Using Deoxybenzoin Monomers to Generate Low Flammability Polymers for Aircraft

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Research Support

FAA
BASF-NORA
Boeing
Center for UMass-Industry Research on Polymers

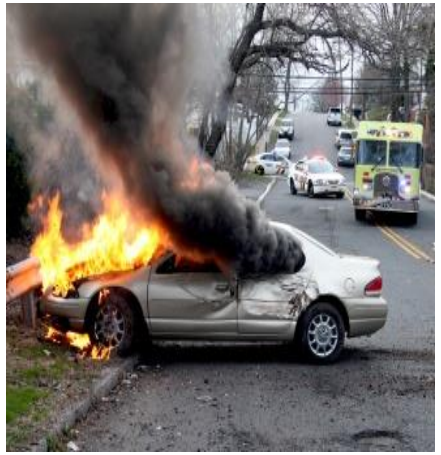
Polymers for a safer society – addressing flammability

Synthetic organic polymers

A mainstay of modern society, used in textiles, upholstery, construction materials, vehicles, and electronic devices

Pose a significant threat due to their inherent flammability

Transportation

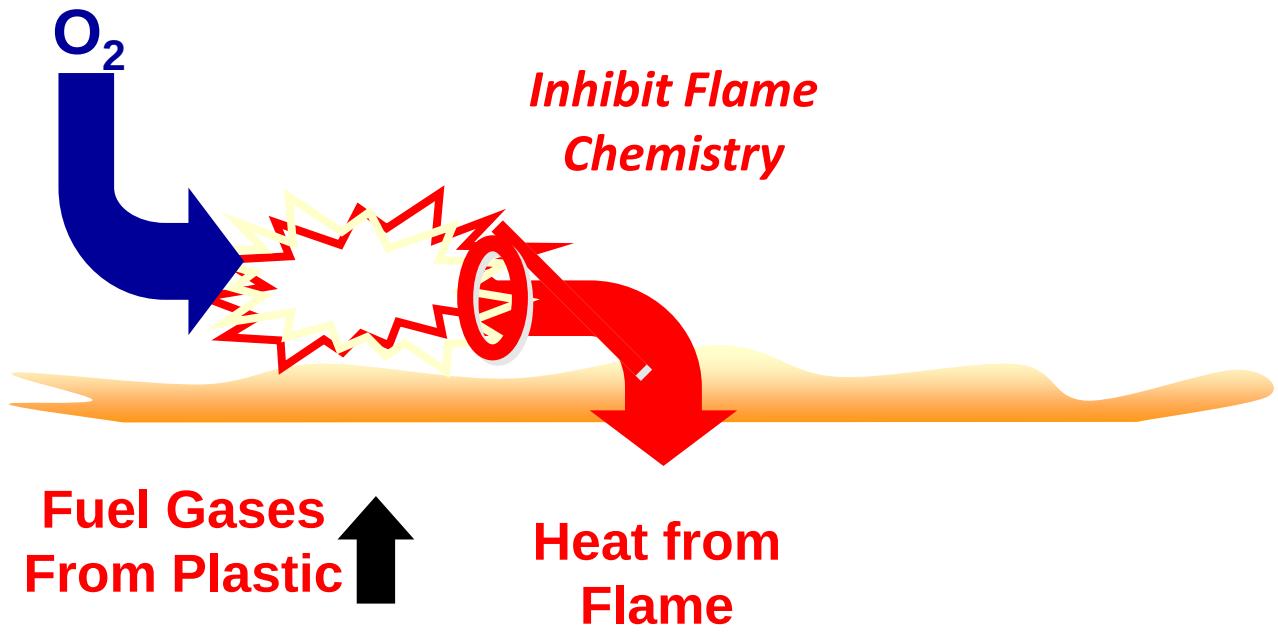


Sound insulation foam

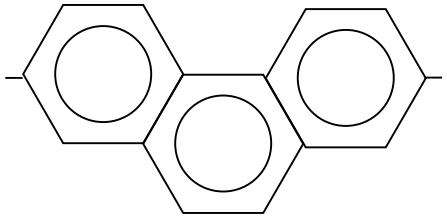
How advanced plastics saved lives on Asiana Flight 214

Plastics Today July 2013

Char residue impedes evolution of flammable gas

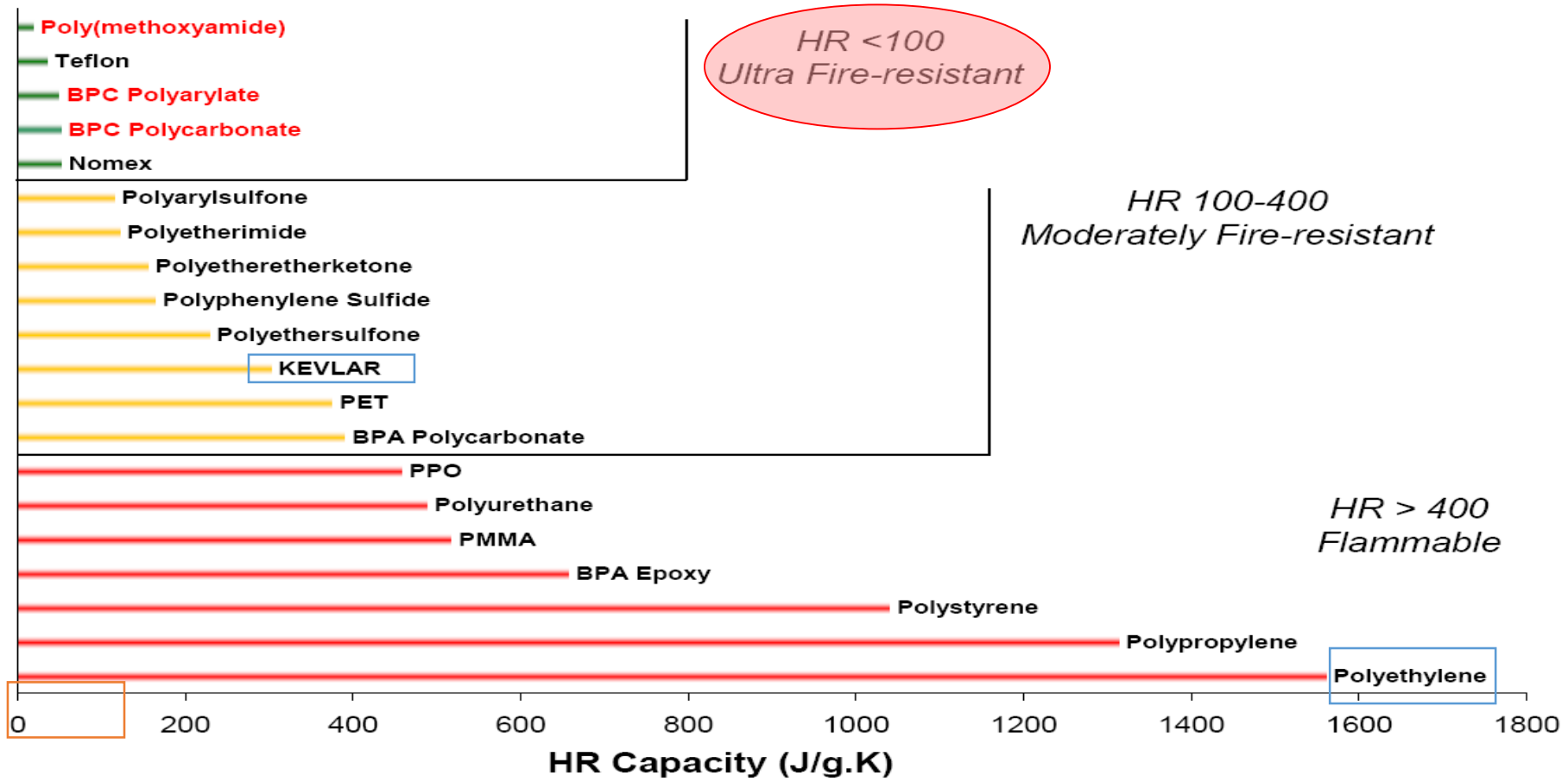


The char produced reduces the amount of flammable gas evolved and thermally insulates the underlying polymer



Char residue

Heat Release Capacity (HRC) measurements on synthetic polymers



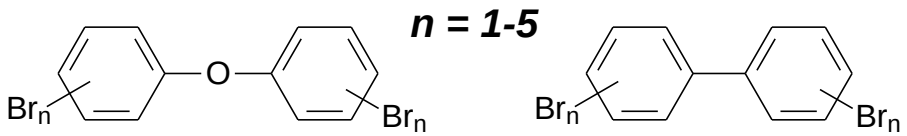
Walters, R.N.; Lyon, R.E. J. Appl. Polym. Sci. 2003, 87, 548

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

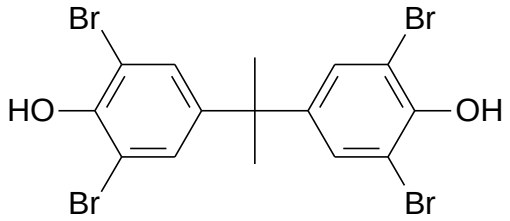
Richard Lyon
Federal Aviation Administration

Small molecule flame-retardants

Halogenated aromatics



n = 1-5



additive or monomer

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

- Leaching from polymer material
Environmental persistence
Toxicity
Restrictions and legislation

Inorganic fillers: non-halogenated

Aluminum trihydrate

Magnesium hydroxide

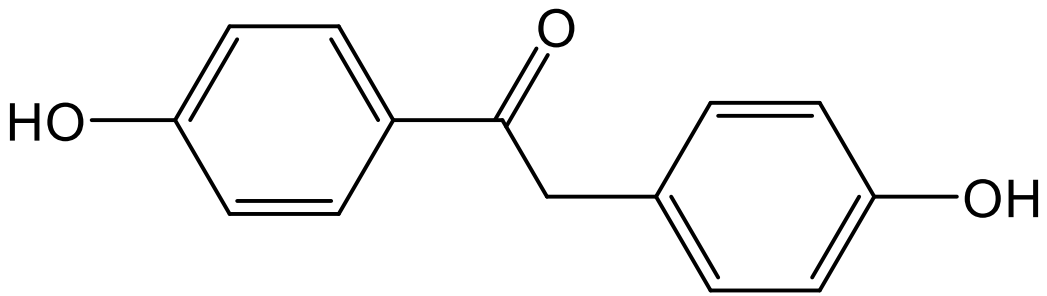
Phosphorus, nitrogen, and silicon-based inorganics

Environmentally-friendly
Used in commodity polymers

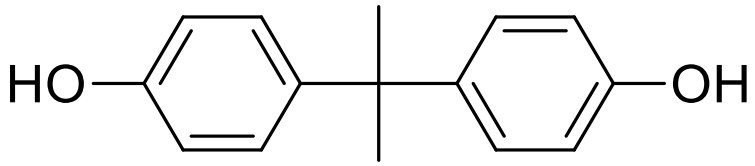
High loading needed for FR activity
Negative impact on mechanical properties of host polymer materials
Limitations in high-temperature applications

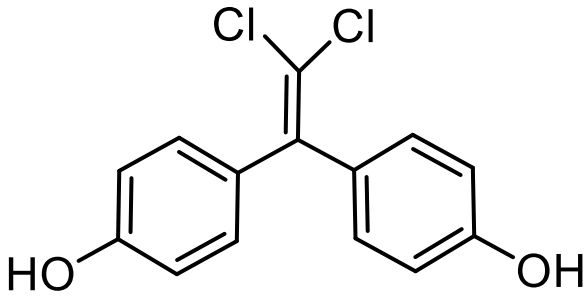
Alternatives: 1) include halogenation directly on the polymer backbone (prevents leaching) or 2) develop polymers that are *both* non-halogenated and non-flammable

Deoxybenzoin as a new monomer in polymers, networks, foams, etc.



Plastics *Gels/networks* *Foams* *Elastomers*





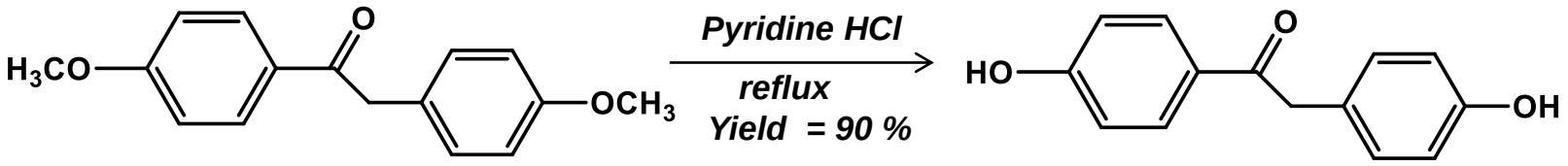
Presentation Topics

I. Background studies on the integration of deoxybenzoin into synthetic polymers
   - Reducing flammability of flammable polymers

II. Deoxybenzoin as a comonomer in polysulfones
   - Making low flammability polymers even less flammable

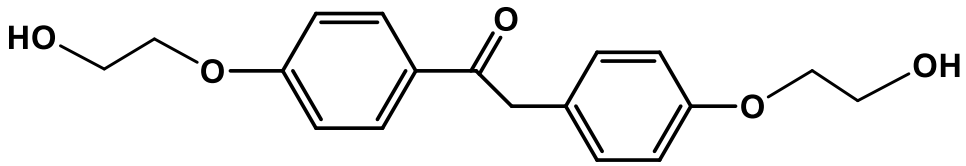
III. An easy route to functional deoxybenzoins

BHDB preparation from desoxyanisoin and integration into polyarylates

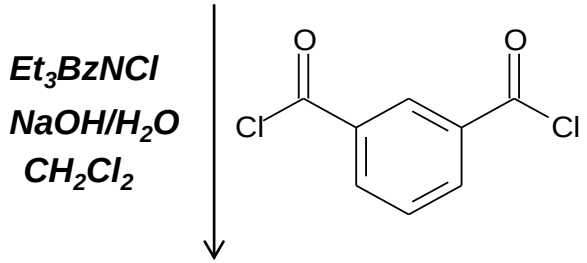


Desoxyanisoin

4,4'-bishydroxydeoxybenzoin (BHDB)

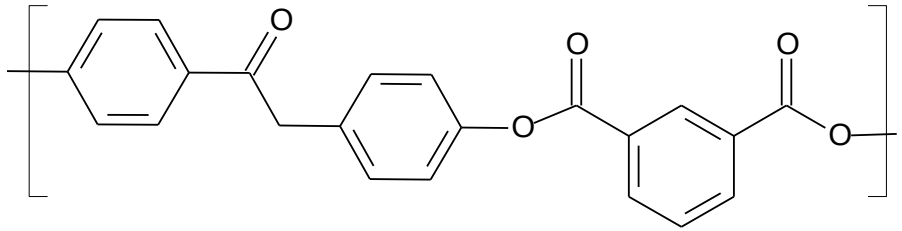


Another useful diol: ethanol-extended version



One step synthesis of monomer in high yield; up to 500 g scale

<u>Polyarylate</u>: HRC = <100 J/g-K; Char yield = 45%



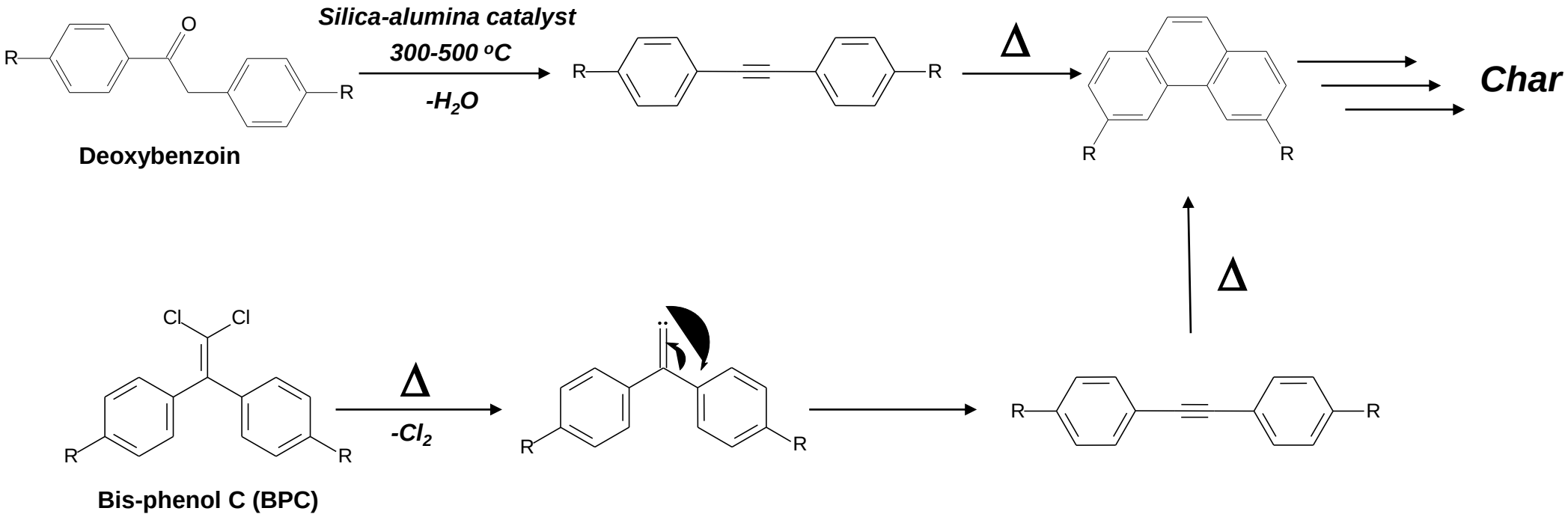
BHDB-Polyarylate

Macromolecules 2006

No prior reports of polymerization chemistry using BHDB

Deoxybenzoin: pathway to char formation

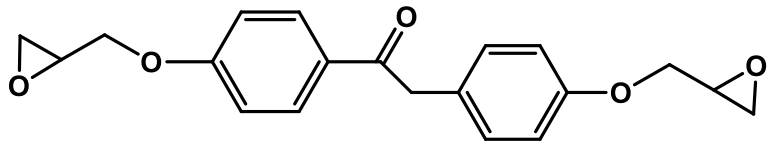
Deoxybenzoin conversion to diphenylacetylene at high temperatures



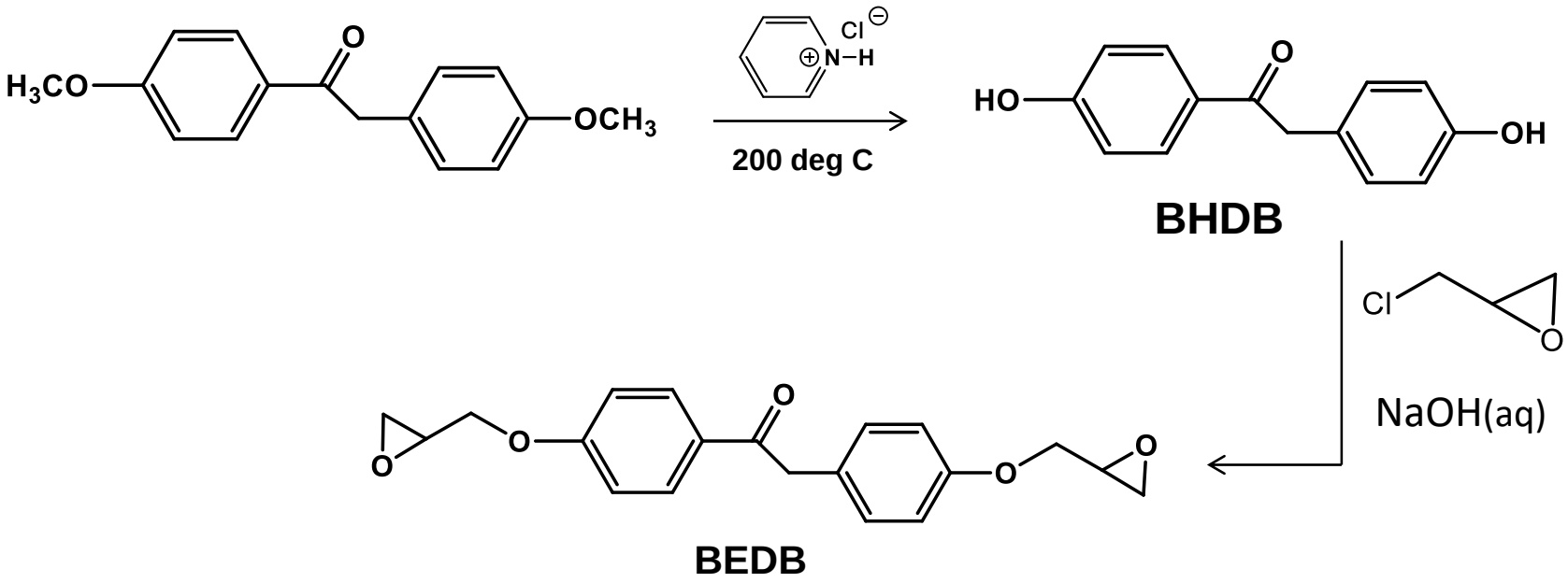
Polyesters, polyurethanes, epoxy polymers, polysulfones, polyester/triazoles, polyamides, vinyl polymers

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

Deoxybenzoin-based epoxy resins



Bis-epoxydeoxybenzoin (BEDB)
(deoxybenzoin diglycidyl ether (DB-DGE))



BEDB: Easily prepared at 250 gram scale; very large scale would be easy to achieve

Polymer 2009 p. 767

Cured BEDB resins: thermal and mechanical properties

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)
BPA	EBPA/4,4′-DDS	198	12	513 ± 10	25.3 ± 0.2
BPA	EBPA/4,4′-$DDS_{0.8}$ 4,4′-$DDM_{0.2}$	196	14	454 ± 30	24.9 ± 0.4
BPA	EBPA/4,4′-$DDS_{0.5}$ 4,4′-$DDM_{0.5}$	185	15	577 ± 28	25.4 ± 0.2
BPA	EBPA/4,4′-$DDS_{0.2}$ 4,4′-$DDM_{0.8}$	178	16	693 ± 21	26.2 ± 0.4
BPA	EBPA/4,4′-DDM	179	16	737 ± 24	26.8 ± 0.4
BEDB	BEDB/4,4′-DDS	181	30	420 ± 14	17.2 ± 0.2
BEDB	BEDB/4,4′-$DDS_{0.8}$ 4,4′-$DDM_{0.2}$	180	33	342 ± 4	17.5 ± 0.5
BEDB	BEDB/4,4′-$DDS_{0.5}$ 4,4′-$DDM_{0.5}$	173	34	321 ± 10	16.9 ± 0.3
BEDB	BEDB/4,4′-$DDS_{0.2}$ 4,4′-$DDM_{0.8}$	160	35	378 ± 29	16.9 ± 0.1
BEDB	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 / heating rate

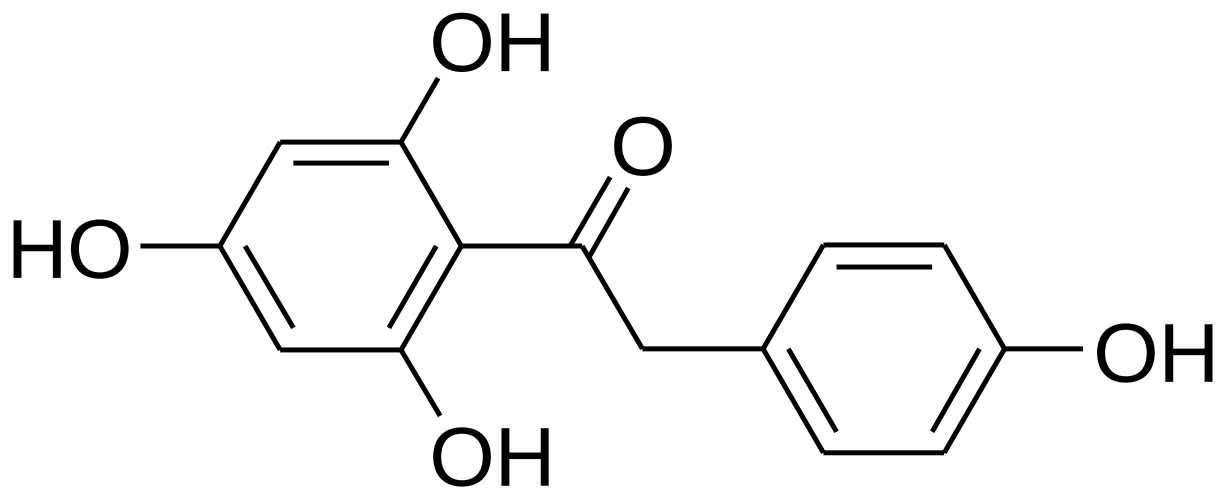
Lap shear strengths: BEDB/DDS: 15.4 MPa; BEDB/DDM: 12.8 MPa
ASTM D 1002 protocol EBPA/DDS: 11.0 MPa; EBPA/DDM: 9.2 MPa

BEDB vs. EBPA:
comparable storage modulus; higher plain-strain fracture toughness

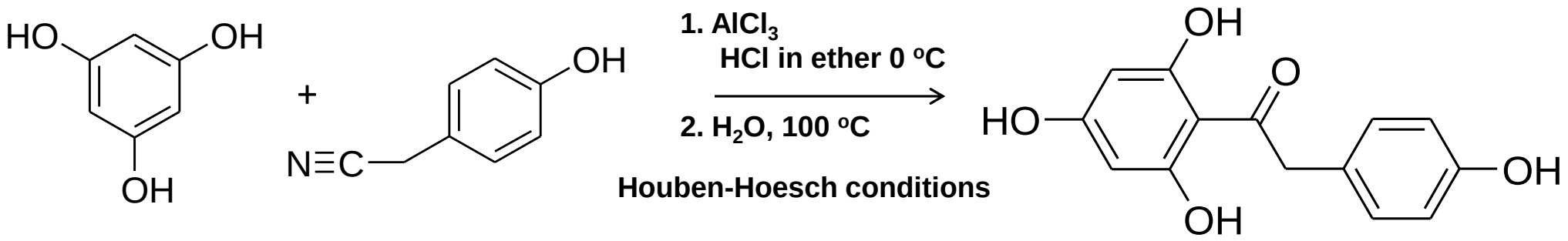
Polymer 2009 p767

Tetrahydroxydeoxybenzoin (THDB)

A multifunctional monomer and additive for anti-flammable materials



Tetrahydroxydeoxybenzoin (THDB)
A new multifunctional compound for anti-flammable materials



Bioorg. Med. Chem. 2007, 15, 3703-3710

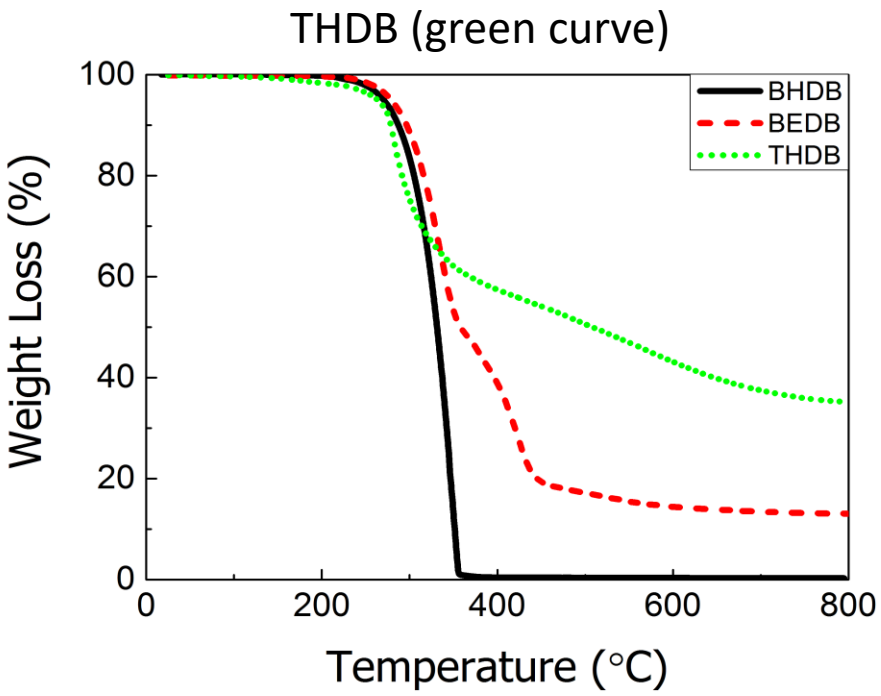
86% yield on 10 g scale
Pale yellow powder

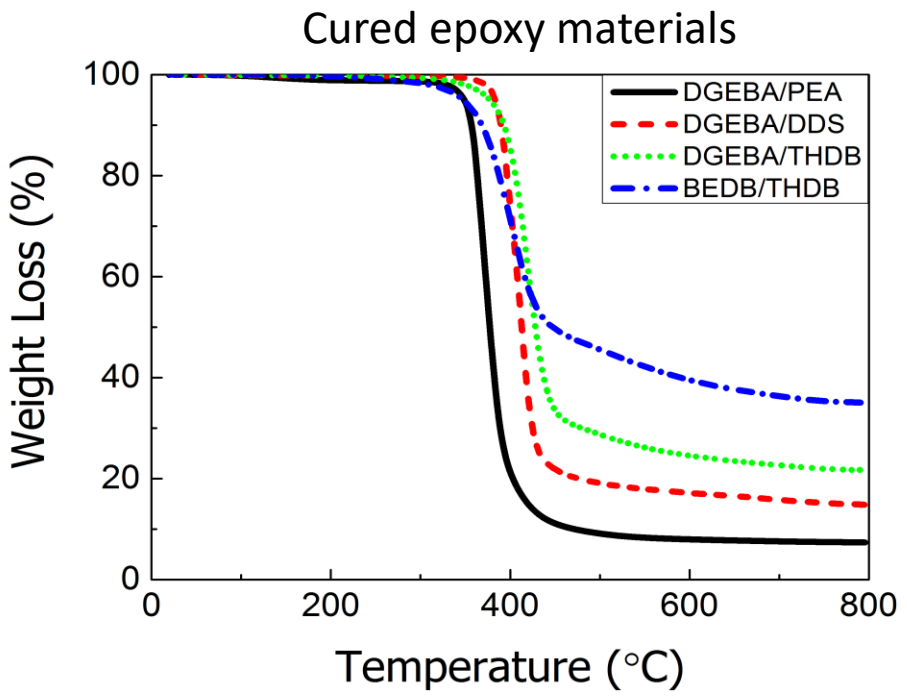
No reported polymer or curing chemistry for THDB found in literature searches (web-of-knowledge and Sci-Finder)

Potentially useful structure for anti-flammable materials as a new monomer, additive, or a cross-linker

Polymer 2014

THDB: alone and in cross-linked resins

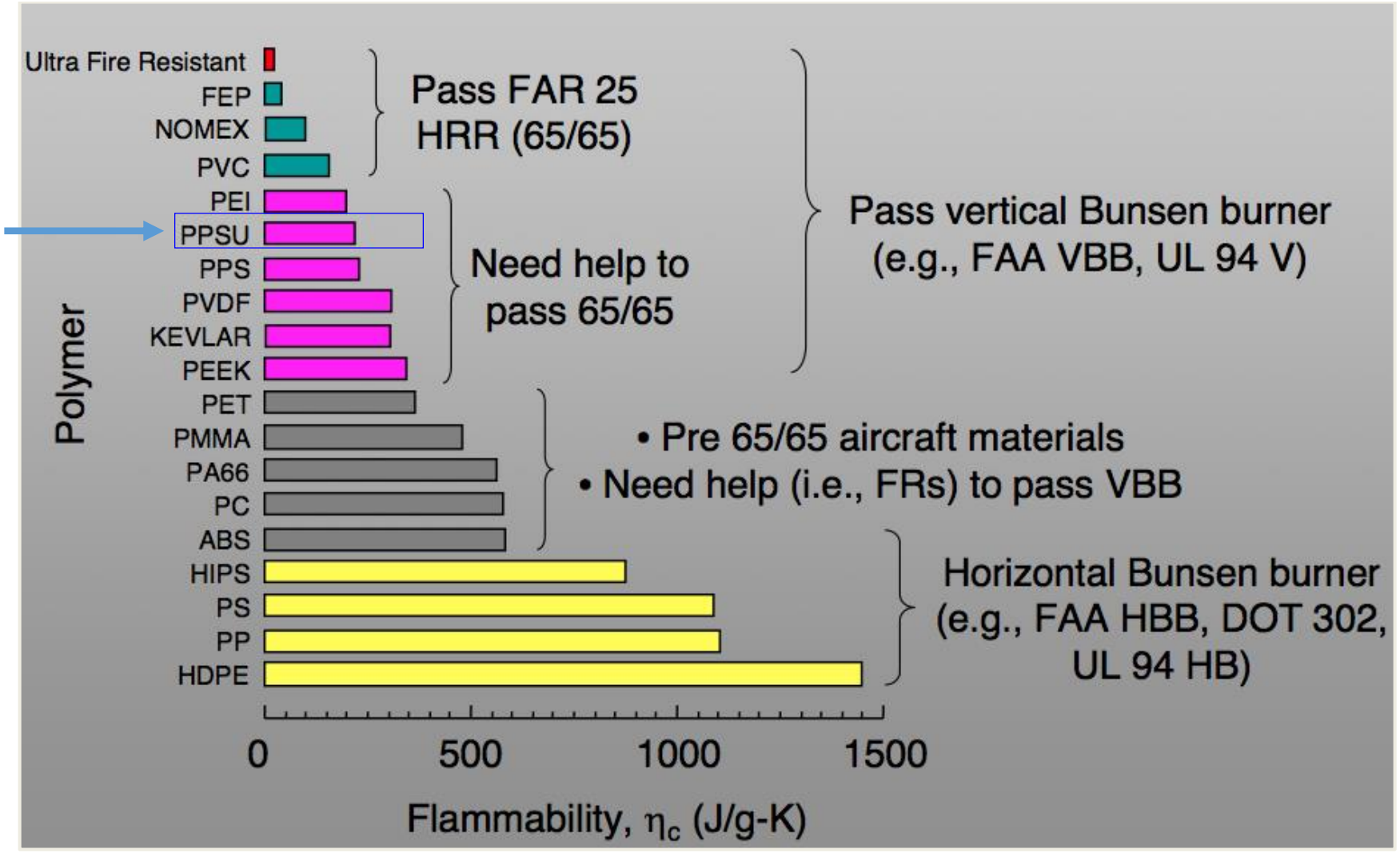




Polymer 2014

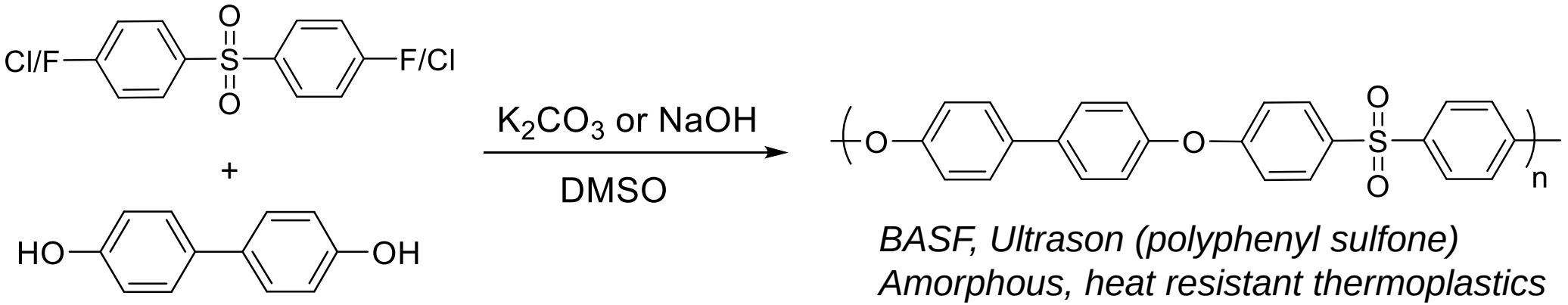
Polymer Flammability – microcalorimetry data

polysulfones



Rich Lyon, Federal Aviation Administration

Aromatic polysulfones

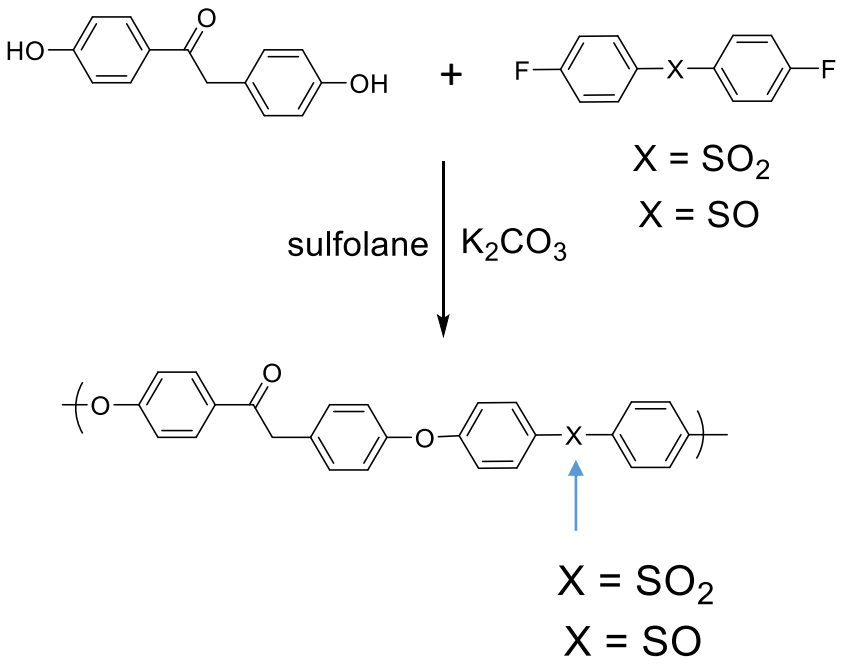


BASF, Ultrason (polyphenyl sulfone)
Amorphous, heat resistant thermoplastics

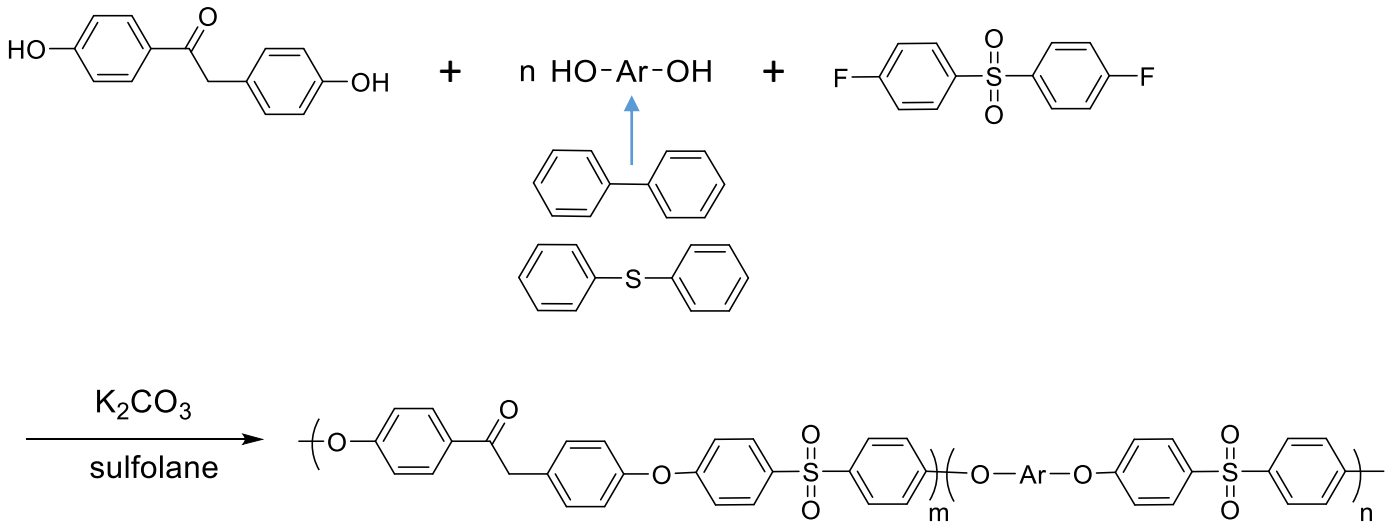
Applications

Deoxybenzoin in polysulfone/sulfoxide/sulfide preparation

Deoxybenzoin in every repeat unit



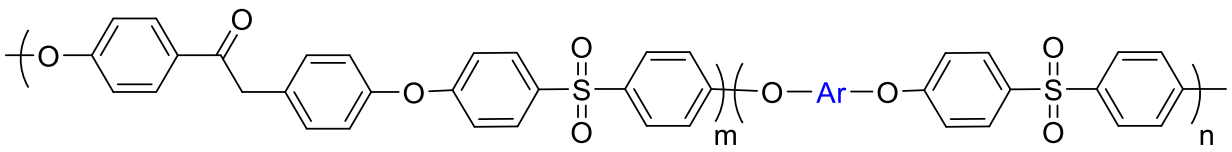
Mixture of bis-phenols in polymer backbone



Results: all polymerizations work well; sulfones proceed faster than sulfoxides (more reactive C-F bonds)

Polymer 2016

Thermal Properties: deoxybenzoin-containing polysulfones



Polymer	*m*	*n*	*X*	*HRC [J g^{-1} K^{-1}]*	*THR [KJ g^{-1}]*	*Char [%]*[a]
BHDB-sulfone **1**	0	1	SO_2	120	10	42
BHDB sulfoxide **2**	0	1	SO	66	6.5	54
BHDB/biphenyl **9**	0.5	0.5	SO_2	86	8	46
BHDB/sulfide **10**	0.5	0.5	SO_2	138	10.7	43
Poly(aryl ether) **9**[b]	0	1	SO_2	228[b]	13.5[b]	c

[a]Obtained from TGA at 800 deg C in nitrogen (heating rate 20 ^{O}C/min.) [b] Data obtained from reference
[c] Not determined

Solution cast film of deoxybenzoin-containing polysulfone

Polymer 2016