

Non-halogenated Anti-flammable Polymers prepared from Deoxybenzoin Monomers

NIST Annual Fire Conference April 4,5 2007



Funding: Federal Aviation Administration, National Institute for Standards and Technology, U.S. ARMY
corporate sponsors:

General Electric Co., International Association of Fire Fighters, Boeing, Johns Manville
Multina, Inc, Rogers Corp., Schneller, Inc., Solvay Advanced Polymers

Polymer Flammability Effort at UMass Amherst

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

A property-driven research cluster, encompassing the synthesis, characterization, and modeling of polymers, centered on the development of low heat release polymers and polymer composites

Current efforts

Synthesis: Halogen-free anti-flammable polymers

Modeling: pyrolysis kinetics and mechanisms

Processing: Films, Fibers, Electrospinning

Characterization: Flammability (pyrolysis combustion flow calorimetry);
Mechanical properties

Personnel: 5 PIs, 6 students and postdoctoral associates

Characterization Techniques in Cluster F Research

Techniques for evaluating thermal properties on a small scale



Py-GC/MS:
Pyrolysis GC/MS
(1 mg)

- Decomposition products
- Mechanism of decomposition



TGA:
Thermogravimetric
Analysis
(10 mg)

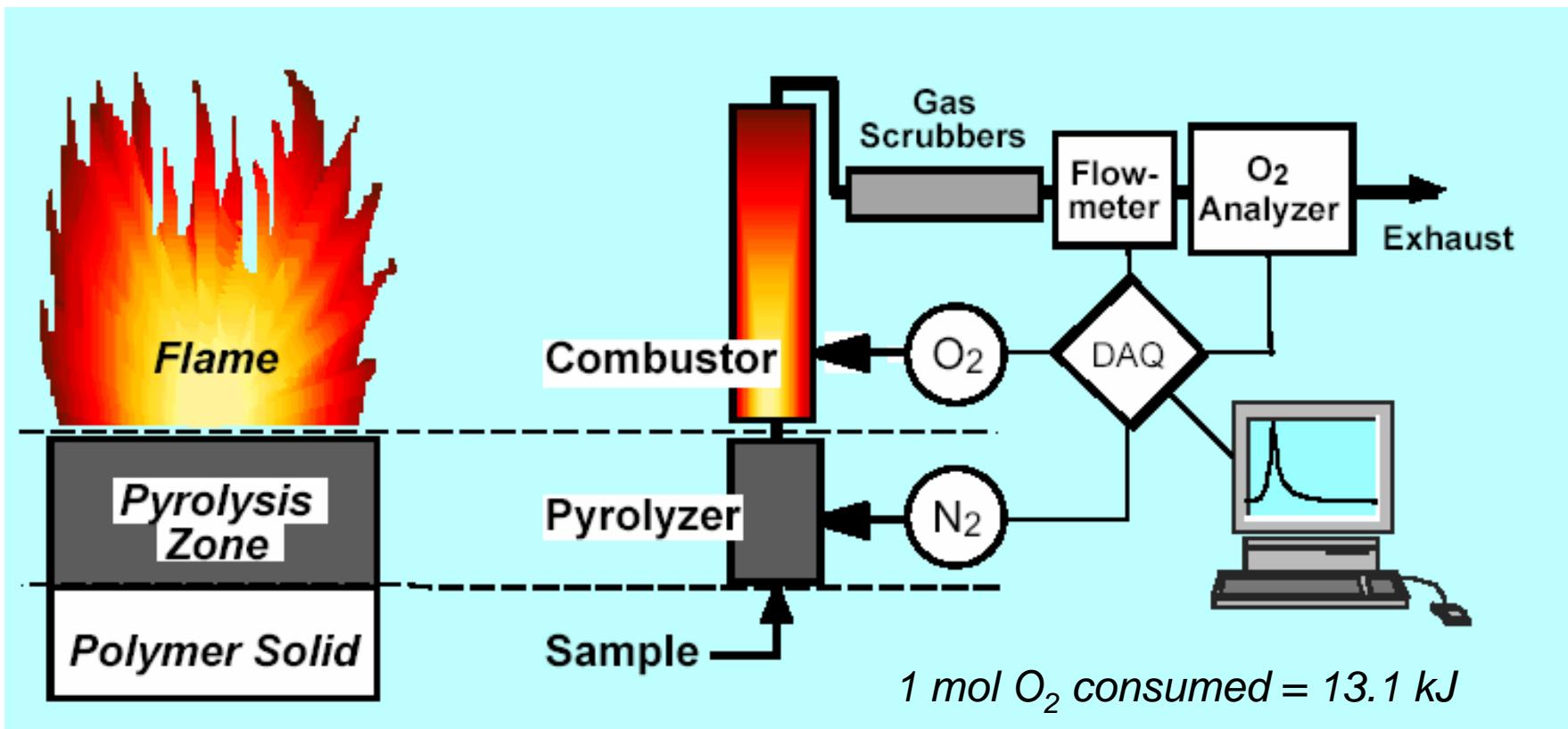
- Thermal stability
- Char yield



PCFC (FAA):
Pyrolysis-combustion
flow calorimeter
1 mg samples!!!

- Heat release capacity
- Total heat of combustion
- Char yield

Pyrolysis Combustion Flow Calorimetry



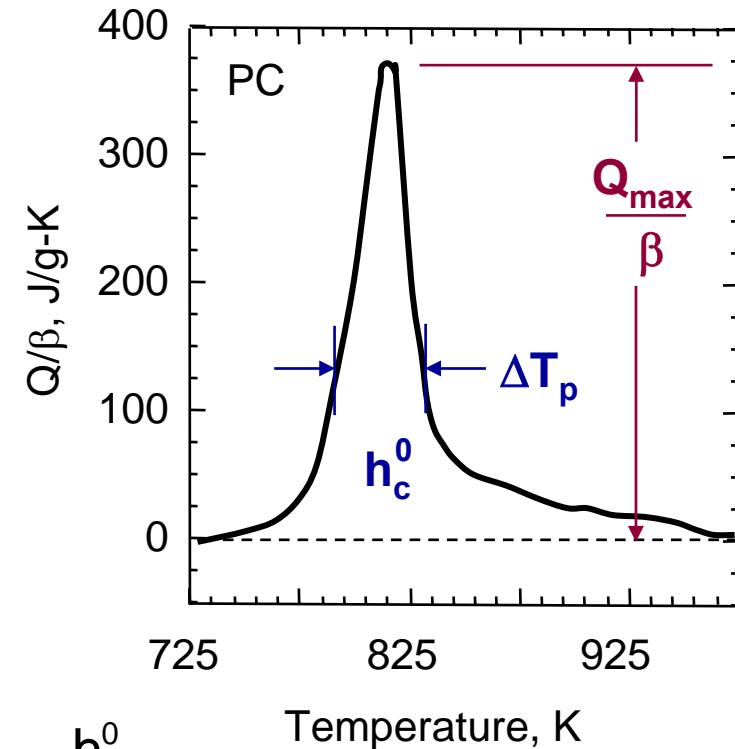
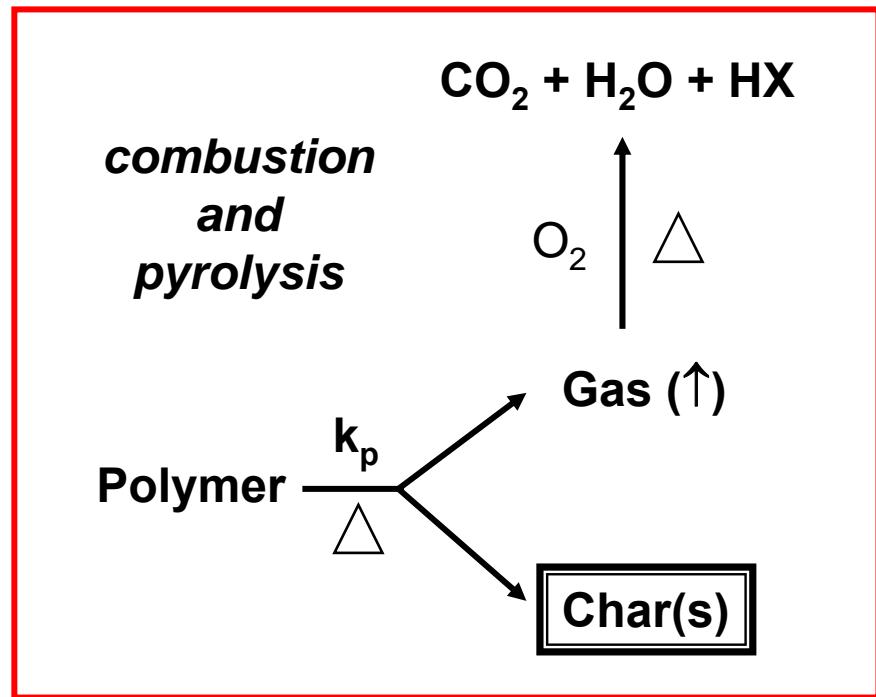
$$\text{Heat Release Capacity} \equiv \frac{\dot{Q}_c^{\max}}{\beta} = h_c^o \frac{(1-\mu)E_a}{eRT_p^2}$$

PCFC provides Heat Release (HR) Capacity as a material property and key parameter in determining flammability.

- h_c^o = Heat of combustion
- E_a = Activation energy
- μ = Char fraction
- T_p = T at peak mass loss
- R = gas constant
- Q_c^{\max} = Peak heat release rate
- β = Heating rate

HEAT RELEASE RATE MODEL

Rich Lyon, Rich Walters, Stanislav Stoliarov
Federal Aviation Administration



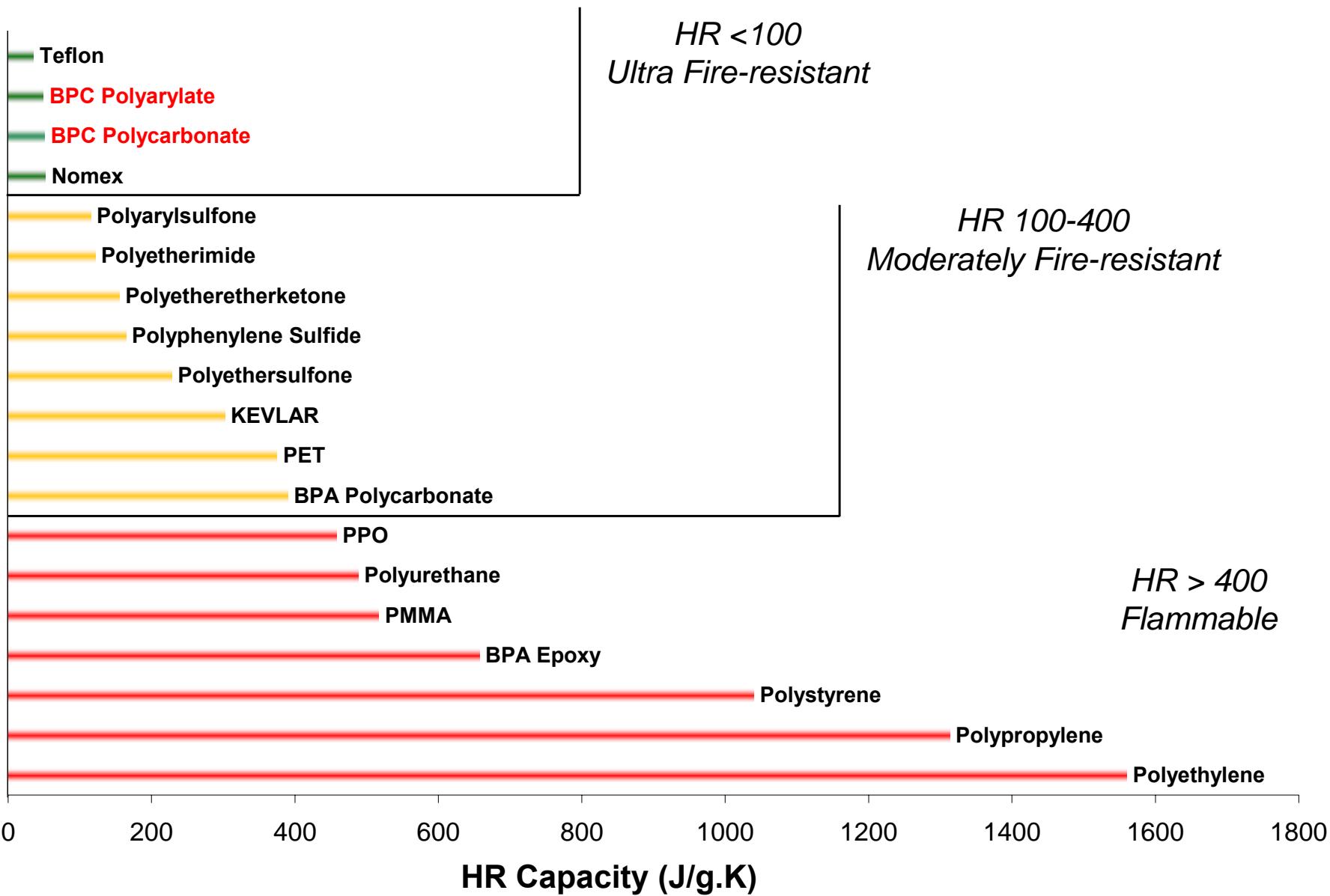
Heat Release Capacity: $\eta_c = \frac{Q_{\max}}{\beta} = \frac{h_c^0}{\Delta T_p}$

Peak Height Method

Peak Area Method

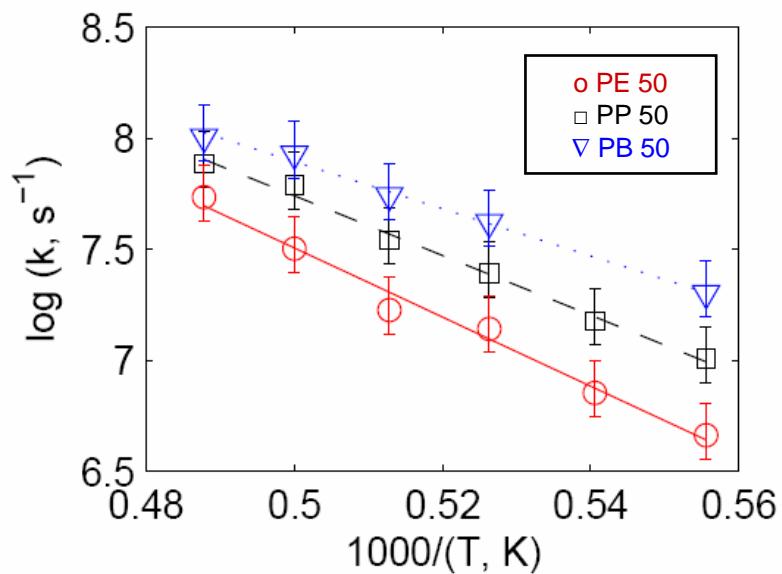
Heat Release Capacity of Polymers

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



Reactive Molecular Dynamics to simulate polymer decomposition, and guide new polymer development: Ken Smith, Phil Westmoreland

- Developed a new reactive forcefield method, RMDff
- Developed a new Reactive Molecular Dynamics code, RxnMD
- Objective: Use microscopic reaction mechanisms to describe entire macroscopic polymer decomposition *a priori* via Kinetic Monte Carlo (KMC).

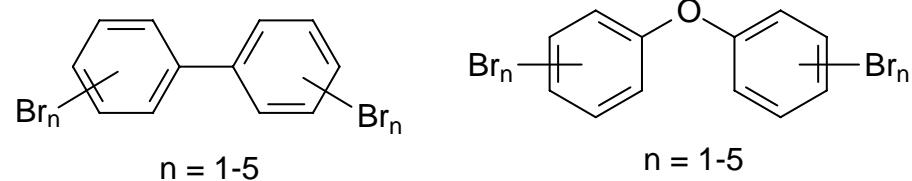


Polymer	$A \times 10^{15} (\text{s}^{-1})$	$E_A (\text{kJ/mol})$
PE 50	1.92	297.7
PP 50	0.289	257.3
PB 50	0.0159	203.2

Brominated anti-flammable additives

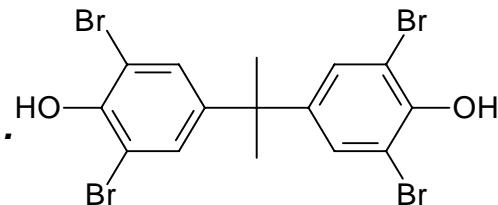
Halogenated additives, and halogenated polymers, give low flammability but are environmentally hazardous/questionable, and/or politically unfavorable

Polybrominated biphenyls (PBBs)



Problems: leaching from polymer, toxicity, environmental persistence

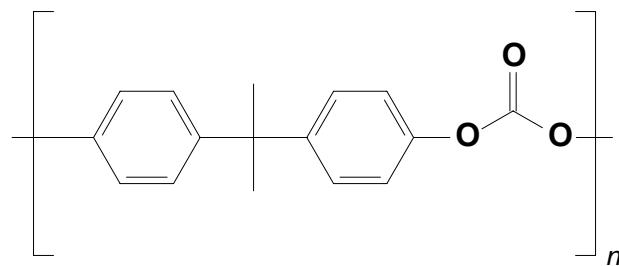
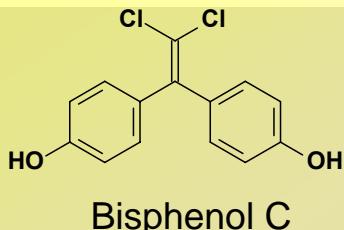
Brominated monomers for integration into polycarbonate, polyesters, polyethers, epoxies...



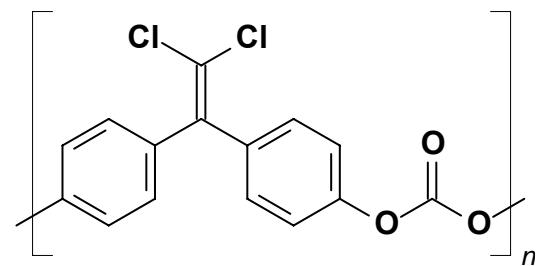
Clay-polymer and nanotube-polymer composites show flame resistance...

Challenge: new polymers with inherently low flammability but no halogen

Bisphenol C vs. Bisphenol A



**Bisphenol A Polycarbonate
(Lexan)**

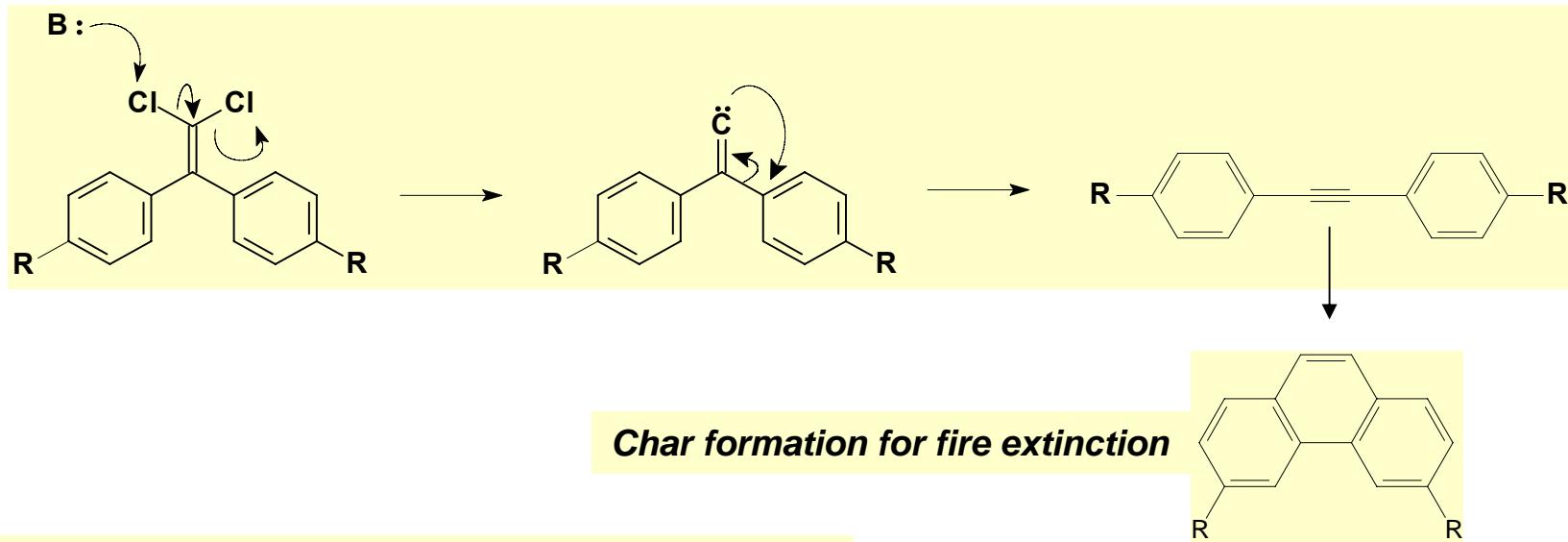
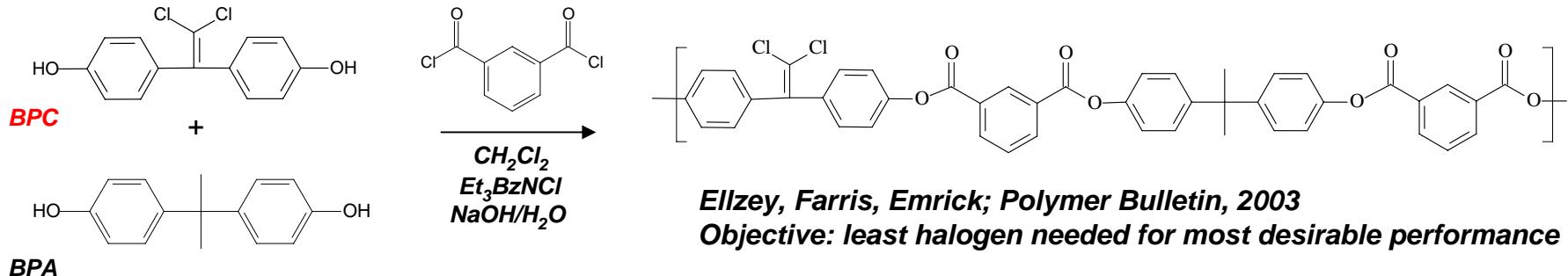


Bisphenol C Polycarbonate

Morphology	Amorphous	Amorphous
Tg (°C)	152	168
Flex Modulus (ksi)	336	376
Flex Strength (psi)	16,300	16,200
Tensile Yield Strain (%)	10	11
NBS Smoke (Dm)	165	75
Oxygen Index (%)	26	56
HR Capacity (J/g.k)	390	29

Source: Dr. Richard Lyon, FAA

Bis-phenol C containing polymers

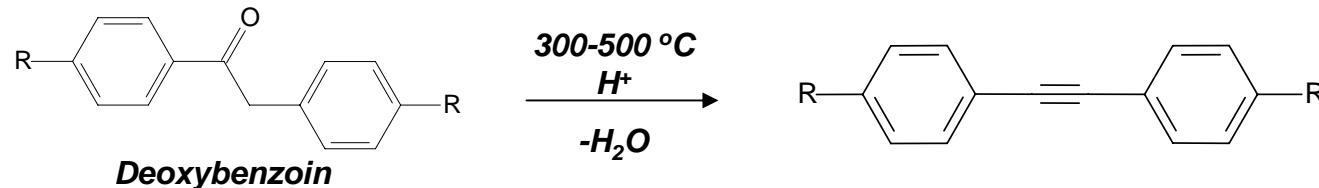


1. Chlorine content in BPC prevents widespread use;
2. Chlorine content in BPC may not be the key feature that leads to its anti-flammable properties; setting up rearrangement chemistry appears to be crucial

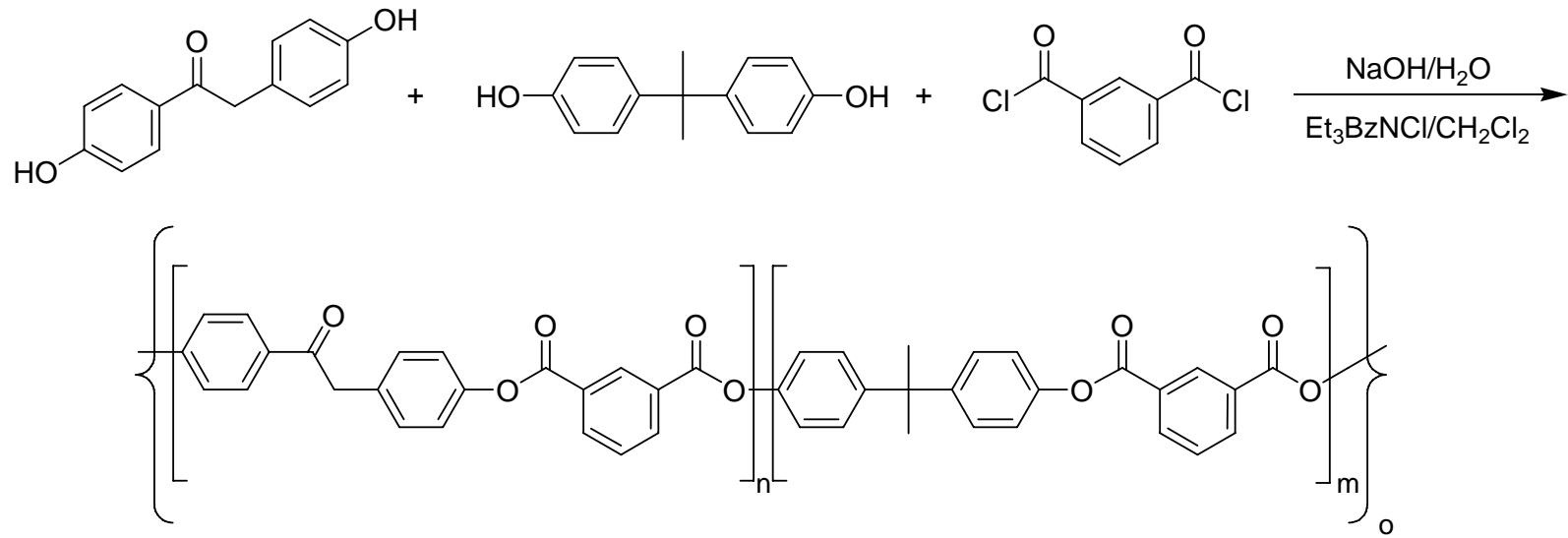
Ramirez, M. L. Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers. DOT/FAA/AR-00/42.; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001;
Stoliarov, S.I.; Westmoreland, P.R. *Polymer*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

Halogen-free anti-flammable polymers

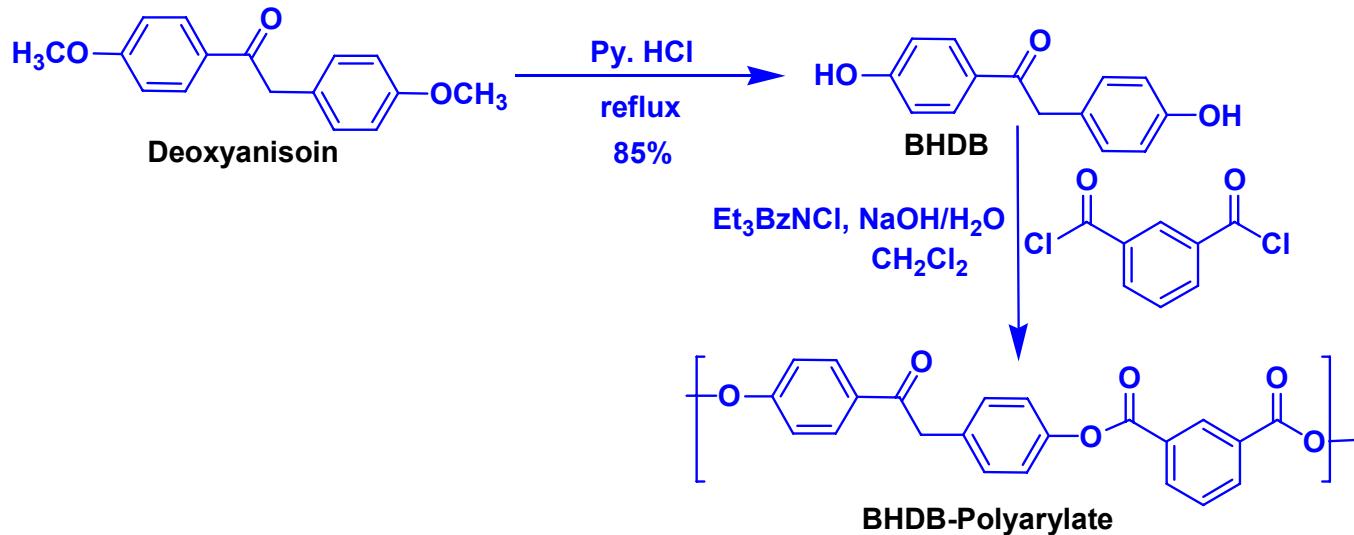
Deoxybenzoin-based polymers



van der Waals et al. J. Mol. Cat. A 1998, p.179



Deoxybenzoin-based Polyarylates

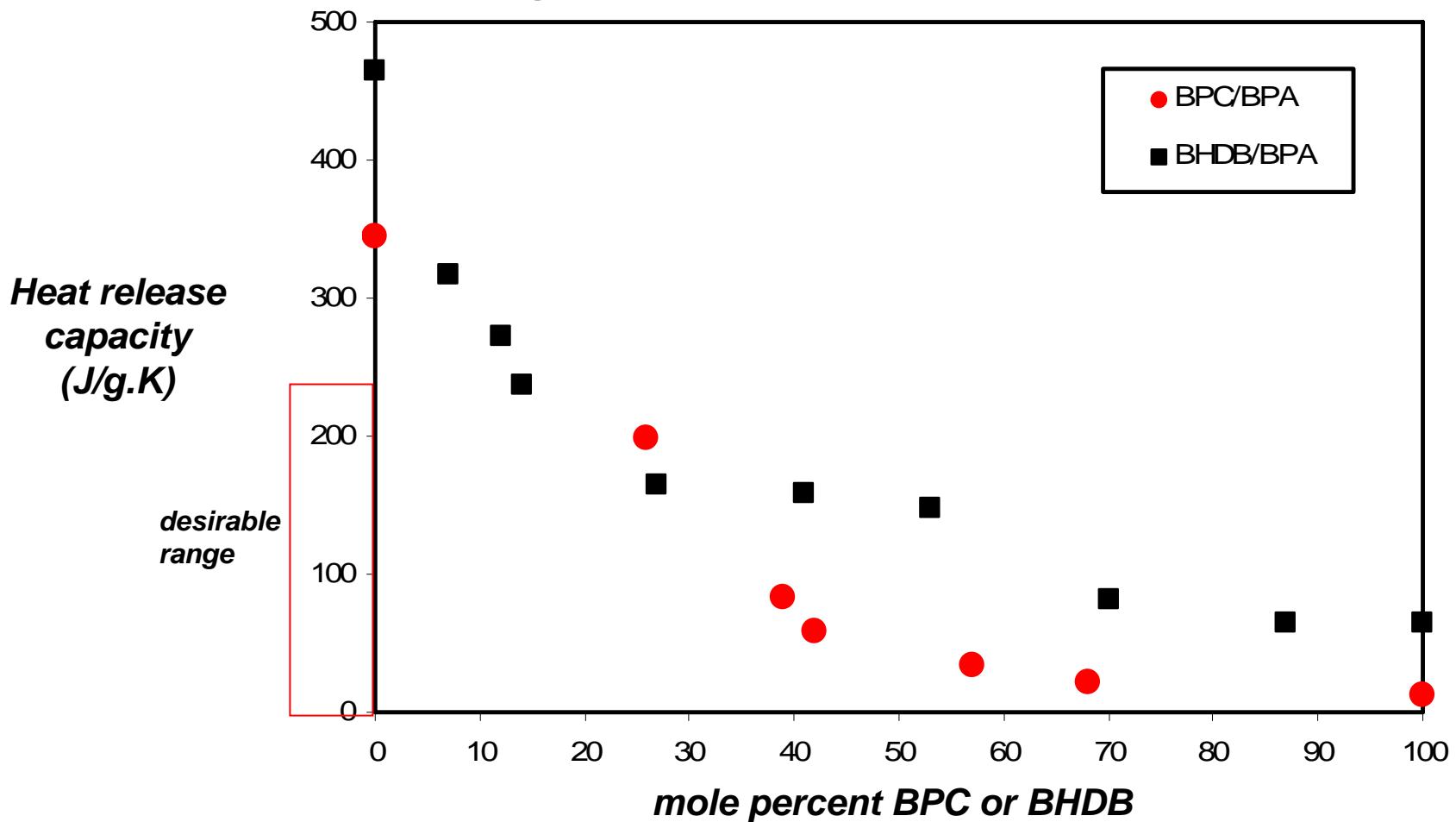


- Demethylation of desoxyanisoin gives 4,4'-bishydroxydeoxybenzoin (**BHDB**)
- **BHDB-polyarylate:**
 - Low solubility in common organic solvents
 - Relatively low molecular weights obtained (10-25K)
 - Use BPA as bisphenolic comonomer: increase solubility, increase flammability

Ellzey, K. A.; Ranganathan, T.; Zilberman, J.; Coughlin, E. B.; Farris, R. J.; Emrick, T. Macromolecules 2006, 39, 3553.

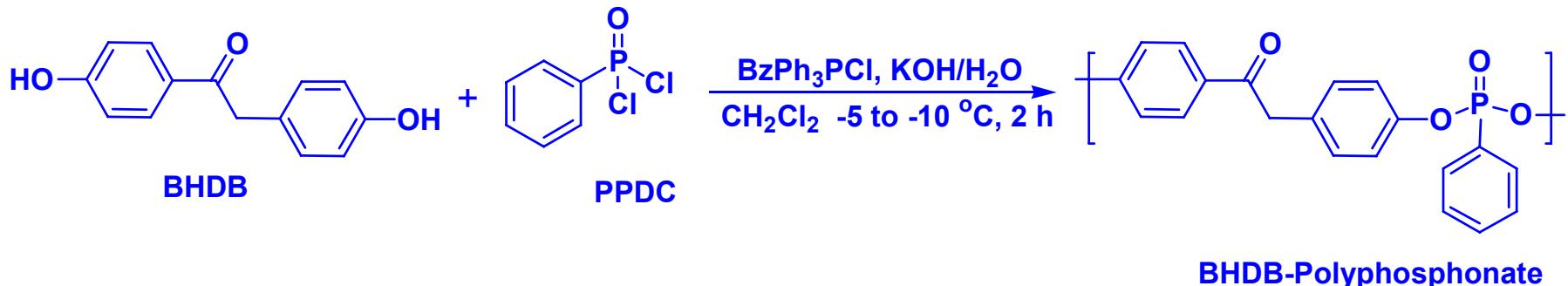
Performance of BPC vs. BHDB polymers

non-halogenated BHDB vs. chlorinated bis-phenol C



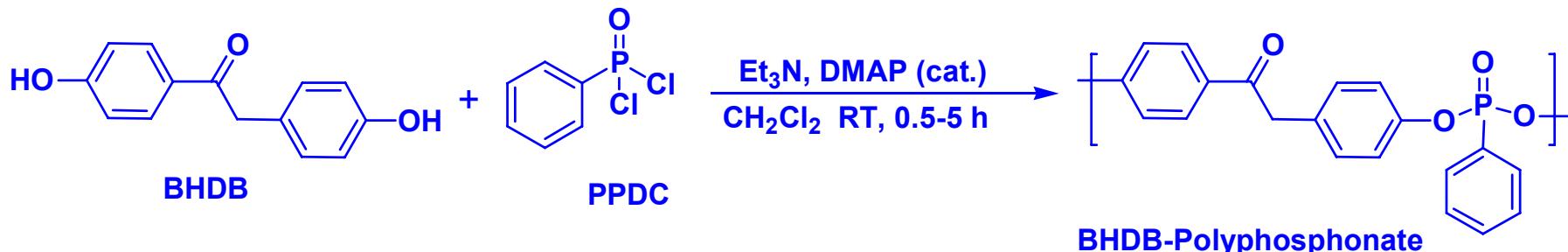
Synthesis of BHDB Polyphosphonates

Interfacial polymerization



- Soluble in most of common organic solvents like dichloromethane, chloroform, THF, DMSO, DMF etc.
- ^{31}P NMR: δ 12.7 ppm (-O-PO-O)
Three overlapping peaks due to regio-isomers (H-H, T-T and H-T)
- FT-IR: 1681 (ν_{CO}), 1269 ($\nu_{\text{P=O}}$), 1193 ($\nu_{\text{P-O-C}}$)
- GPC (DMF): $M_w=22300$ (PDI=2.6)

Solution polycondensation



End-capping Agent	Reaction Time(h) ^a	Yield (%)	GPC ^b		
			M_w	M_n	PDI
2,6-Me ₂ PhOH	0.5	79	53600	23600	2.27
2,6-Me ₂ PhOH	1	75	115800	39800	2.92
2,6-Me ₂ PhOH	2	78	140300	45800	3.06
2,6-Me ₂ PhOH	4	86	55400	23200	2.39
Phenol	2	75	138300	45500	3.05
Phenol	3	79	164900	43700	3.77
Phenol	5	80	52000	22200	2.34
Phenol ^c	3	75	5000	1900	2.64
None	3	77	74700	22700	3.29

^a Reactions were continued for another hour after the addition of end- capping agents;

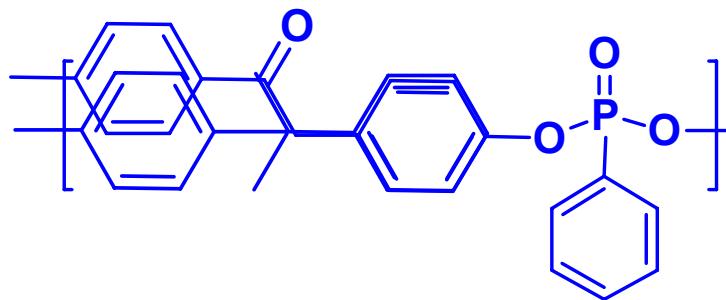
^b DMF as eluent against polystyrene standards; ^c Without catalyst.

- Anhydrous conditions
- End-capping to increase hydrolytic stability
- Phenol converts labile P-Cl bonds into more stable P-OPh bonds
- Catalyst helps to achieve high molecular weight

PCFC, TGA and DSC studies

- Heat Release Capacity = 80-100 J/g.K
- Char yield = 50-52%
- Decomposition temperature = 340-360 °C (5% weight loss)
- Glass transition temperature = 100-110 °C
- No melting point up to 300 °C

BHDB vs. BPA Polyphosphonates



Heat Release Capacity = ~430-560 KJ/g.K
Char yield = 15%

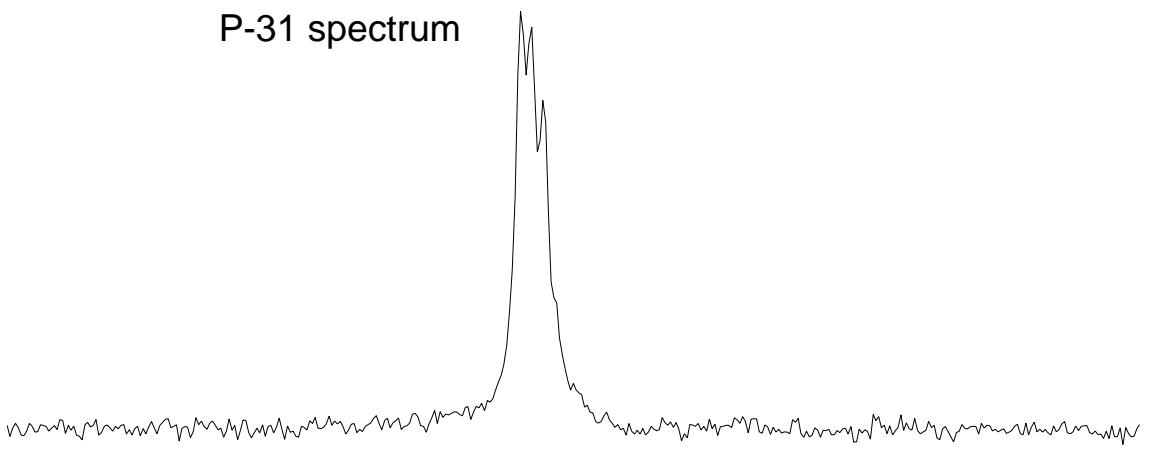
Flammability characterization: BHDB Vs BPA

Polymer	Bisphenol part	PCFC	TGA
		HRC (J/g-K)	Char yield (%)
Polyarylate	BPA	400	30
	BHDB	65	45
Polyphosphonate	BPA	450	20
	BHDB	80	52

- Choice of bisphenol part is key determinant of flammability
- Inherently fire-resistant properties evident when using deoxybenzoin unit

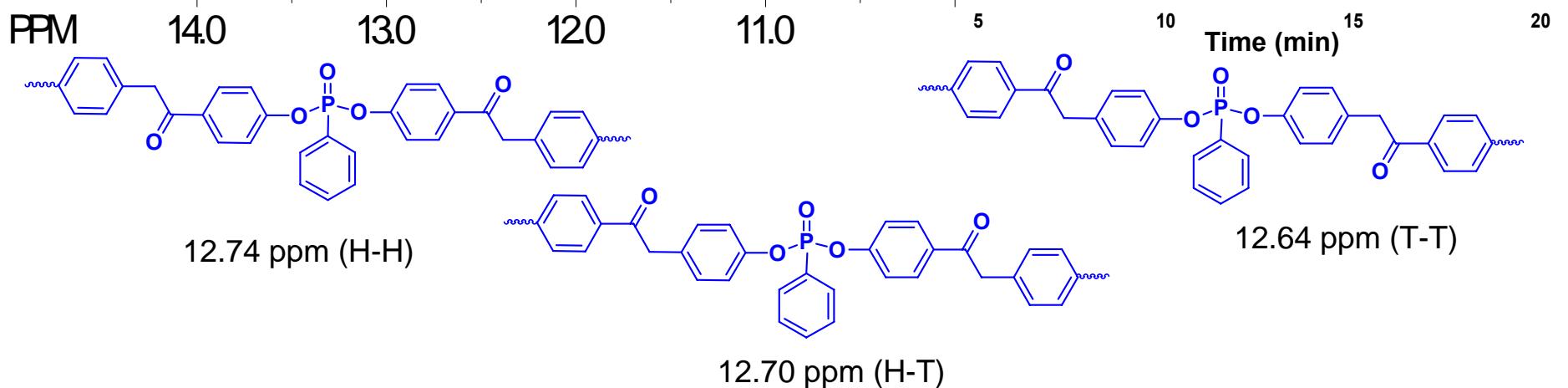
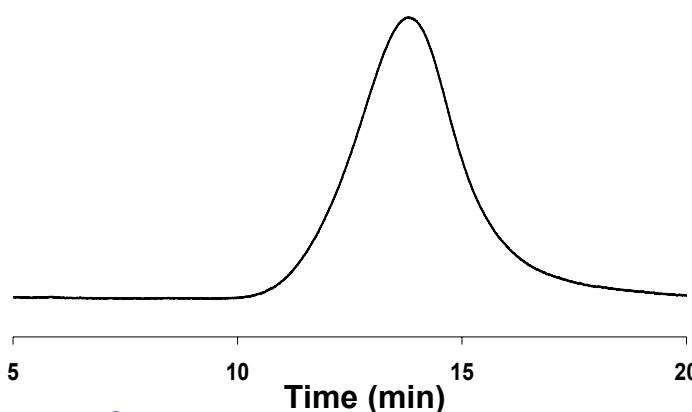
BHDB polyphosphonates

P-31 spectrum

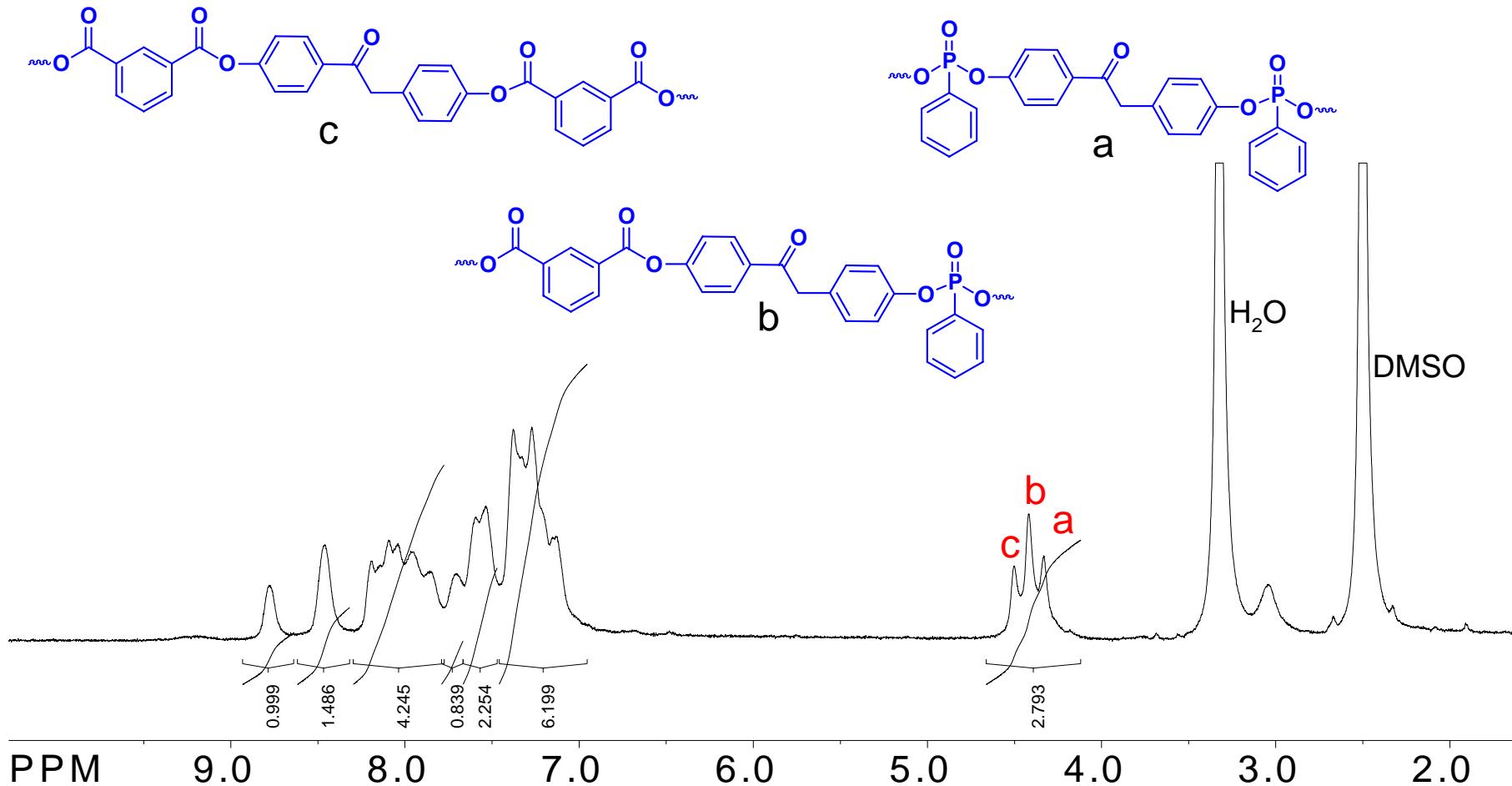


Size exclusion chromatography

$M_w = 54,600$; $M_n = 24,100$
 $PDI = 2.27$



^1H NMR spectrum of BHDB polyphosphate/polyarylate copolymers



Molecular weight characterization

Isophthaloyl chloride: PPDC (molar ratios)		Yield (%)	GPC ^b		
Feed	Incorporated ^a		M_w (g/mol)	M_n (g/mol)	PDI
100:0	100:0	80	15,100	11,700	1.29
80:20	77:23	88	65,600	37,000	1.78
60:40	57:43	85	50,700	28,500	1.78
50:50	46:54	95	54,600	24,100	2.27
40:60	39:61	92	83,700	31,200	2.69
20:80	23:77	90	61,000	37,000	1.65
0:100	0:100	89	92,700	41,000	2.26

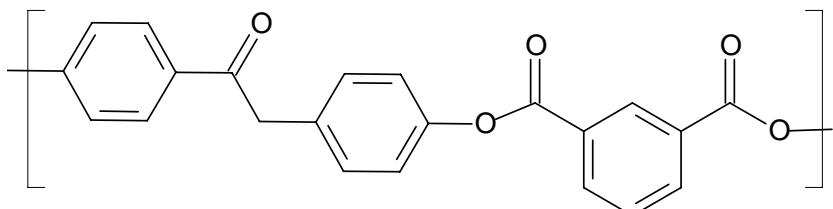
^a Calculated from ¹H NMR spectroscopy; ^b Using DMF as eluent, against polystyrene standards

Thermal and Flammability Studies

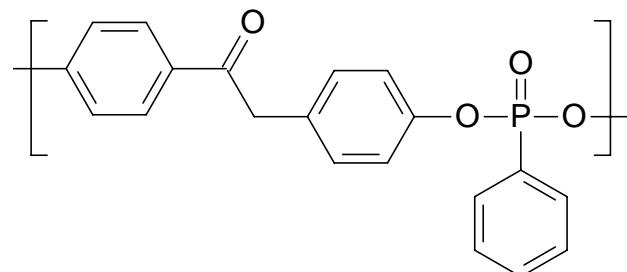
Isophthaloyl chloride: PPDC (molar ratios)	PCFC	TGA		DSC
	Heat release capacity (J/g-K)	5% Weight loss temperature (°C)	Char yield at 800 °C (%)	Glass transition temperature (°C)
100:0	65	340	45	157
77:23	48	346	50	142
57:43	41	383	56	133
46:54	36	367	54	131
39:61	40	390	57	124
23:77	59	394	55	110
0:100	80	397	52	100

- ❖ Phosphorus promote char formation efficiently in “oxygen-rich” polymers
- ❖ “Synergism” between phosphonate and isophthalate units

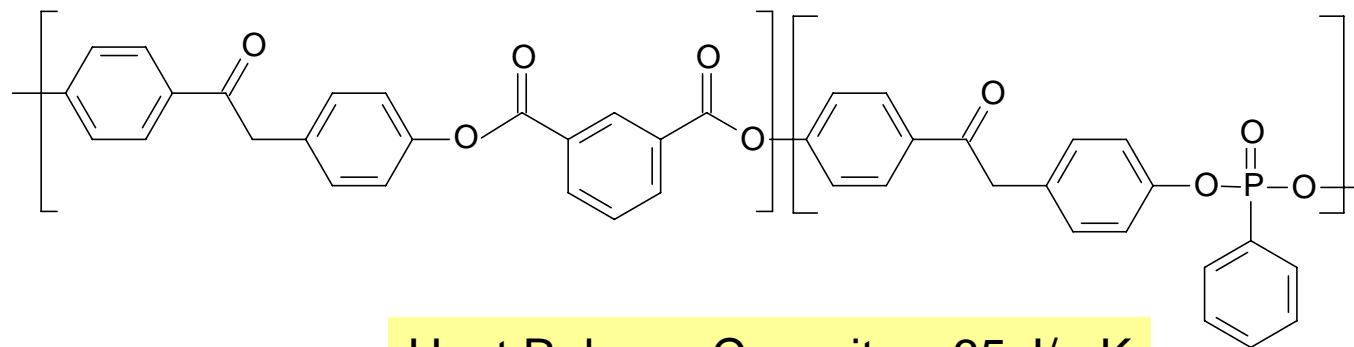
Summary: BHDB-containing polymers with low heat release capacity values



Heat Release Capacity = 65 J/g-K
Char yield = 45 %



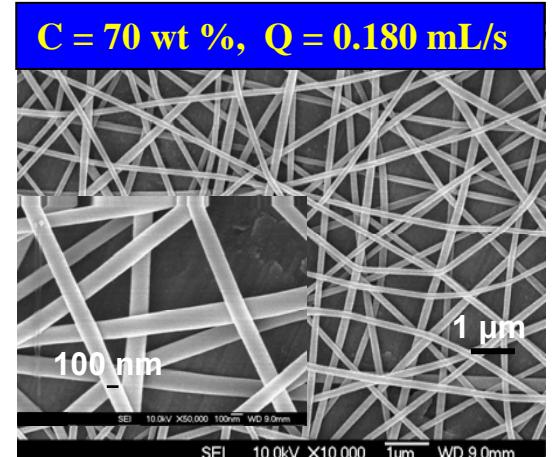
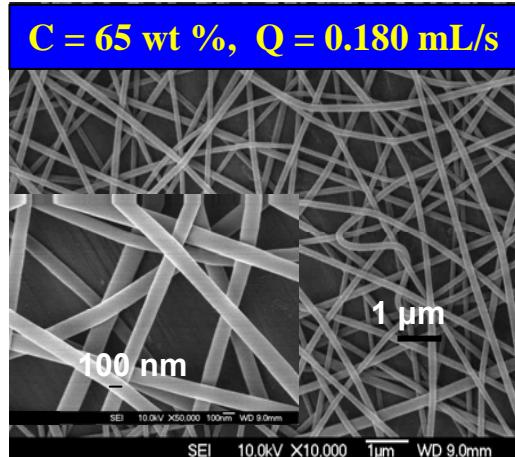
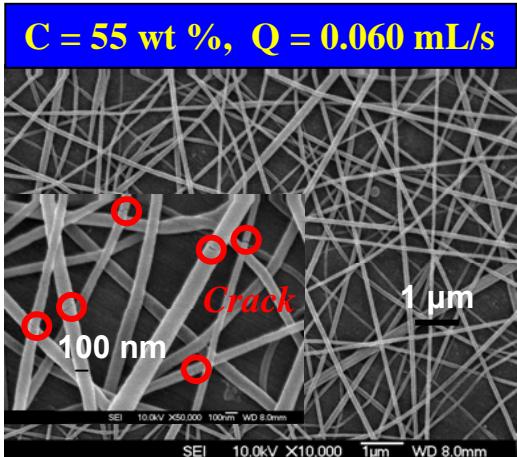
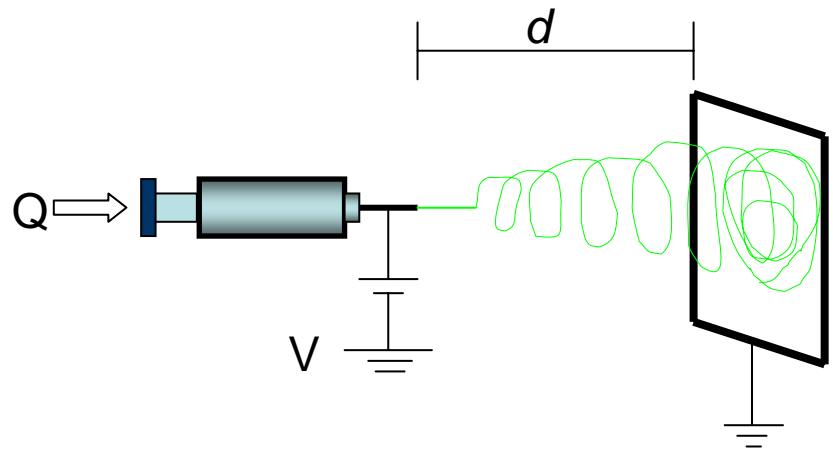
Heat Release Capacity = 80 J/g-K
Char yield = 52 %



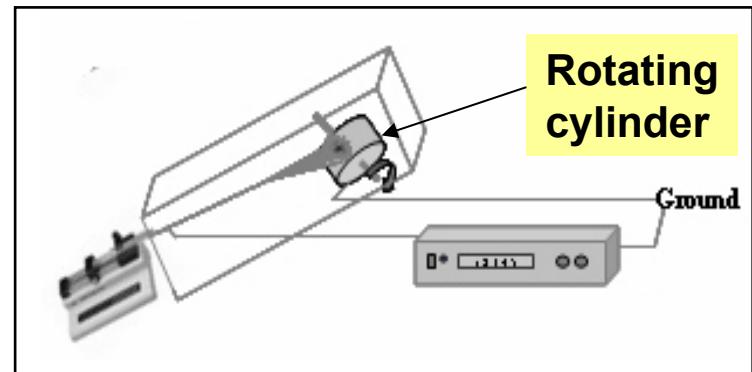
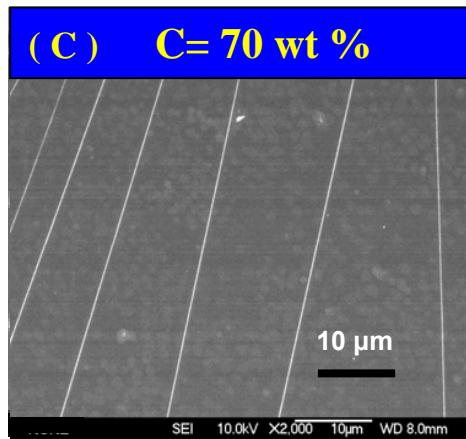
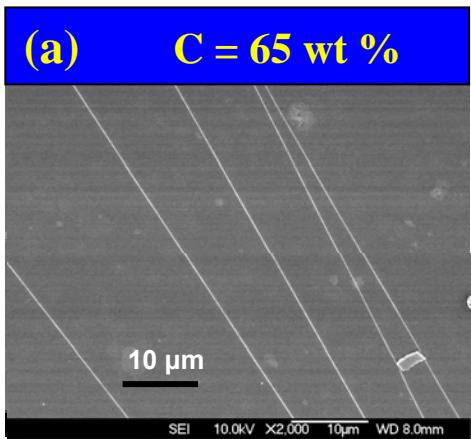
Heat Release Capacity = 35 J/g-K
Char yield = 57 %

Electrospun Nanofibers with BHDB polymers

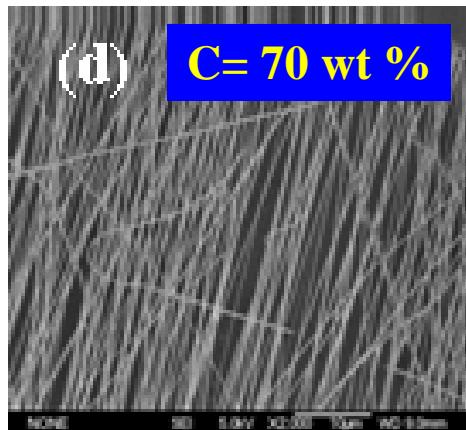
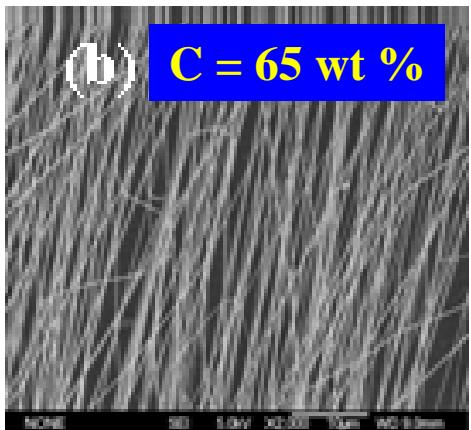
- Polymer : BHDB-polyphosphonate
- Molecular Weight: **44,700** (PDI = 3.28)
- Voltage (V) : **10 kV**, Solvent : **DMF**
- Flow Rate (Q): **0.06 ~ 0.18 mL/sec.**
- Polymer concentration (C): **55 ~ 70 wt %**
- Distance (*d*) between needle and target:**12 cm**



Oriented Electrospun Nanofibers



Rotating speed : **9.8 m/sec**



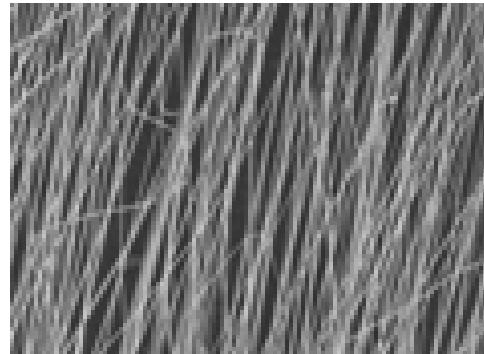
Wt (%)	Diameter (nm)
65	101 ± 11
70	145 ± 28

Properties of Electrospun Nanofibers

Heat Release Capacity (HRC)

Nanofibers: **70 ± 3 J/(g-K)** (SD = 6)

Diameter: **100 nm**, Mw: 44,700 (PDI = 3.28)



Polymer Powder: **80 ± 11 J/(g K)** (SD = 14)

T. Ranganathan et al., *Macromolecules*, 2006, 39, 5974

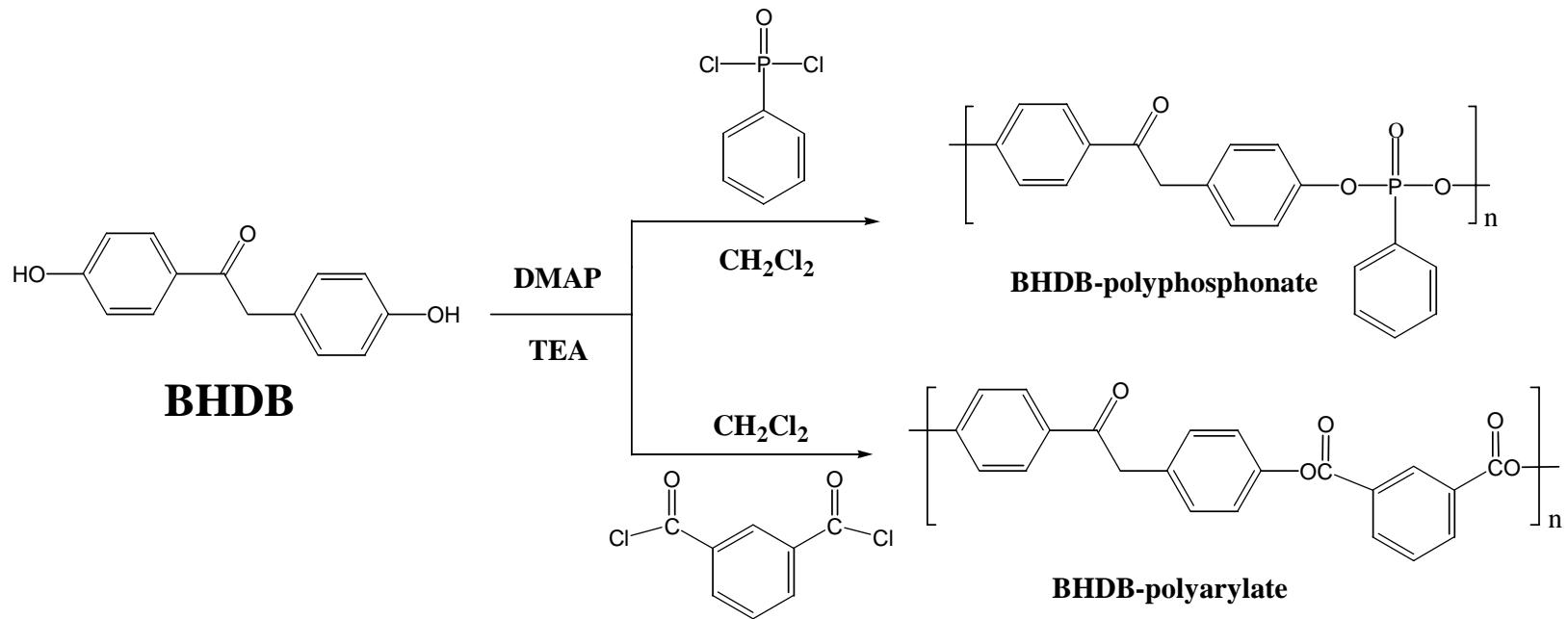
Mechanical Properties

	Mw (g/mol)	PDI	Tensile Strength @ Break (MPa)	Tensile Modulus (GPa)	Elongation @ break (%)
Fiber U ¹	69,500	2.29	50 ± 4	0.9 ± 0.1	113 ± 4
Fiber D ²	69,500	2.29	78 ± 2	2.9 ± 0.1	N/A
Cast Film	76,000	2.9	16.3 ± 2.7	1.49 ± 0.28	2.5 ± 1.7

- 1) Undrawn fiber (U)
- 2) 50 % drawn fiber (D)

density: 0.77 g/cm³, diameter: 588 ± 87 nm

BHDB-Polyphosphonate & arylyate



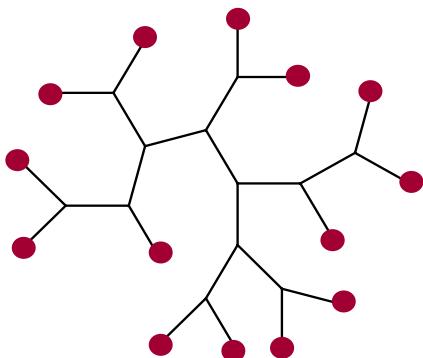
#	IPC: PPDC	Yield (%)	Solubility (mg/mL)	Solvent	GPC		
					M_w (g/mol)	M_n (g/mol)	PDI
1	0:100	90	700	DMF	44,700	13,600	3.28
2	100:0	64	< 3	DMSO	3,200	2,600	1.22

Summary and Future Directions

- BHDB-polyarylates showed excellent fire-resistant behavior (HRC ~ 65 J/g.K; Char yield ~ 45%); limited solubility in common organic solvents
- BHDB-polyphosphonate exhibited excellent solubility, while retaining flame-resistant properties (HRC ~ 80 J/g.K; Char yield ~ 52%)
- BHDB-poly(arylate-co-phosphonate)s showed HRC as low as ~35 J/g.K and char yield as high as ~57%
- Phosphorus acts efficiently in “oxygen-rich” polymers in promoting char formation
- Synthesis of BHDB polyarylate/phosphonate copolymers have been scaled up to >30 g, and mechanical properties are currently being studied

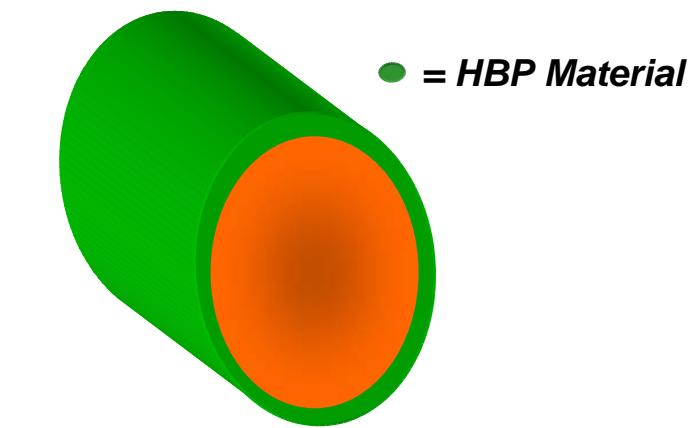
Application of hyperbranched polymers to flame-retardants

Hyperbranched polymers have been shown to migrate to polymer surfaces during co-extrusion processes



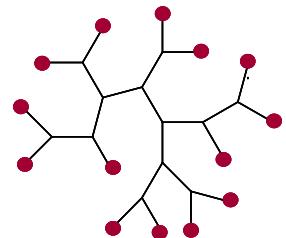
5% HBP

*Co-extrusion with
polymer of interest
(polyethylene,
polypropylene,
polystyrene, etc...)*



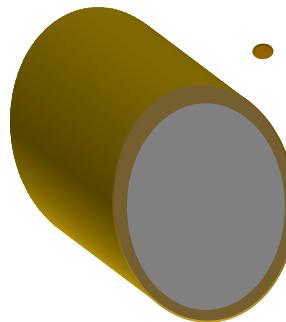
*Fiber cross-section showing
HBP coating on polymer surface*

Hyperbranched Polymer Flame-retardants



Hyperbranched Polymer (HBP)

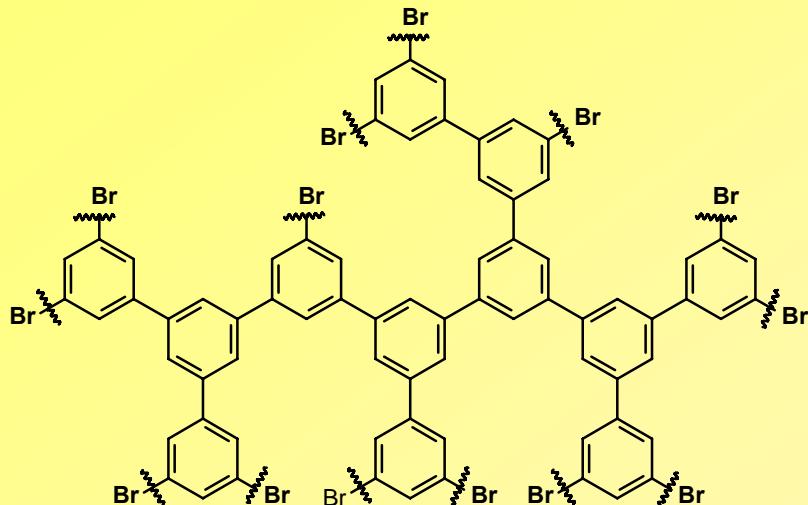
Extrusion
Bulk Polymer



● = HBP Material

May be used to deliver functionality to surface

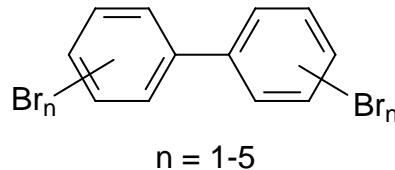
Fiber Cross-Section showing
HBP coating on surface



Hyperbranched Polyphenylene
(HBPP-Br)

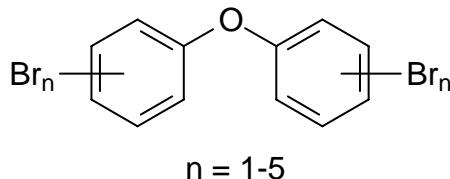
HR Cap (j/g.K)	6
THR (kJ/g)	0.7
Char Yield (%)	44

Halogenated Flame-retardants



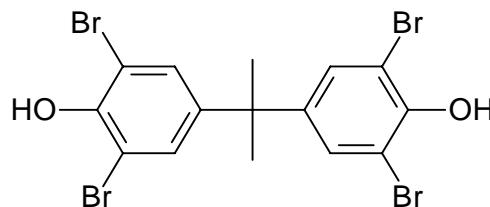
- *Environmentally persistent*
- *Lipophilic*
- *Toxic*
- *Banned worldwide*

Polybrominated biphenyls (PBB's)



- *Lipophilic; found in breast tissue*
- *Expected toxin*
- *May soon be banned*

Polybrominated diphenylethers (PBDE's)



- *Found in human blood samples in computer technicians*

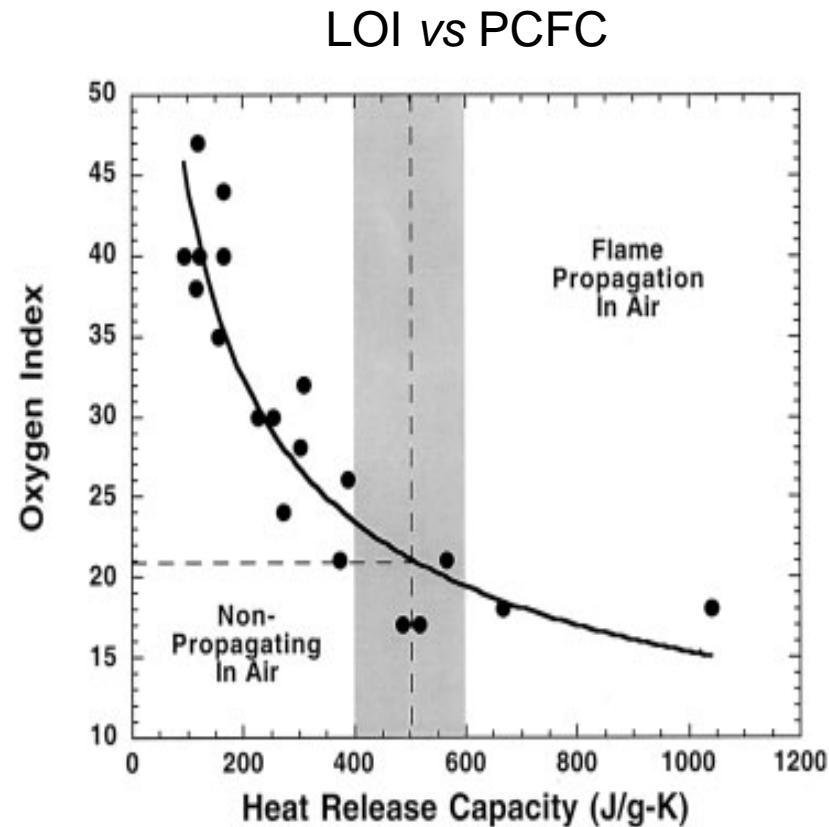
new flame-retardant materials needed

Background

- Flame Retardants (FR) are added to Polymers to
 - Increase resistance to ignition
 - Reduce flame spread
 - Suppress smoke formation
 - Prevent polymer from dripping
- Brominated FR additives
 - Very efficient and cost-effective
 - Leaching from polymer matrices
 - Environmental and health concerns
- Use of several polybrominated diphenyl ethers is restricted/banned in California, Michigan, and Oregon; others to follow...
- Non-halogenated FR, example Aluminum trihydrate (ATH)
 - Requires high loading (as high as 65%); affects mechanical properties of polymer products
 - Limitations in high processing temperatures

Flammability Characterization

- Traditional methods (~100g sample)
 - Cone calorimetry
 - UL-94 (vertical and horizontal)
 - Limiting oxygen index (LOI)
- Pyrolysis combustion flow calorimetry (PCFC)
 - Measures HRC, a material property that determines flammability
 - Correlates well with



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

BHDB-Poly(arylate-phosphonate) copolymers

Polyarylate:

- ✓ Rigid, thermally robust aromatic ester backbone
- ✓ Excellent fire-resistant properties
- ✗ Low solubility and moderately low molecular weight

Polyphosphonate:

- ✓ Good solubility
- ✓ Phosphorus improves char yield in “oxygen-rich” polymers

Copolymers:

- ✓ Combine the advantages of homopolymers
- ✓ Possible increment in char yield due to presence of two oxygen-rich species (deoxybenzoin and isophthalate units)
- ✓ Optimize phosphonate percent to improve solubility and processibility without diminishing mechanical properties

Synthesis of BHDB-Poly(arylate-co-phosphonate)s

