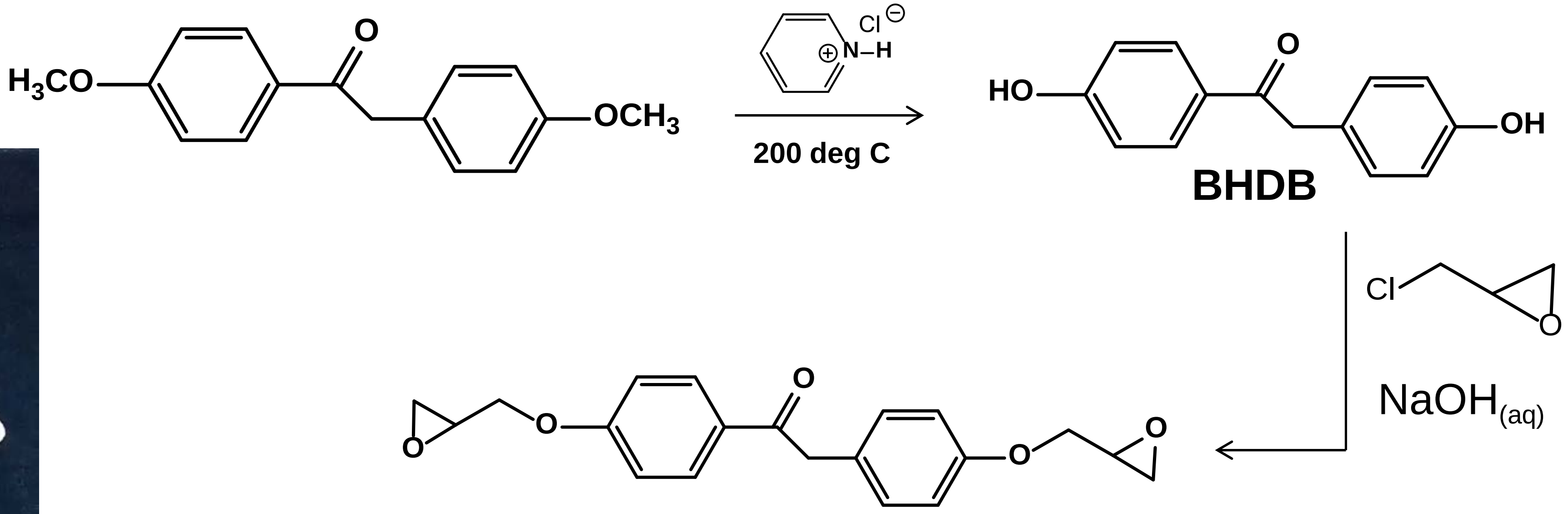


Increasing deoxybenzoin content (up to 15 weight percent)

Bis-epoxy Deoxybenzoin (BEDB)



BEDB



BEDB

BPA-epoxy

BEDB-epoxy

BEDB is easy to scale up: 200 gram batches in UMass labs

Deoxybenzoin Doubles Char and Halves Heat Release

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

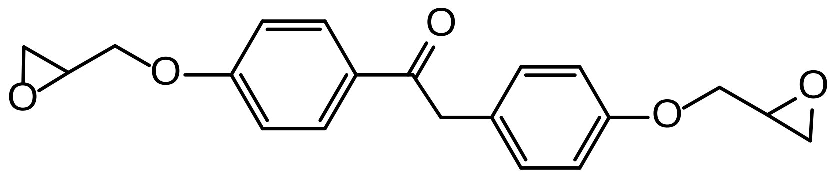
Thermal properties and flammability of the resins cured with mixed amines.

	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′-$DDS_{0.5}$ 4,4′-$DDM_{0.5}$	173	34	321 ± 10	16.9 ± 0.3
	BEDB/4,4′-$DDS_{0.2}$ 4,4′-$DDM_{0.8}$	160	35	378 ± 29	16.9 ± 0.1
	BEDB/4,4′-DDM	145	35	439 ± 7	17.6 ± 0.2

[a] Subscripts mean mole fraction of compounds.
[b] T_gs were obtained from DSC.
[c] Char residues were obtained from TGA at 850 °C in nitrogen (heating rate 10 °C/min).

THR: heat of combustion of pyrolysis gas

HRC: maximum heat release rate divided by the heating rate



BEDB

Lap shear strengths: BEDB/DDS: 15.4 MPa; BEDB/DDM: 12.8 MPa

ASTM D 1002 protocol EBPA/DDS: 11.0 MPa; EBPA/DDM: 9.2 MPa

BEDB vs. BPA-epoxies

Comparable storage modulus

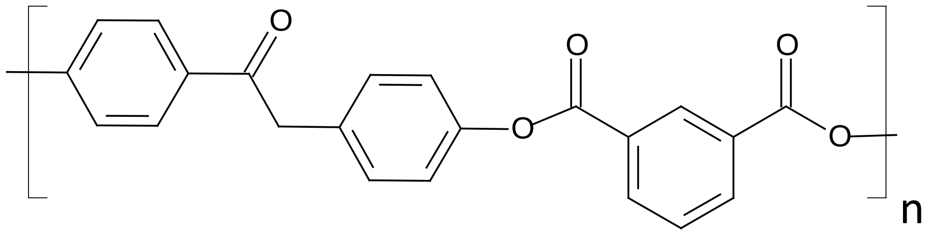
BEDB had higher plane-strain fracture toughness

Polymer 2009

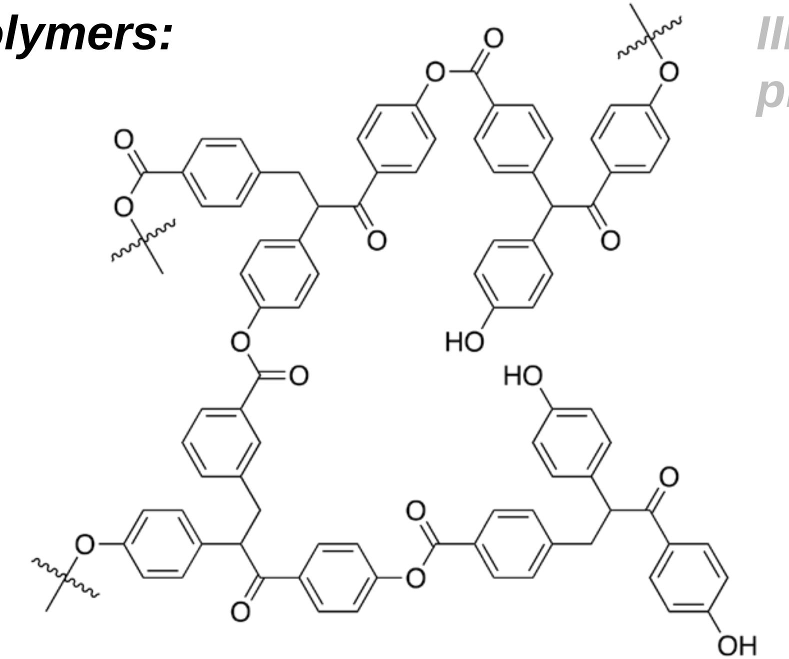
Presentation Outline

Deoxybenzoin as a component of aromatic hydrocarbon flame-retardants

I. Brief background on polymers derived from deoxybenzoin

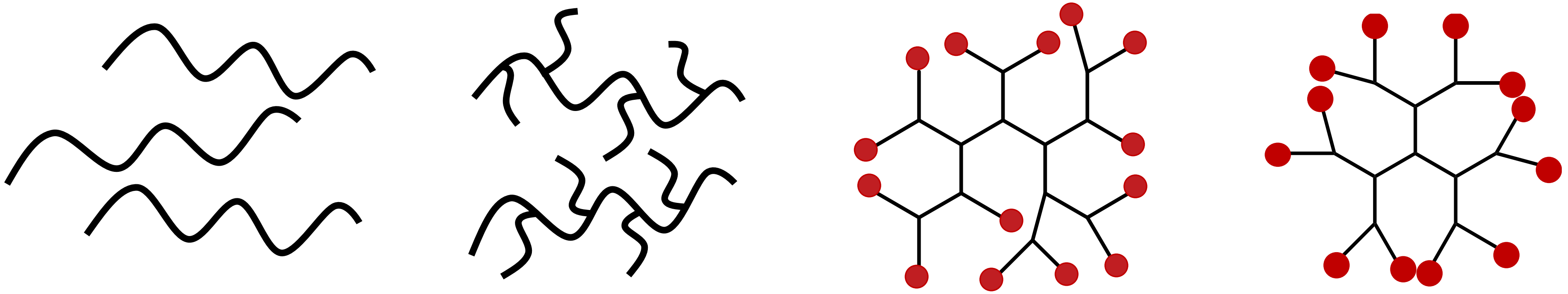


II. Branched deoxybenzoin polymers: new, polymeric additives



III. Deoxybenzoin polymers + phosphorus derivatives

Impact of Branched Polymer Architecture on Properties

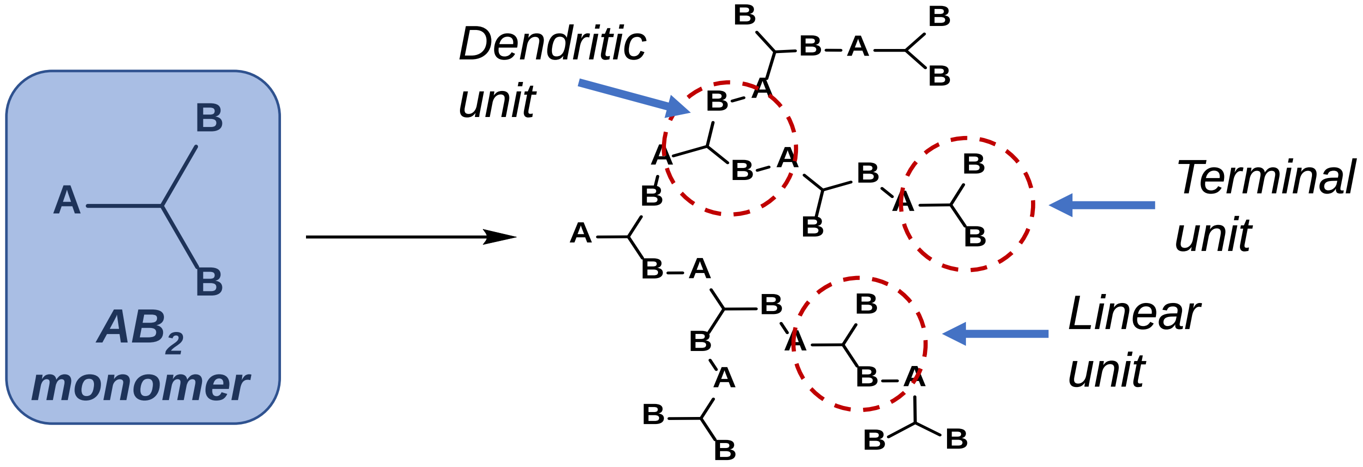


Polymer architecture	Linear	Branched	Hyperbranched	Dendritic
Viscosity	**high**	**low**	**low**	**very low**
Solubility	**low**	**high**	**high**	**very high**
Degree of branching (DB)	**0**	**0-0.4**	**0.4-1**	**1**

$$DB = \frac{D + T}{D + T + L}$$

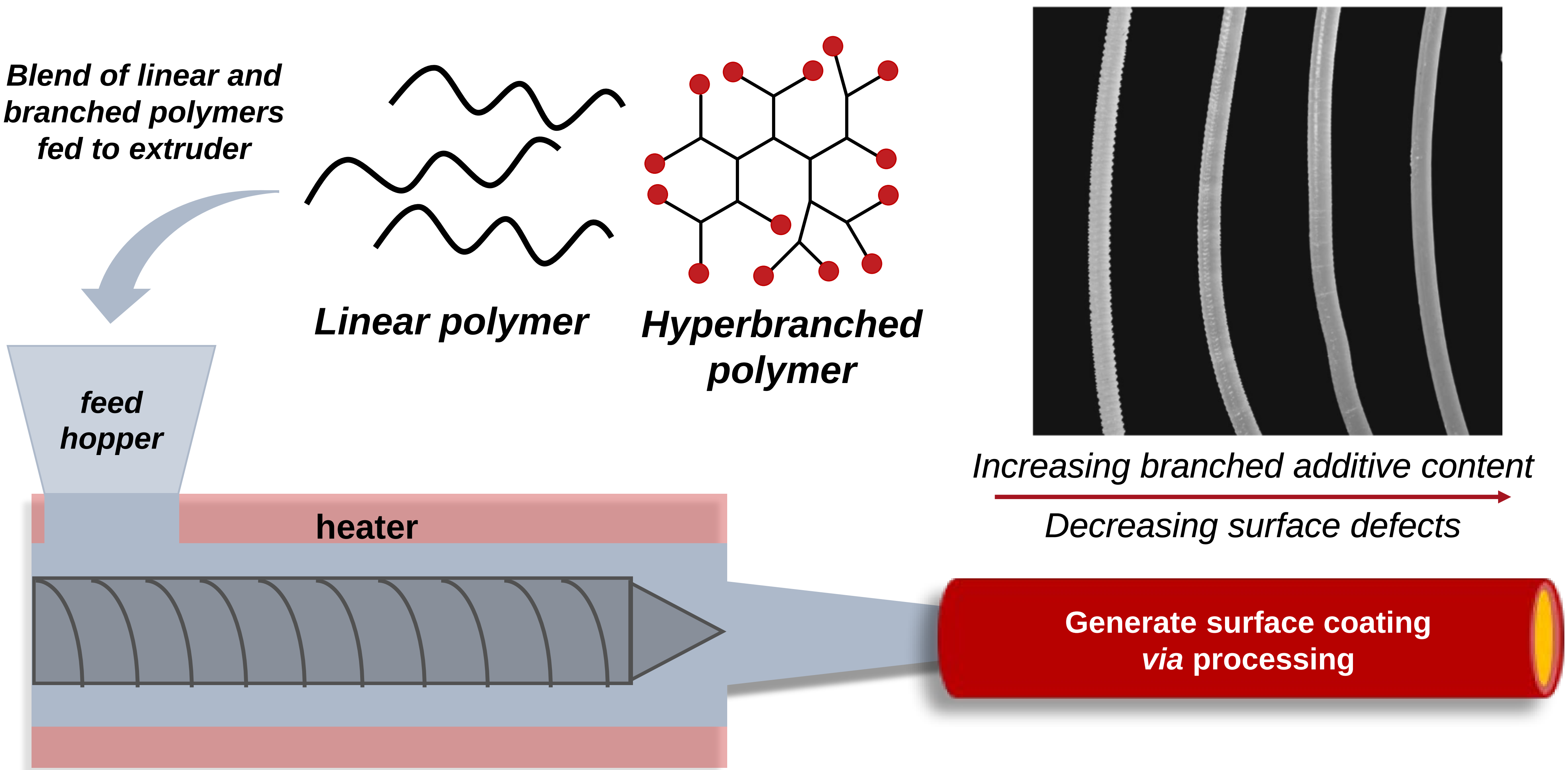
Degree of branching (DB)
determined spectroscopically

D = Dendritic
L = Linear
T = Terminal



Frechet *J. Am. Chem. Soc.* 1991.
Gao *Hyperbranched polymers-Chapter 1* 2011.

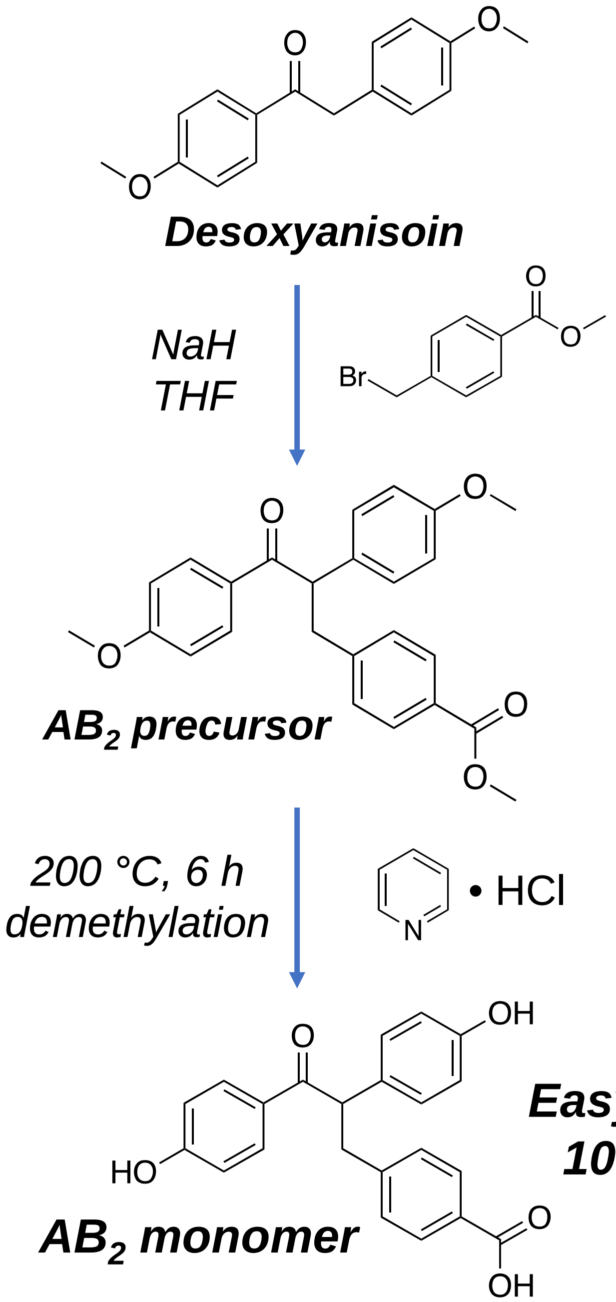
Branched Polymers as Processing Aids



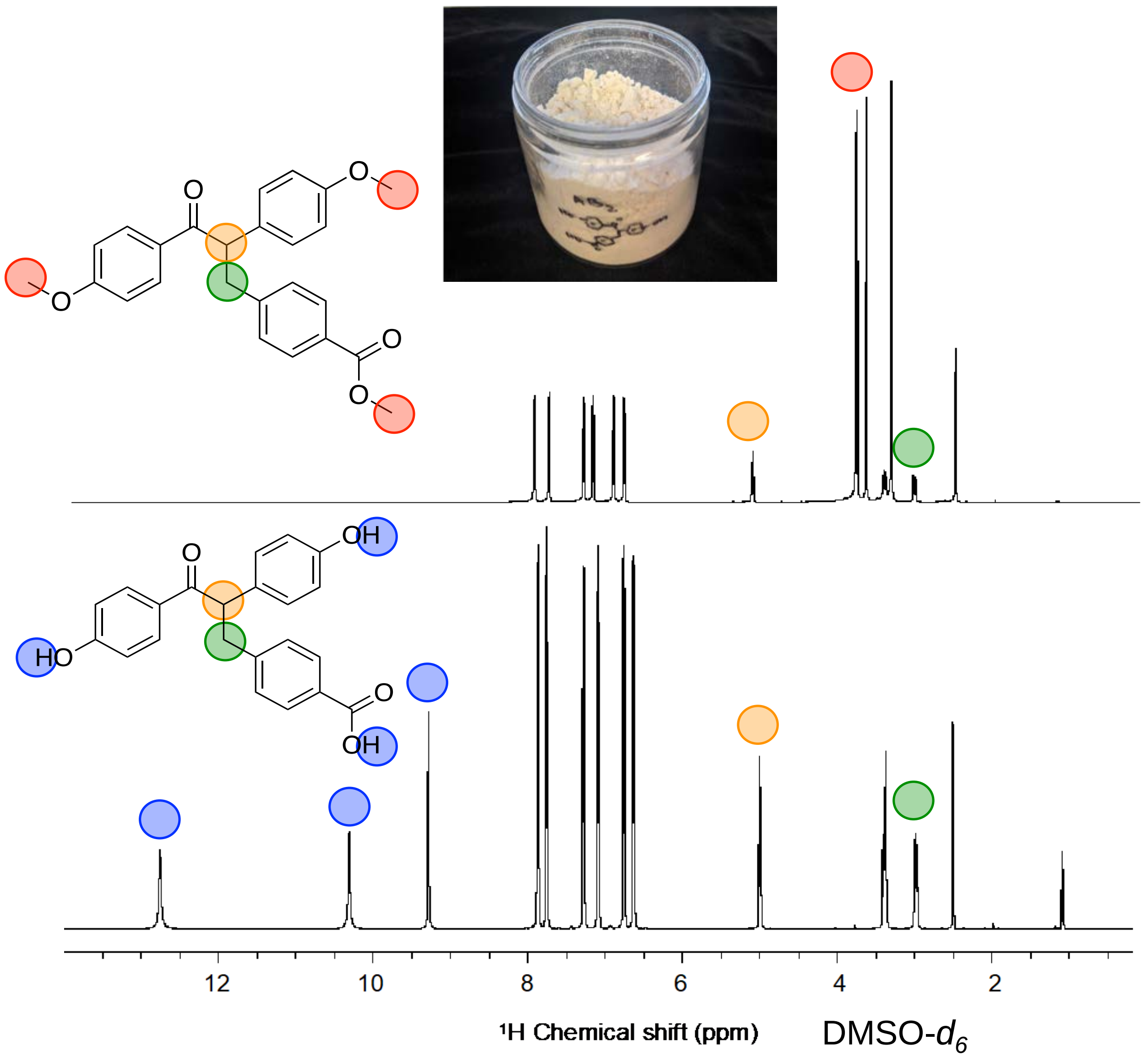
Mackay *Journal of Rheology* 1999

Objective: Combine processing benefits of branched polymers with low flammability

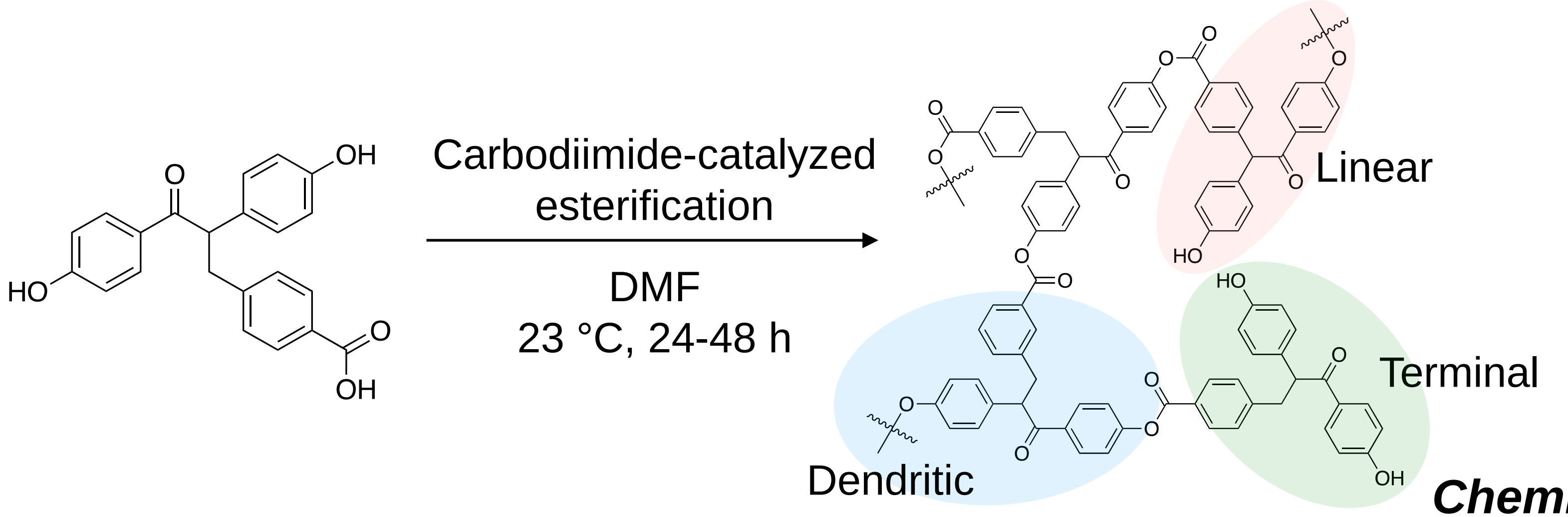
Preparation of Deoxybenzoin AB_2 Monomer



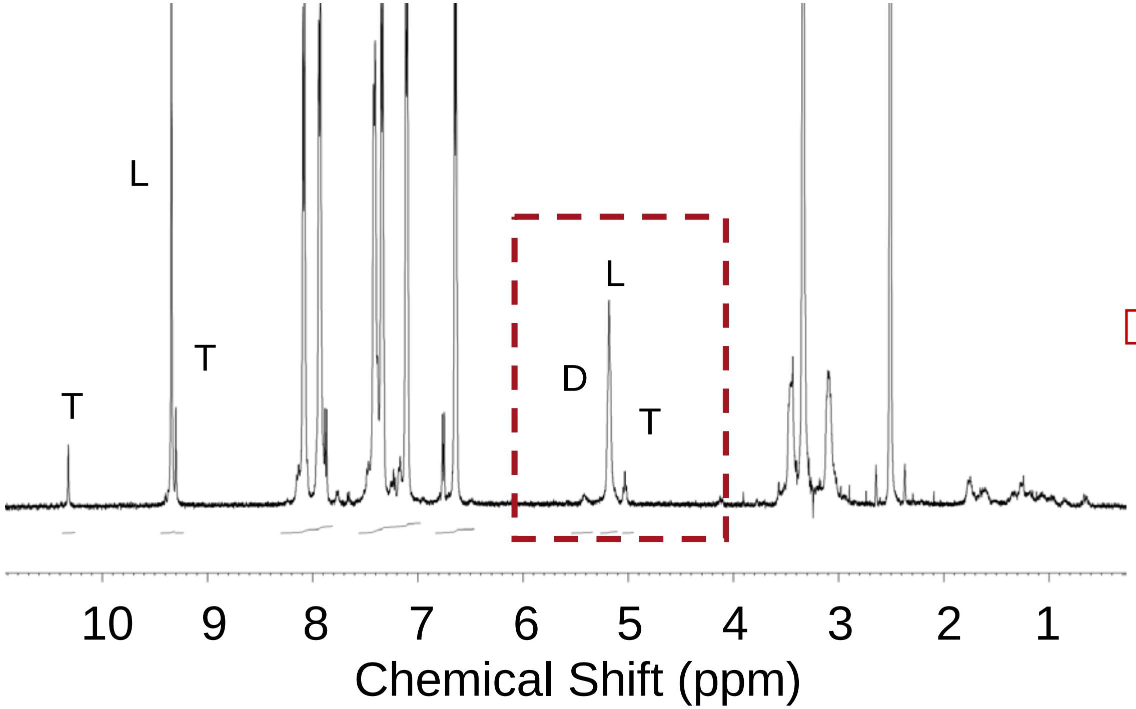
Easy to make 100 grams



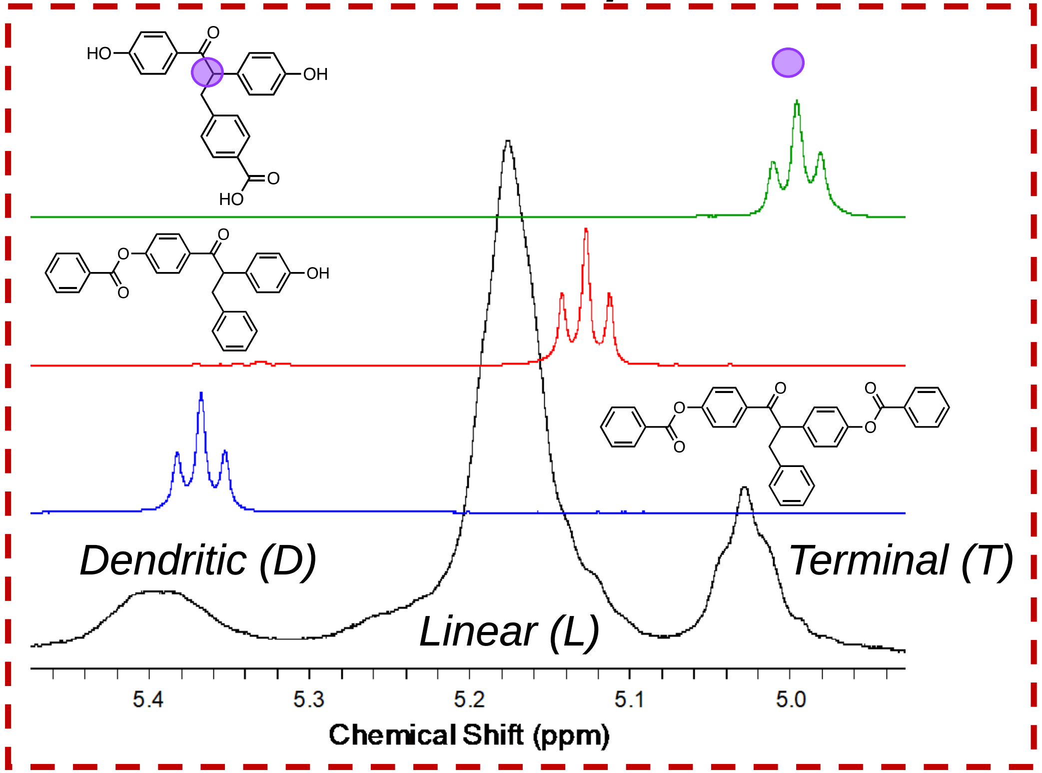
Synthesis of Branched, Deoxybenzoin Aromatic Polyesters



Calculated DB: 0.36
M_w 17,000 g/mol

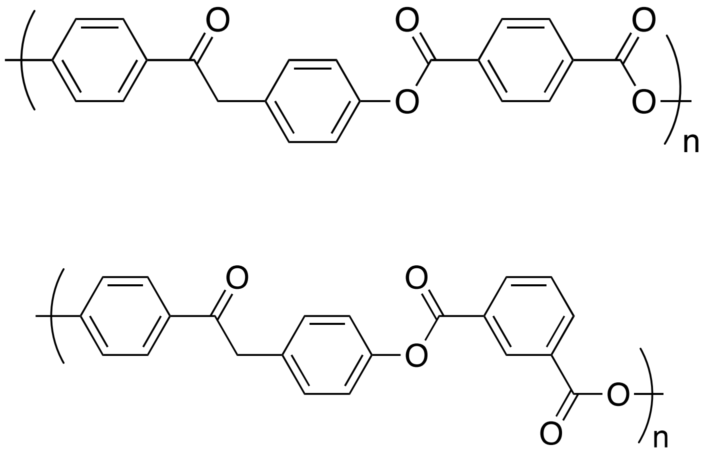


Chemical shift of methine proton defines DB



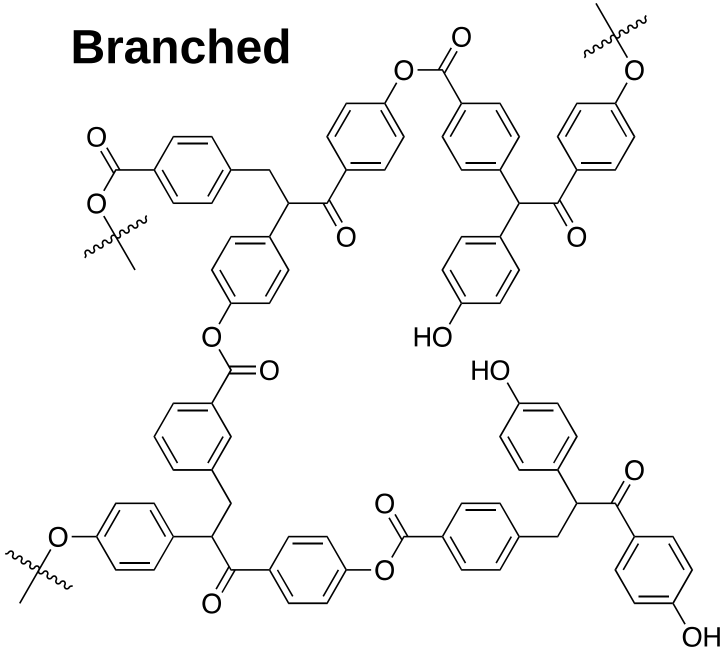
Impact of Branching on Polyester Properties

Linear



vs.

Branched



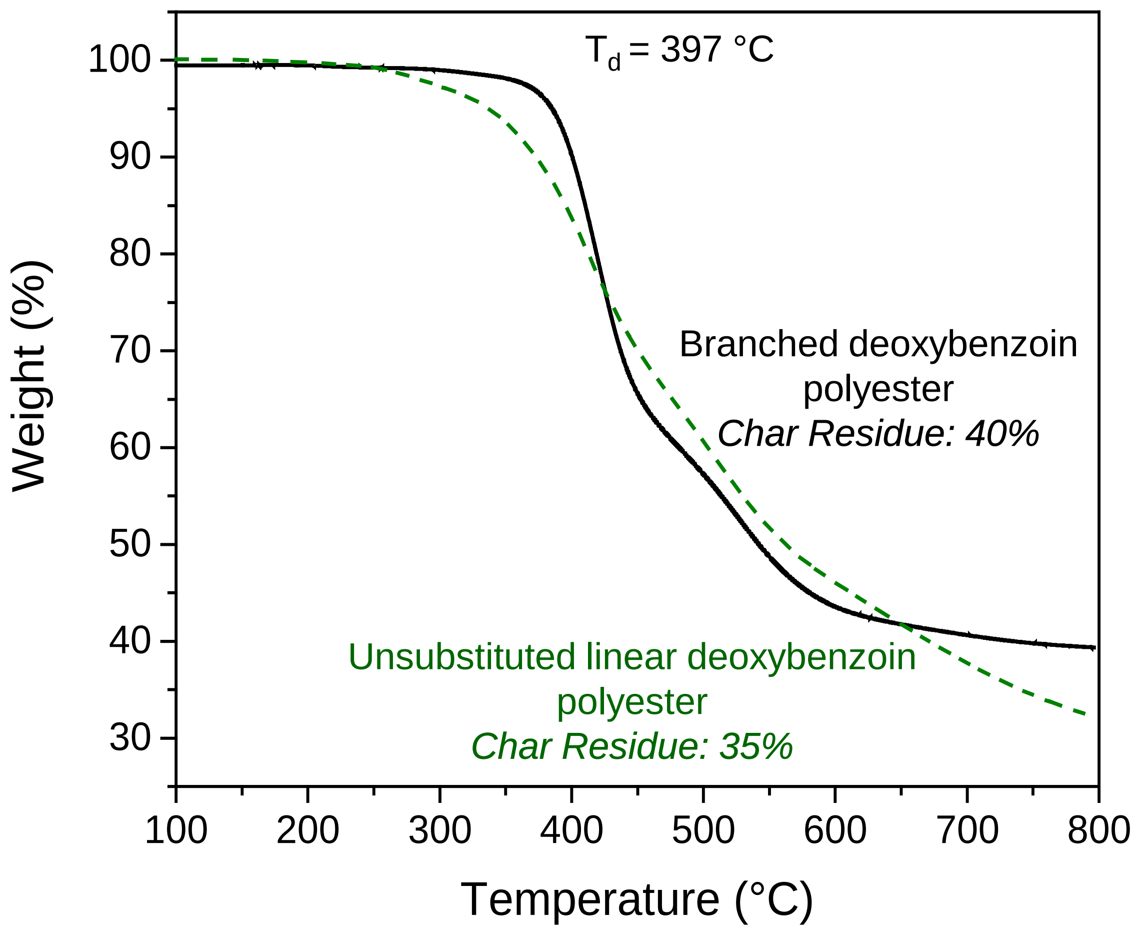
Polymer	Solvent solubility	M_n (kg/mol)	M_w (kg/mol)	Đ
BHDB-TPC*	insoluble	-	-	-
BHDB-IPC*	DMF	3.2	2.6	1.22
Branched	DMF, THF, DMSO	32.9	100	3.20

Molecular weights estimated by GPC, eluting in DMF, relative to PS calibration standards

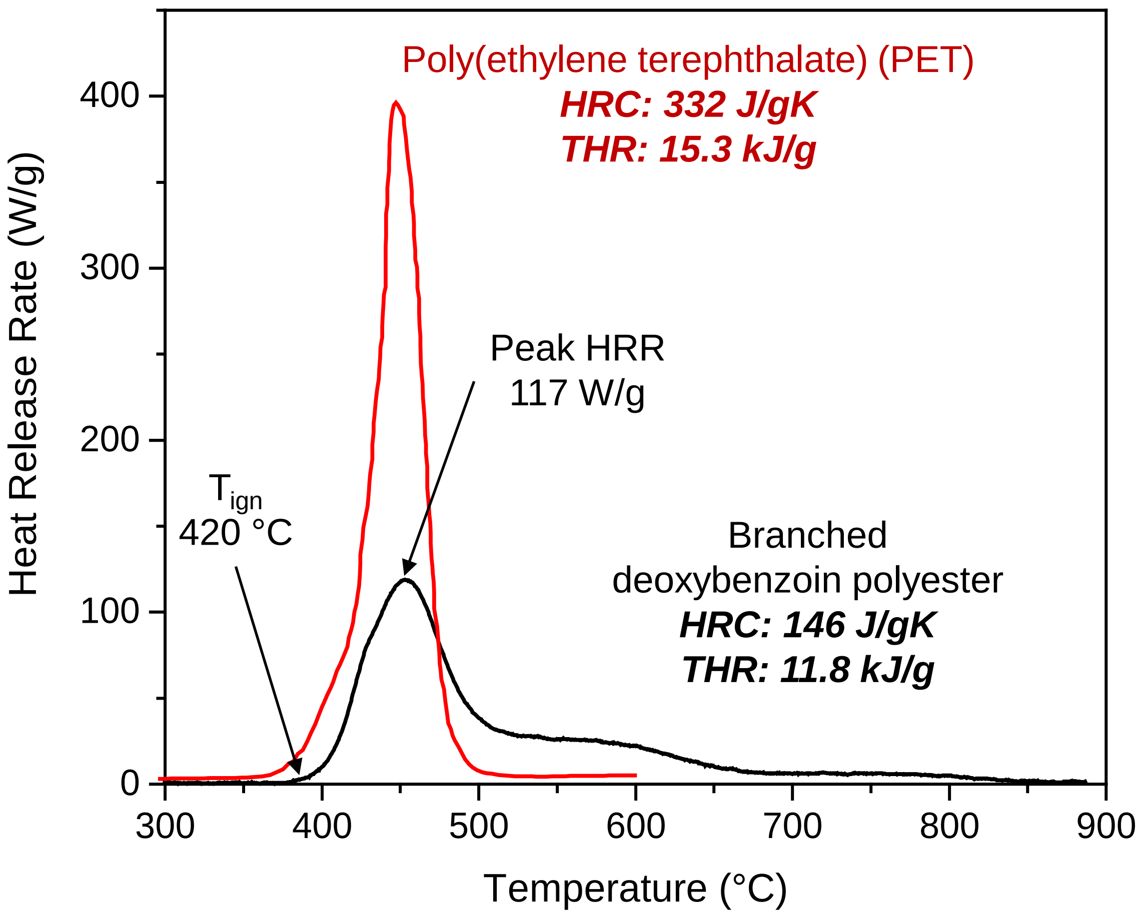
*Ellzey, *Macromolecules* 2006

Thermal Properties of Branched Deoxybenzoin Polymres

Thermogravimetric analysis (TGA)



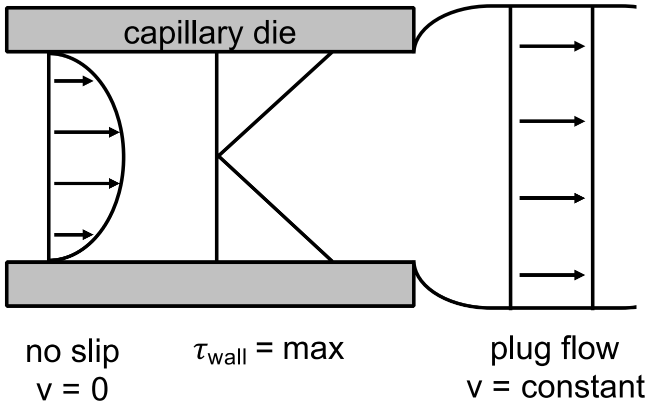
Microscale combustion calorimetry (MCC)



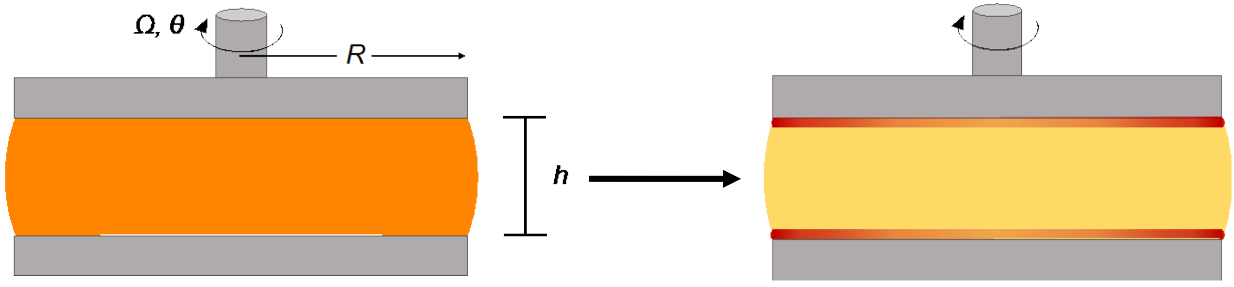
Highly branched deoxybenzoin polyesters exhibit low heat release

Lyon *J. Anal. Appl. Pyrol.* 2004
Zhao *Textile Research Journal* 2016.

Probing Polymer Blends with Parallel-plate Rheology



Shear stress proportional to shear rate



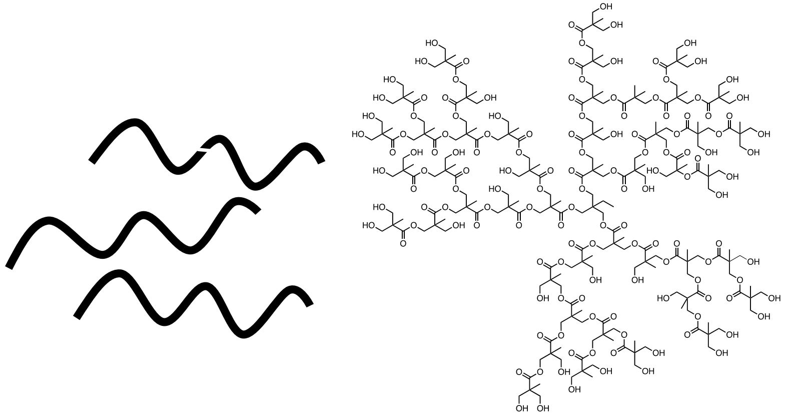
Increasing shear rate

Concentrate branched component in high shear region

Parallel-plate rheology as a tool to determine:

- Differences in blend viscosity
- Kinetics of branched polymer migration
- Probe a range of shear rates

Model system: blends of LLDPE and Boltorn™ H311



Perstorp

4th generation dendrimer

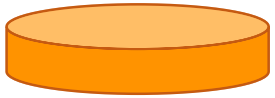
15 wt. %

melt mixed

170 °C
20 min
70 rpm

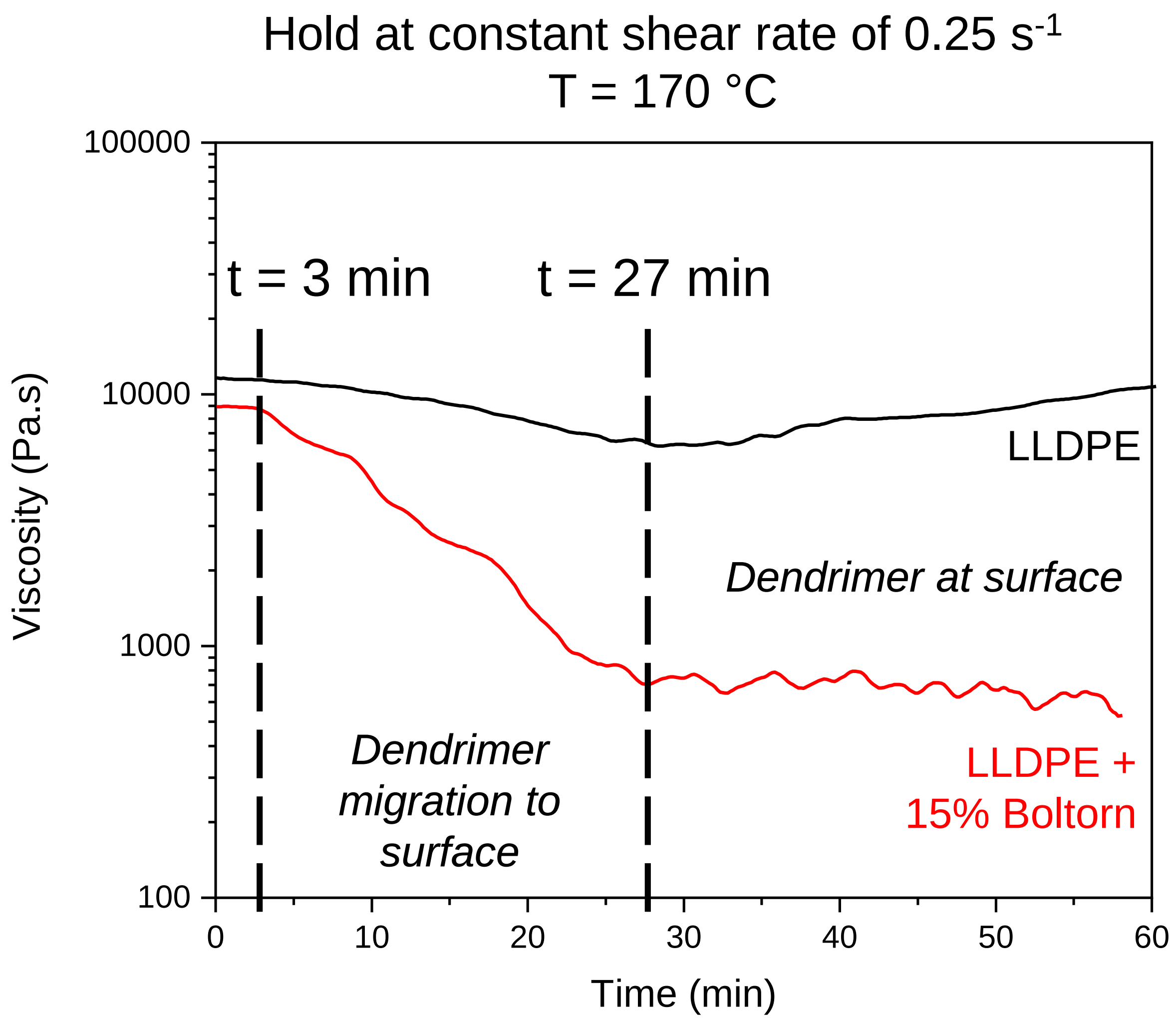
molded

170 °C
10 min

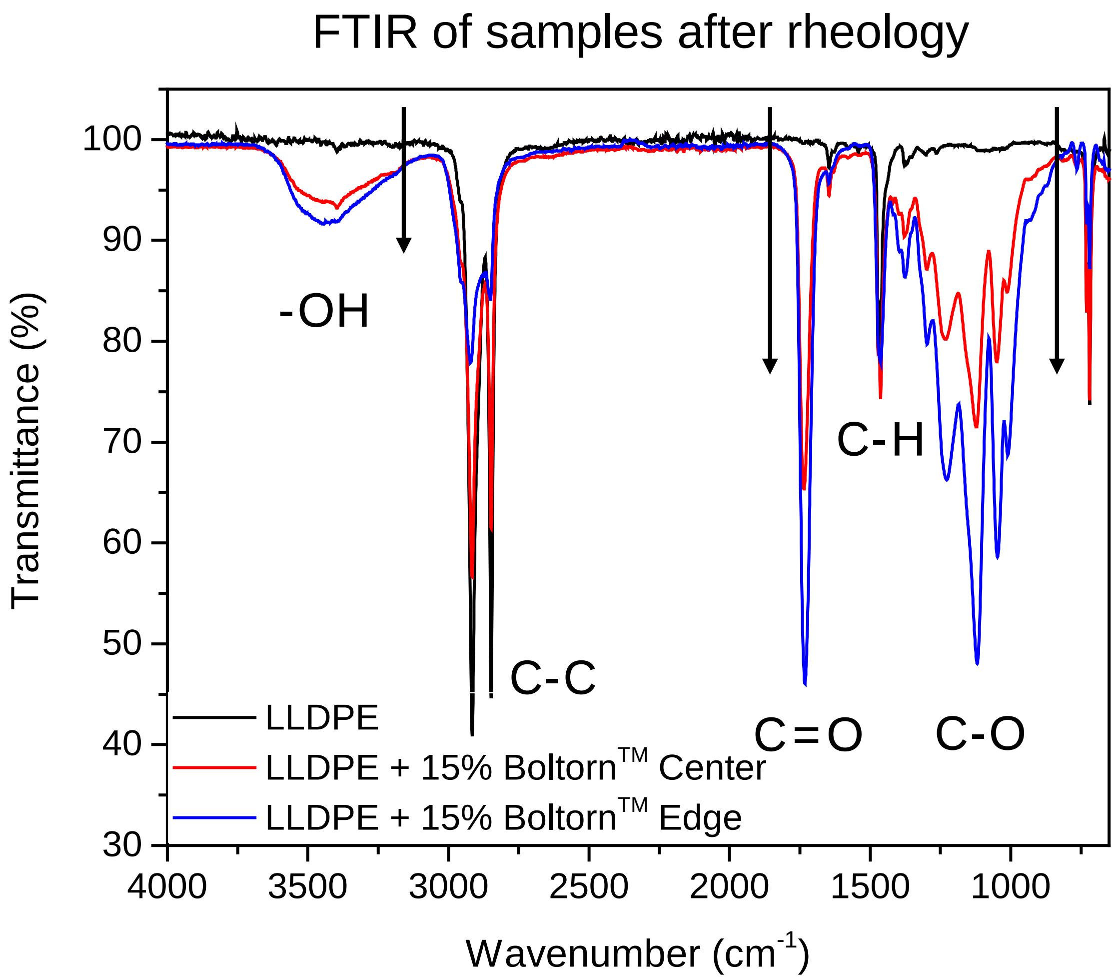


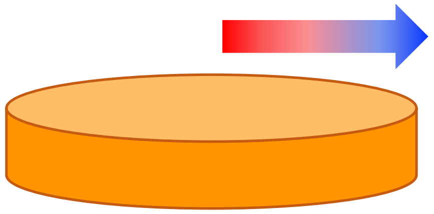
Blended sample for rheology

Model System: Polyethylene-Dendrimer Blends



Viscosity drop suggests dendrimer migration to surface





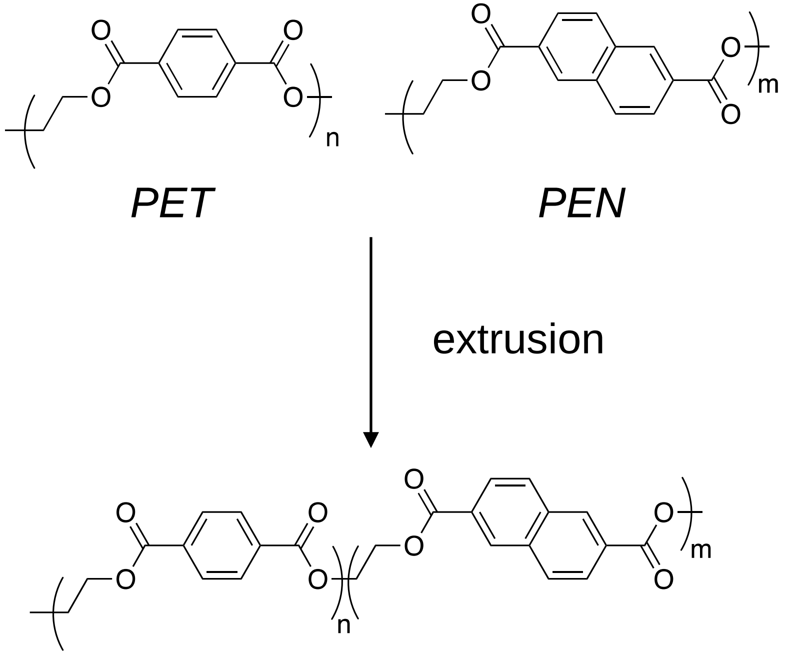
Increasing concentration detected at edge, in region of highest shear

Reactive Processing

Combining chemistry and processing into a single step

Transesterification

Ex. PET-PEN copolymers



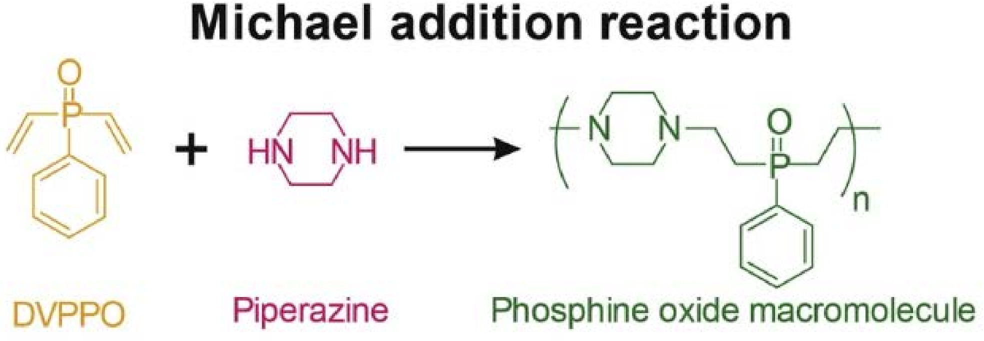
PET-PEN copolymer containing 1-20 % PEN

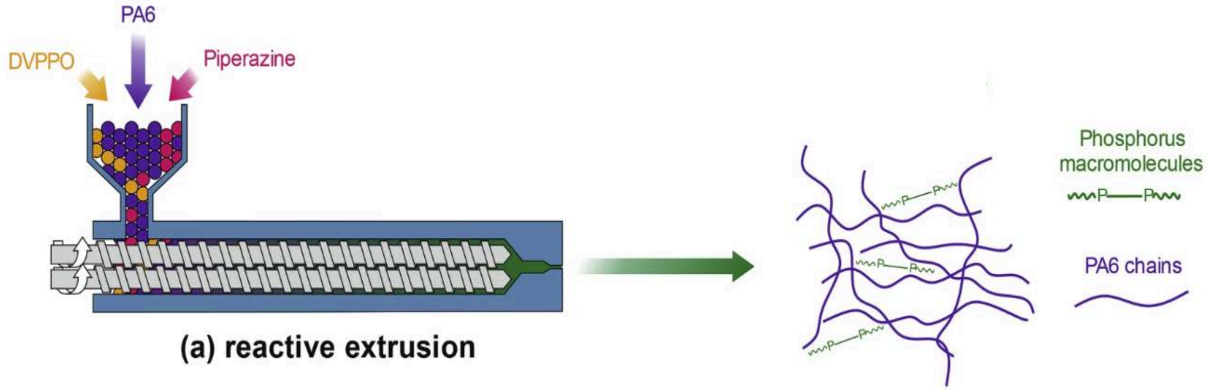
Enhanced mechanical, thermal, and barrier properties for food packaging

Hoechst Celanese Corp. (1996) WO 96/35571

Chemical modification with flame retardant moieties

Michael addition reaction





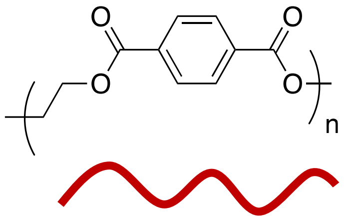
Solvent free method

Prevents leaching of flame-retardant

Gooneie *Poly. Degrad. and Stab.* 2019

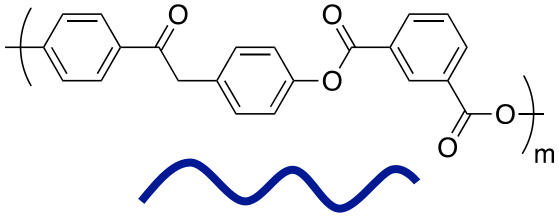
Reactive Processing with Deoxybenzoin Polyesters

Idealized reaction



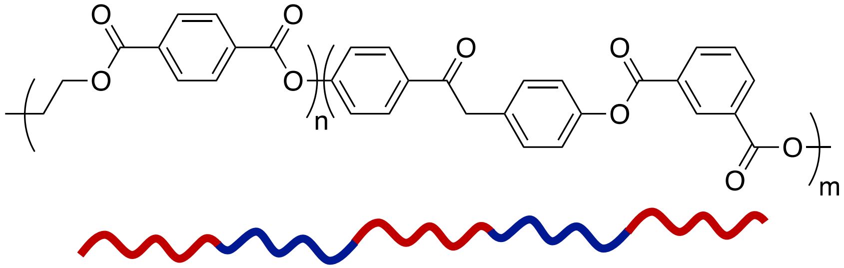
commercial polyester
(ex. PET)

+



deoxybenzoin
polyester

$\xrightarrow{\text{Transesterification catalyst}}$



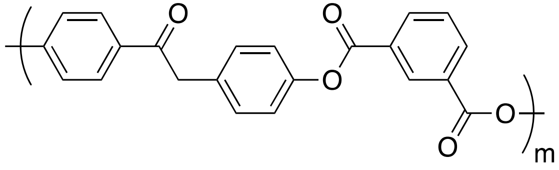
Transesterification product
deoxybenzoin-containing block polymer

Initial experiments

Eastar™ EN052

20 grams

+



Deoxybenzoin polyester
7 grams

$\xrightarrow{\text{0.05 wt.\% zinc acetate hydrate}}$

Brabender batch mix
290 °C, 20 min, 70 rpm

$\xrightarrow{\text{mold 290 °C, 5 min}}$

0 wt.%

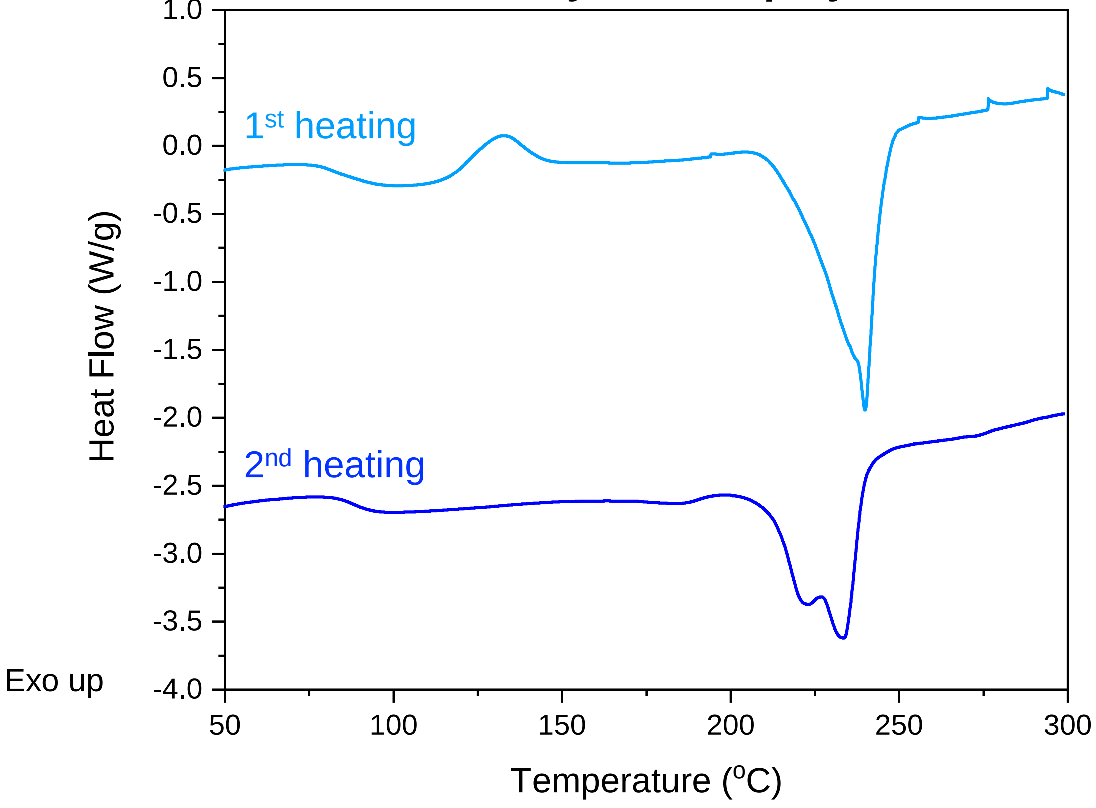
5 wt.%

25 wt.%

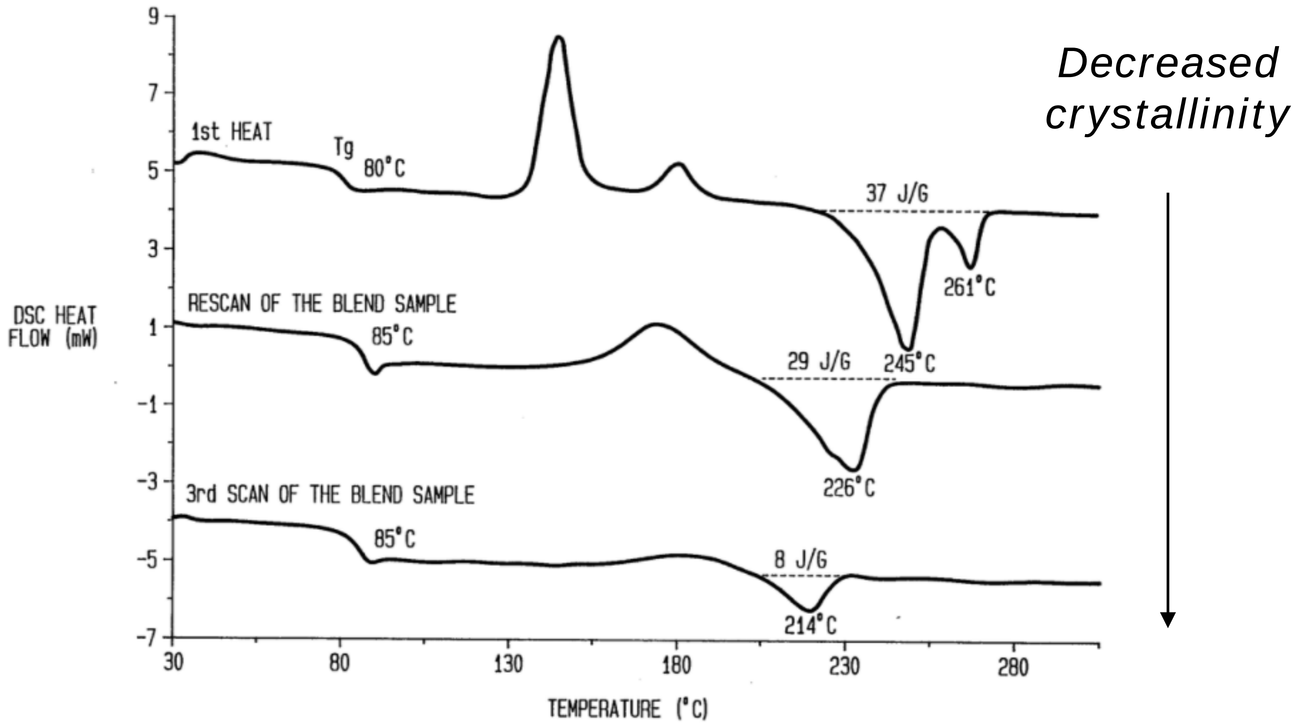
Increasing concentration of deoxybenzoin polyester

Thermal properties: polyester blends

25 wt. % deoxybenzoin polyester



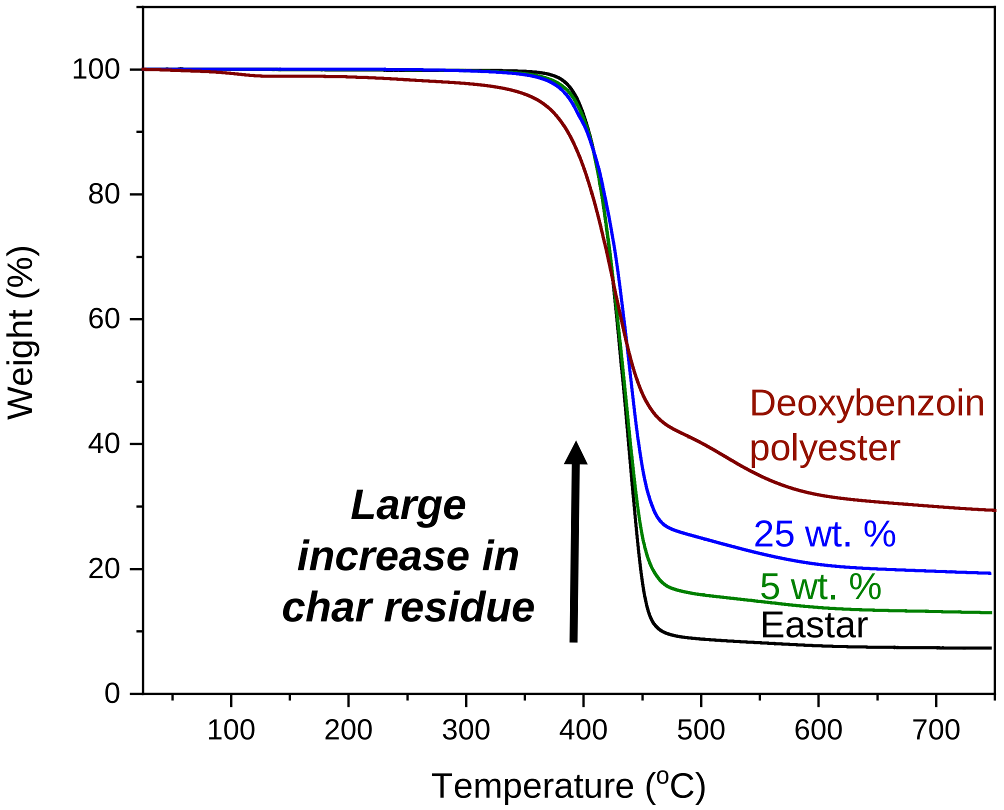
PET-PEN copolymer from reactive extrusion

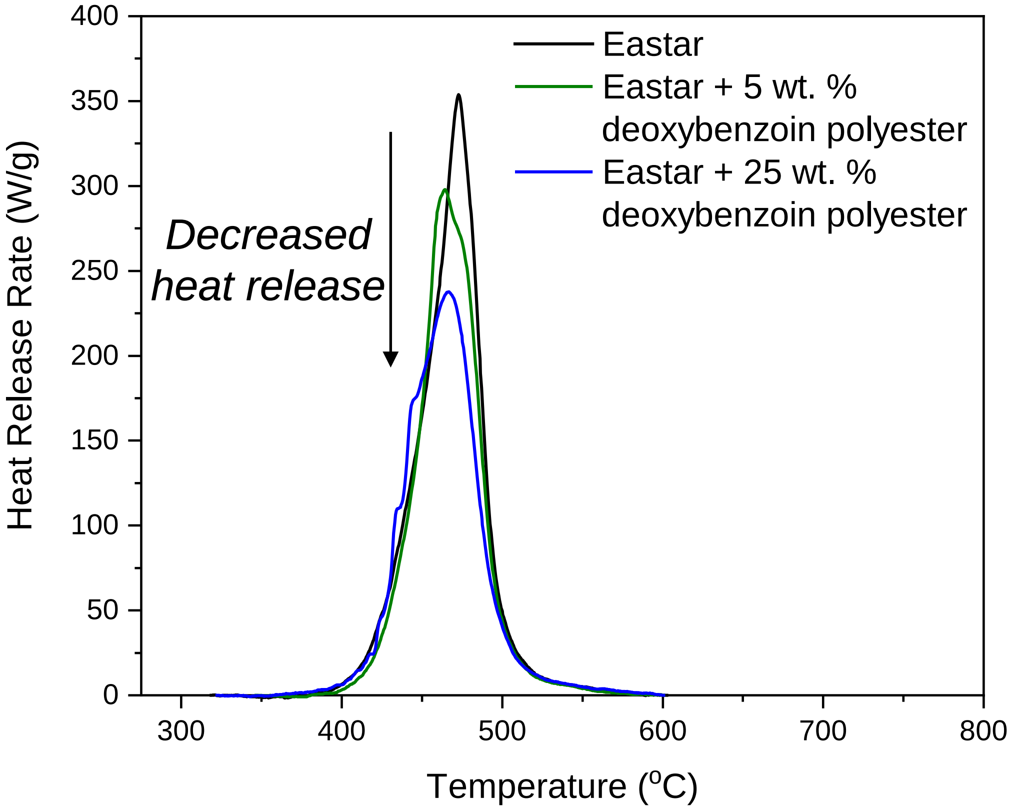


Hoechst Celanese Corp. (1996) WO 96/35571

Deoxybenzoin polyester content (wt. %)	Melting temperature (°C)	Melting enthalpy (J/g)
0	253	46
5	247	42
25	234	29

Heat release properties: polyester blends





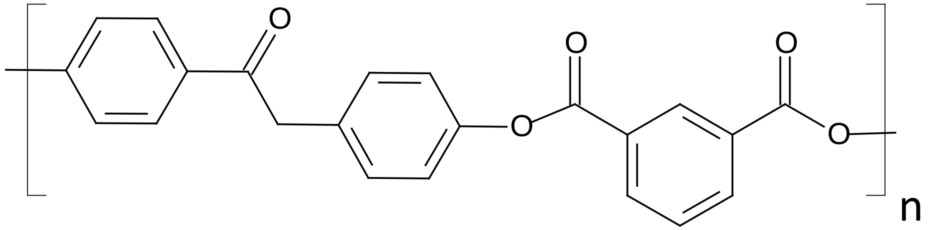
Deoxybenzoin Polyester Concentration (wt. %)	Char Residue (%) at 750 °C	Heat Release Capacity (J/gK)	Total Heat Release (kJ/g)
0	7.3	419 ± 17	15.0 ± 0.1
5	13.0	301 ± 5	13.8 ± 0.1
25	**19.5**	**257 ± 22**	**12.6 ± 0.1**

Deoxybenzoin-containing blends exhibit low heat release properties

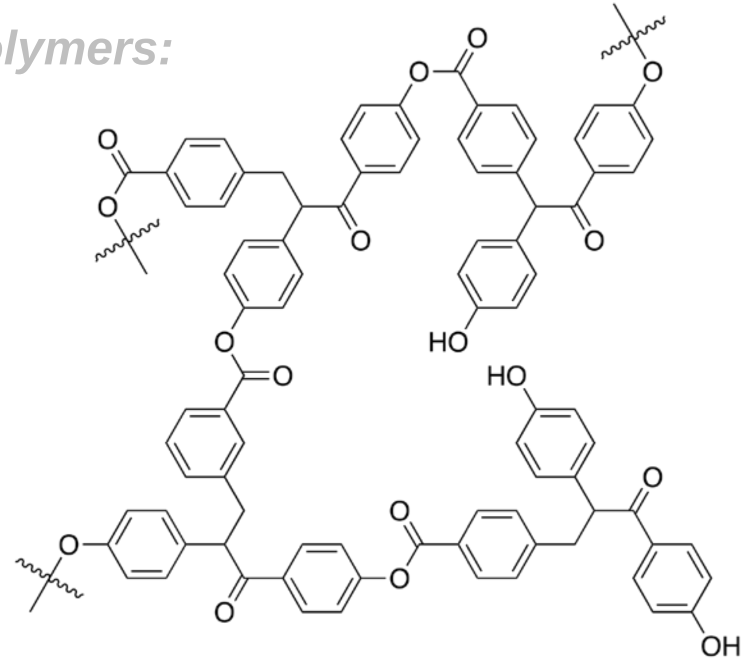
Presentation Outline

Deoxybenzoin as a component of aromatic hydrocarbon flame-retardants

I. Brief background on polymers derived from deoxybenzoin



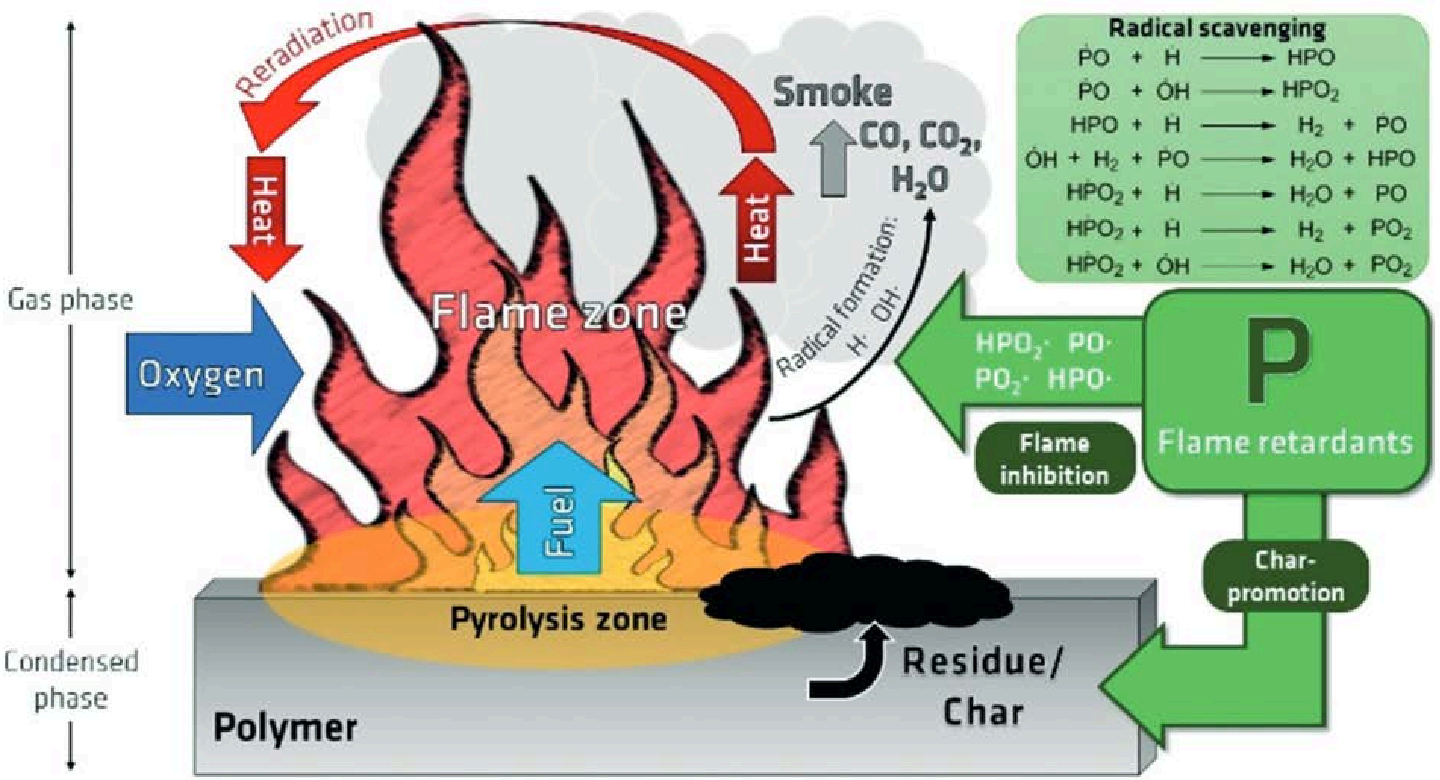
II. Branched deoxybenzoin polymers: new, polymeric additives



III. Deoxybenzoin polymers + phosphorus derivatives

Impact of Phosphorus on Materials Flammability

Battig, A; *Angew. Chem. Int. Ed.* (2018) 10450.

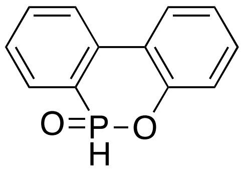


Modes of action

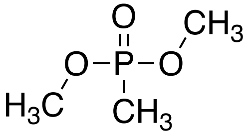
Condensed phase
charring and intumescence

Gas phase
flame dilution/poisoning

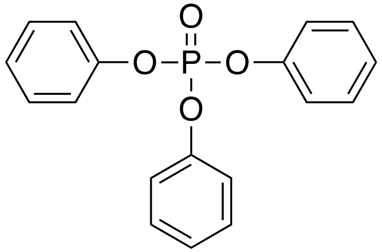
Small molecule additives



DOPO

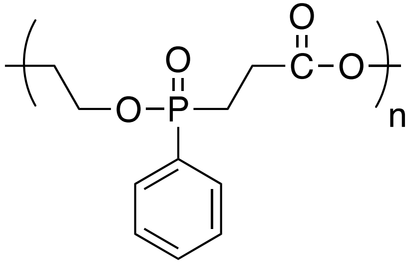


DMMP

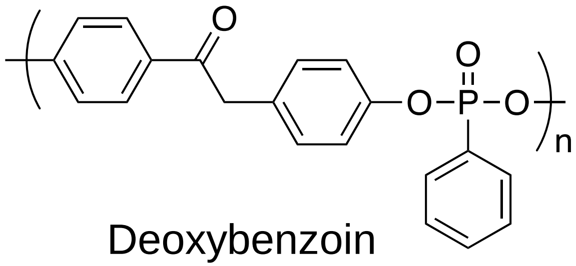


TPP

Polymeric additives

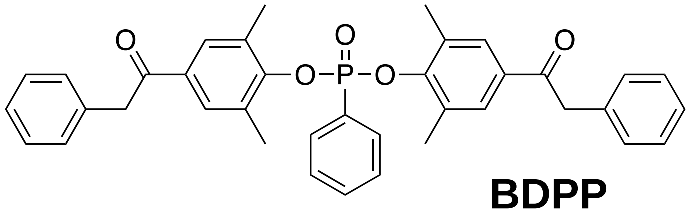


Trevira

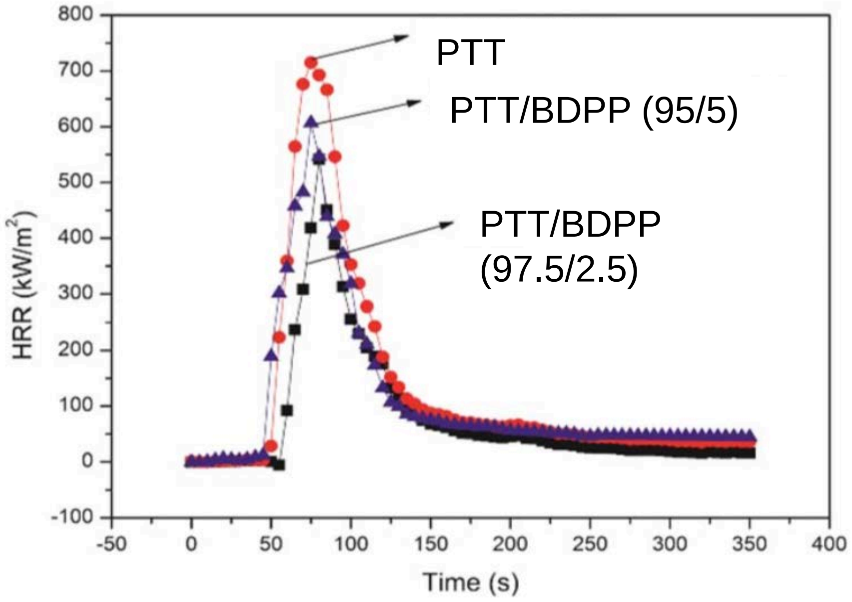


Deoxybenzoin polyphosphonate

Integration of Phosphorus into Deoxybenzoin Structures

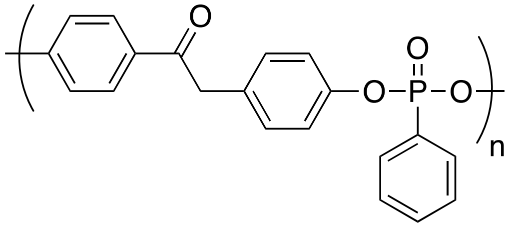


BDPP

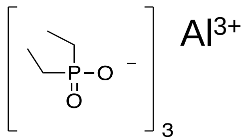


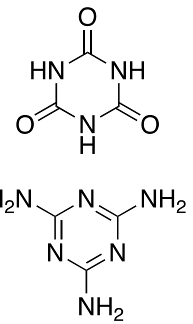
	Peak HRR (kW/m²)	THR (mJ/m²)	LOI (%)	Char residue (%)
PTT	715	55.1	22.5	5.1
PTT/BDPP (97.5/2.5)	608	51.3	23.0	-
PTT/BDPP (95/5)	541	41.4	25.0	7.5

Hu, X.; *J. Appl. Polym. Sci.* (2018) 45904



BHDB polyphosphonate
BHDB-PPN





AlPi/MCA

	PBT/ AlPi	PBT/AlPi/ MCA	PBT/AlPi/ BHDB-PPN	PBT/ BHDB-PPN

Classification	V-0	V-2	V-0	NR

Hu, X.; *J. Appl. Polym. Sci.* (2017) 45537

Deoxybenzoin-containing Polymers:
Combining Tailored Polymer Architectures with Non-halogenated Materials

The Ninth Triennial International Fire & Cabin Safety Research Conference
Atlantic City, NJ   October 29 2019

Todd Emrick
Polymer Science and Engineering Department
University of Massachusetts Amherst

Research Support

Federal Aviation Administration

Industrial support through the Center for UMass-Industry Research on Polymers (CUMIRP)