Non-halogenated antiflammable polymers prepared from deoxybenzoin bisphenol monomers

Conte Center for Polymer Research
Univ. of Massachusetts Amherst

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

Corporate sponsors *Boeing, Johns Mansville, Multina, Inc, Schneller, Inc.*
Solvay Advanced Polymers, General Electric

Research Group

Research group: Samantha McCrae, Elizabeth Glogowski, Maisie Joralemon, Katrina Kratz, Ravindra Revanur, Ravi Tangirala, Debasis Sumatra, P.K. Sudeep, Qingling Zhang, T. Ranganathan, Beth Cooper, Irem Kosef, Hemali Rathnayake, Yunxia Hu, Delphine Chan-Seng

Polymer Flammability Effort at UMass Amherst

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

CUMIRP CENTER FOR RESEARCH ON POLYMERS
UNIVERSITY OF MASSACHUSETTS ↔ INDUSTRY

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

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, 5 students and postdoctoral associates

Characterization Techniques in Cluster F Research

Techniques for evaluating thermal properties on a small scale

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

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

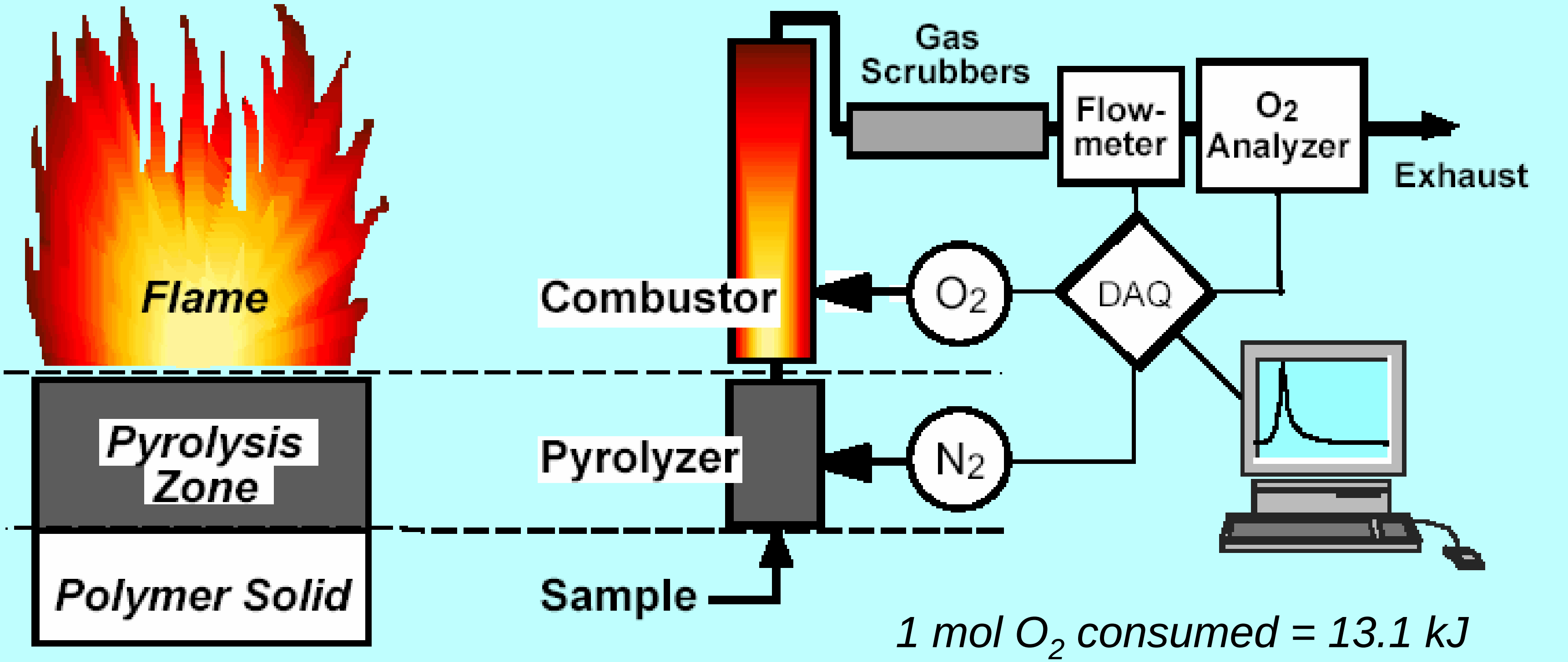
Py-GC/MS:
Pyrolysis GC/MS
(1 mg)

- Decomposition products
- Mechanism of decomposition

TGA:
Thermogravimetric
Analysis
(10 mg)

- Thermal stability
- Char yield

Pyrolysis Combustion Flow Calorimetry



1 mol O_2 consumed = 13.1 kJ

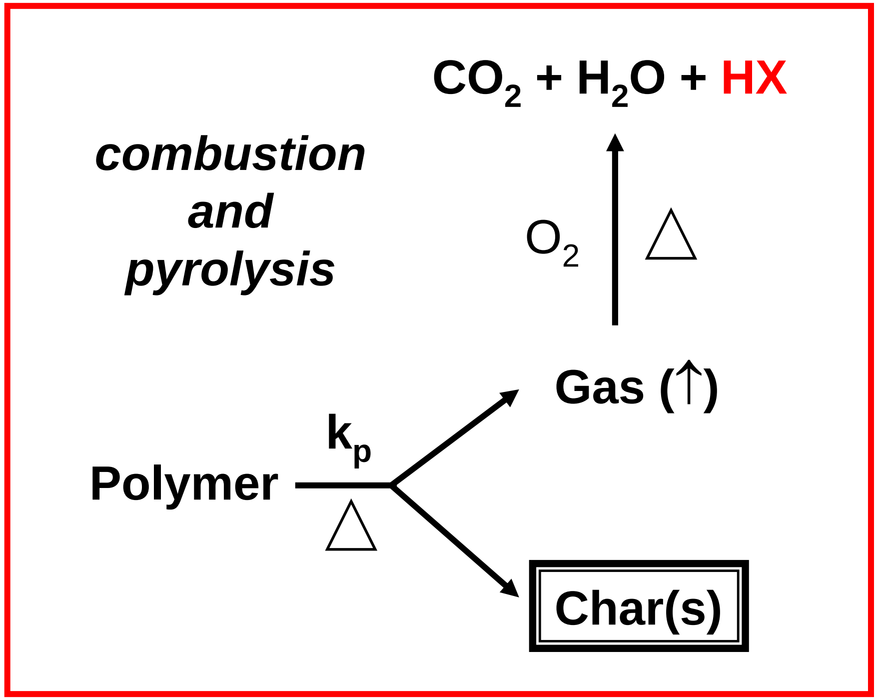
$$\text{Heat Release Capacity} \equiv \frac{\dot{Q}_c^{max}}{\beta} = h_c^o \frac{(1-\mu)E_a}{eRT_p^2}$$

PCFC provides Heat Release (HR) Capacity as a material property and key parameter in determining flammability on small sample scales

$h^o{}_c$ = 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



combustion and pyrolysis

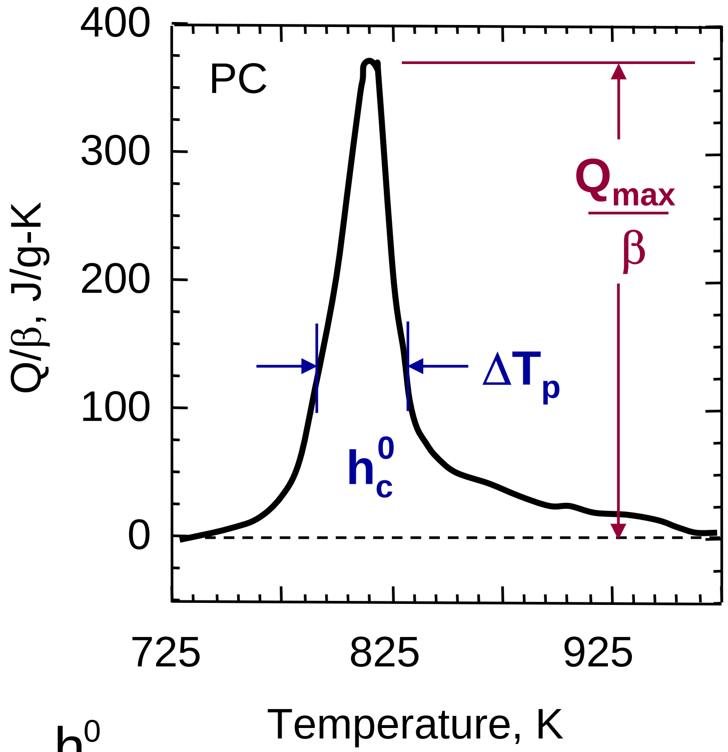
$CO_2 + H_2O + HX$

O_2 △

Gas (↑)

Polymer k_p △

Char(s)



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

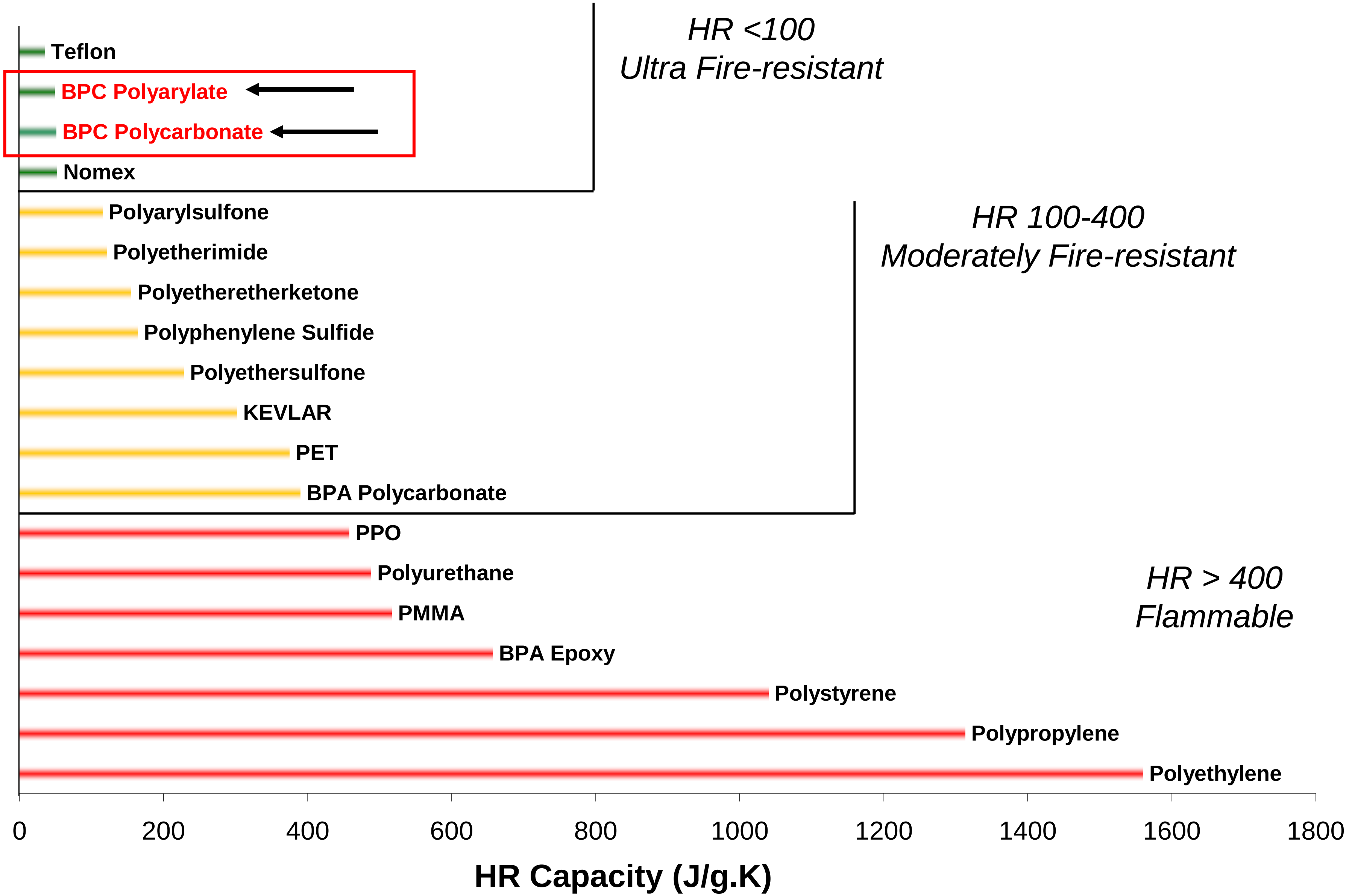
(J/g-K)

Peak Height Method

Peak Area Method

Heat Release Capacity of Polymers

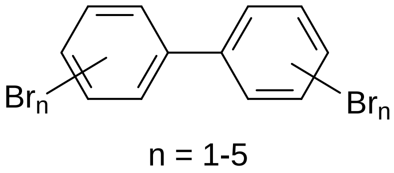
Walters, R.N.; Lyon, R.E. *J. Appl. Polym. Sci.* **2003**, **87**, 548.

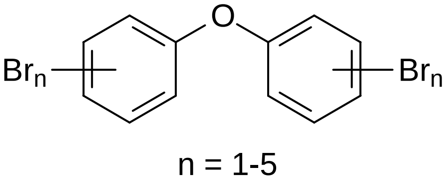


Flame retardant additives

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

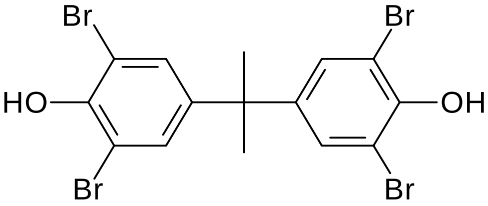
Polybrominated biphenyls (PBBs)





Problems: leaching from polymer, toxicity, environmental persistence

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

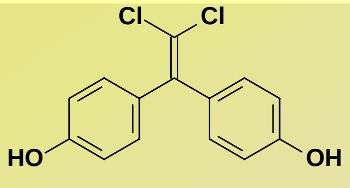


Clay-polymer and nanotube-polymer composites show flame resistance…

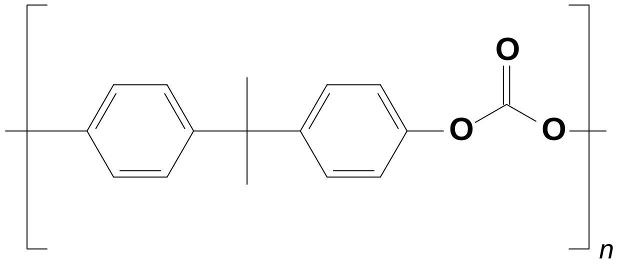
Objective

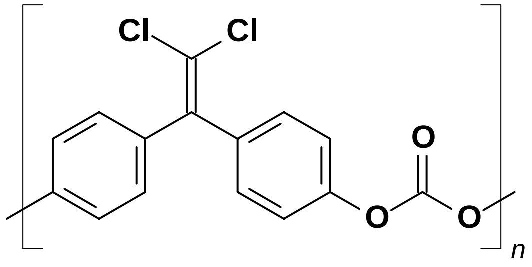
Discover new polymers with inherently low flammability that do not require these additives

Bisphenol C *vs.* Bisphenol A



Bisphenol C

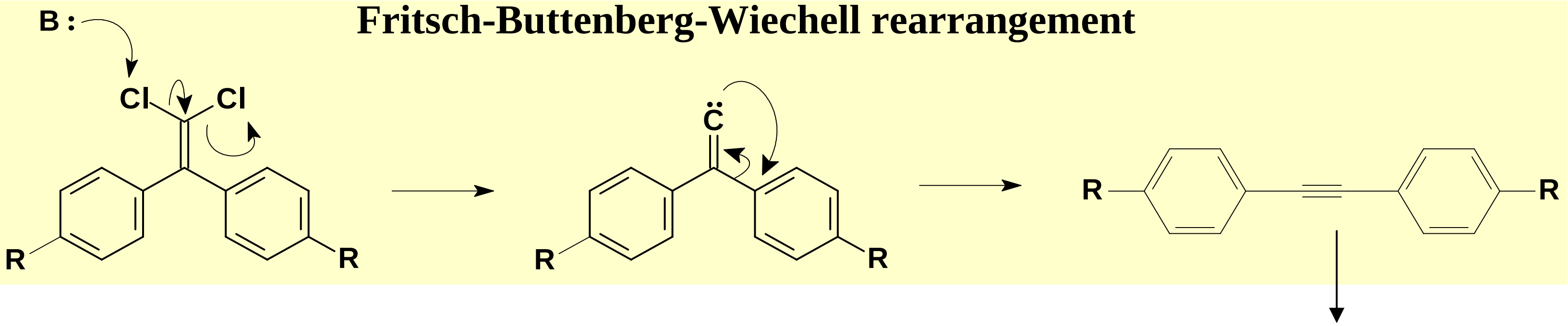




	Bisphenol A Polycarbonate (Lexan)	**Bisphenol C Polycarbonate**
Morphology	Amorphous	Amorphous
Tg (°C)	152	168
Flex Modulus (ksi)	336	376
Flex Strength (psi)	16,300	16,200
Tensile Yield Strain (%)	10	11
NBS Smoke (Dm)	165	75
Oxygen Index (%)	26	56
HR Capacity (J/g.k)	**390**	**29**

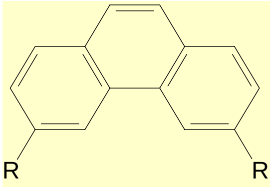
Source: Dr. Richard Lyon, FAA

Dichloroethylene rearrangements



Fritsch-Buttenberg-Wiechell rearrangement

Char formation for fire extinction

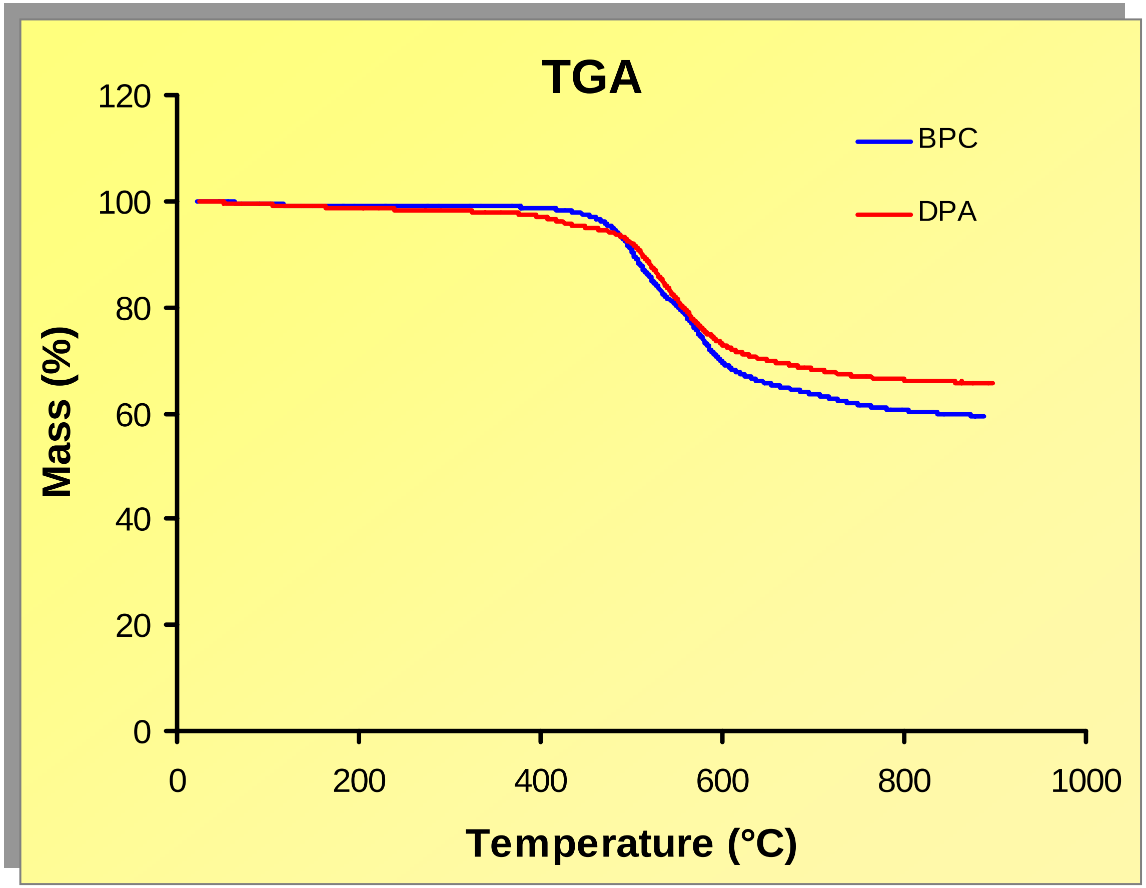


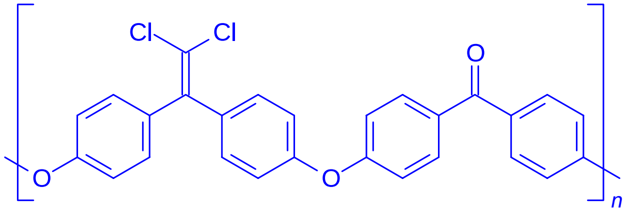
1. ***Chlorine content in BPC prevents widespread use;***
2. ***Chlorine content in BPC provides anti-flammable properties by setting up rearrangement chemistry***

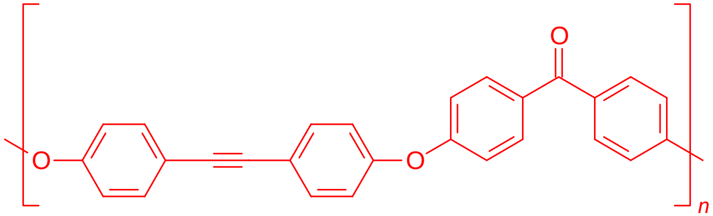
Ramirez, M. L. *Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers. DOT/FAA/AR-00/42.*; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001;

Stoliorav, S.I.; Westmoreland, P.R. *Polymer* **2003**, *44*, 5469; van der Waals et al. *J. Mol. Cat. A* **1998**, *134*, 179

Thermal Properties of Alkyne *vs*. bisphenol C polyethers





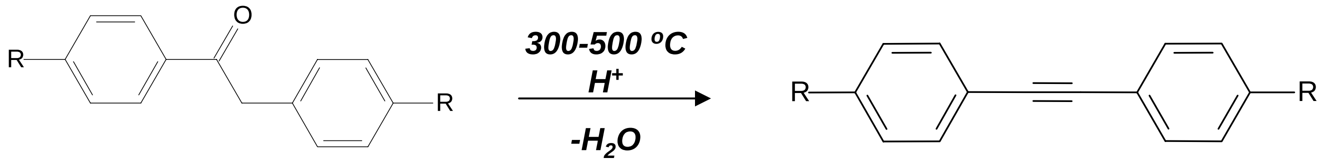


Halogen-free version behaves similarly to BPC version by PCFC and TGA

	Char Yield (%)	**HR Capacity** (J/g·K)	**Total HR** (kJ/g)
BPC	59	30	6.2
DPA	66	24	5.3

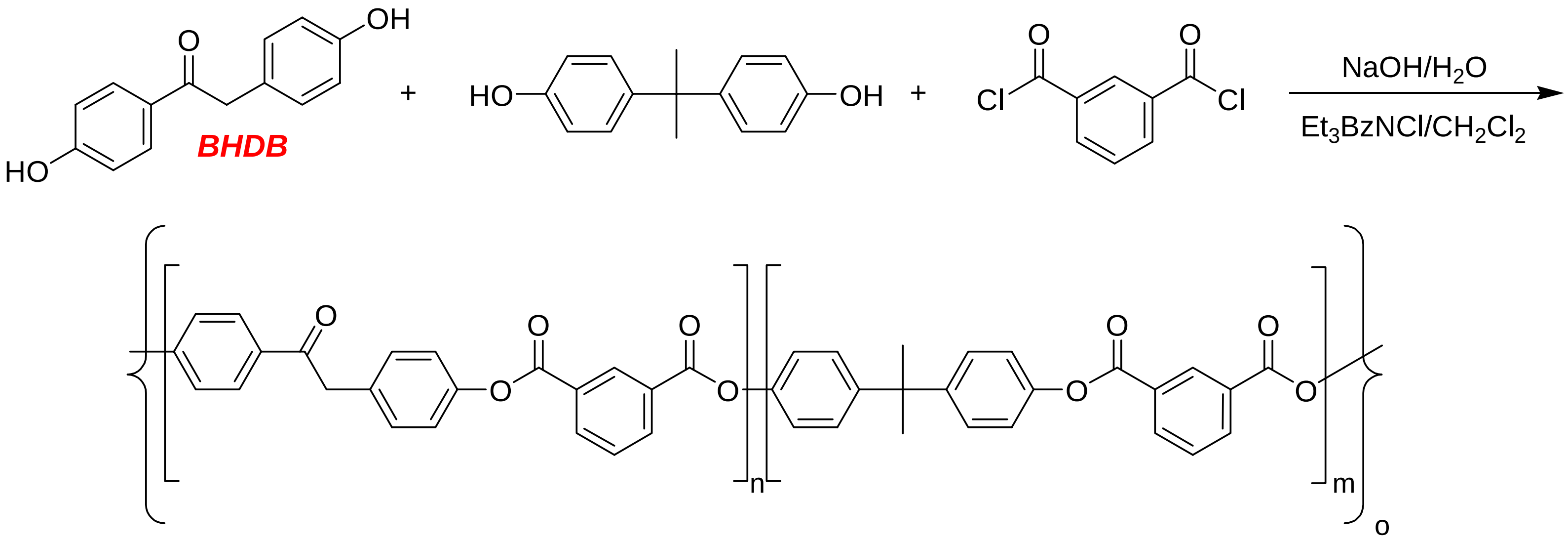
Char Yields, HR Capacity, and Total HR similar to BPC.

Halogen-free anti-flammable deoxybenzoin-based polymers



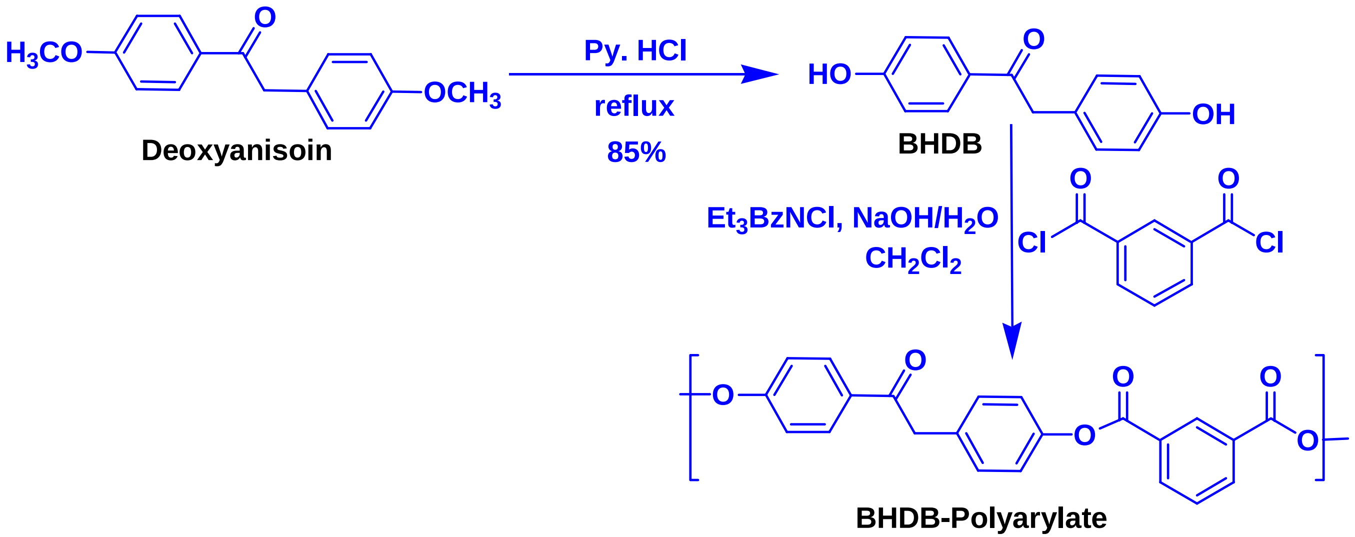
Deoxybenzoin derivatives

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



BHDB

Deoxybenzoin-based polyarylates



- Demethylation of desoxyanisoin gives 4,4’-bishydroxydeoxybenzoin (BHDB)

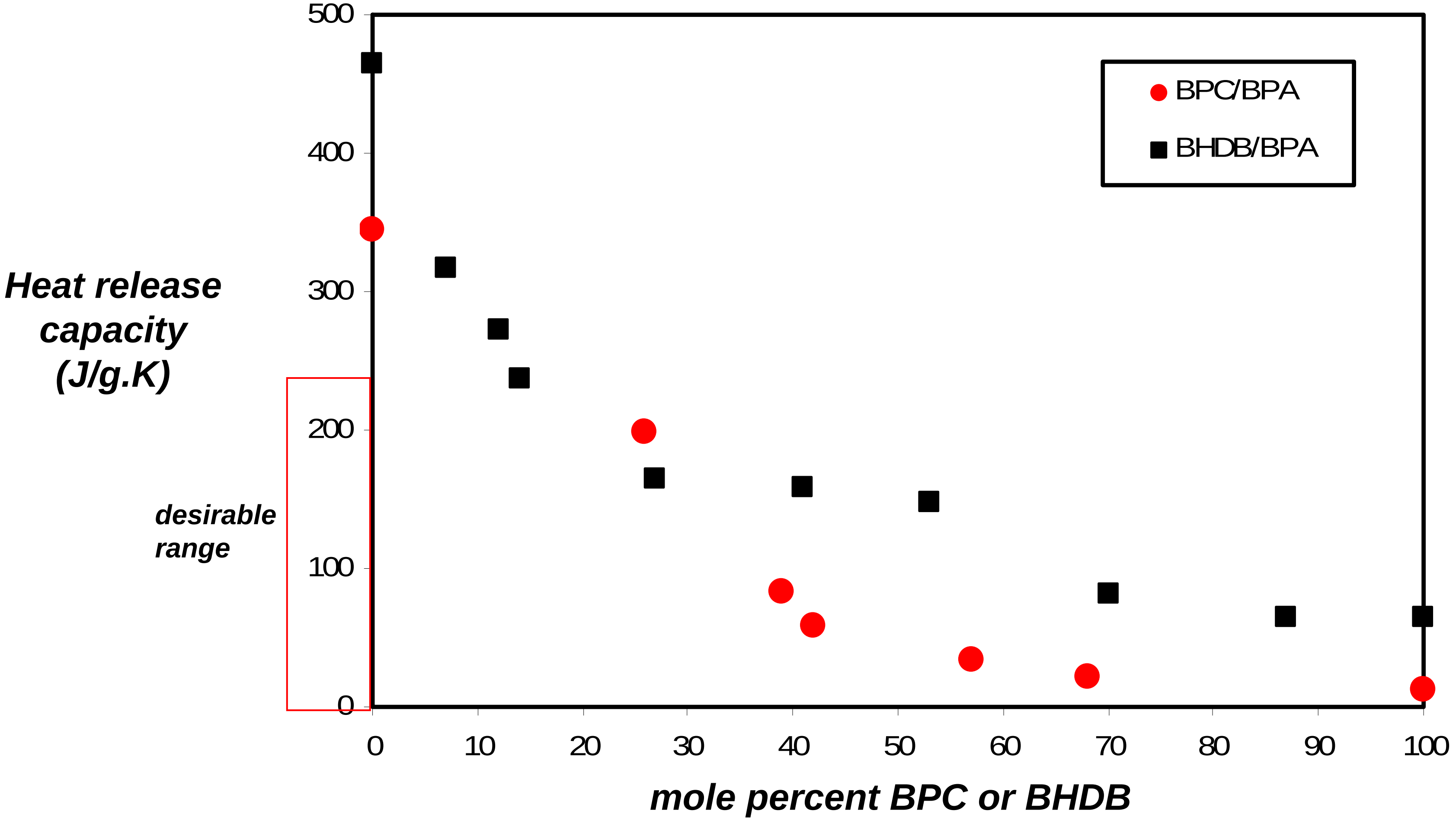
Buo-hoi, N. P.; Sy, M.; Xuong, N. D.
Bull. Soc. Chim. Fr. 1956, 629.

- BHDB-polyarylate:
  - Interfacial or solution polymerization
  - Polymer has low solubility in common organic solvents
  - Interfacial method gives relatively low molecular weights (10-25K)
  - Using BPA as bisphenolic comonomer leads to increased solubility and increased flammability

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

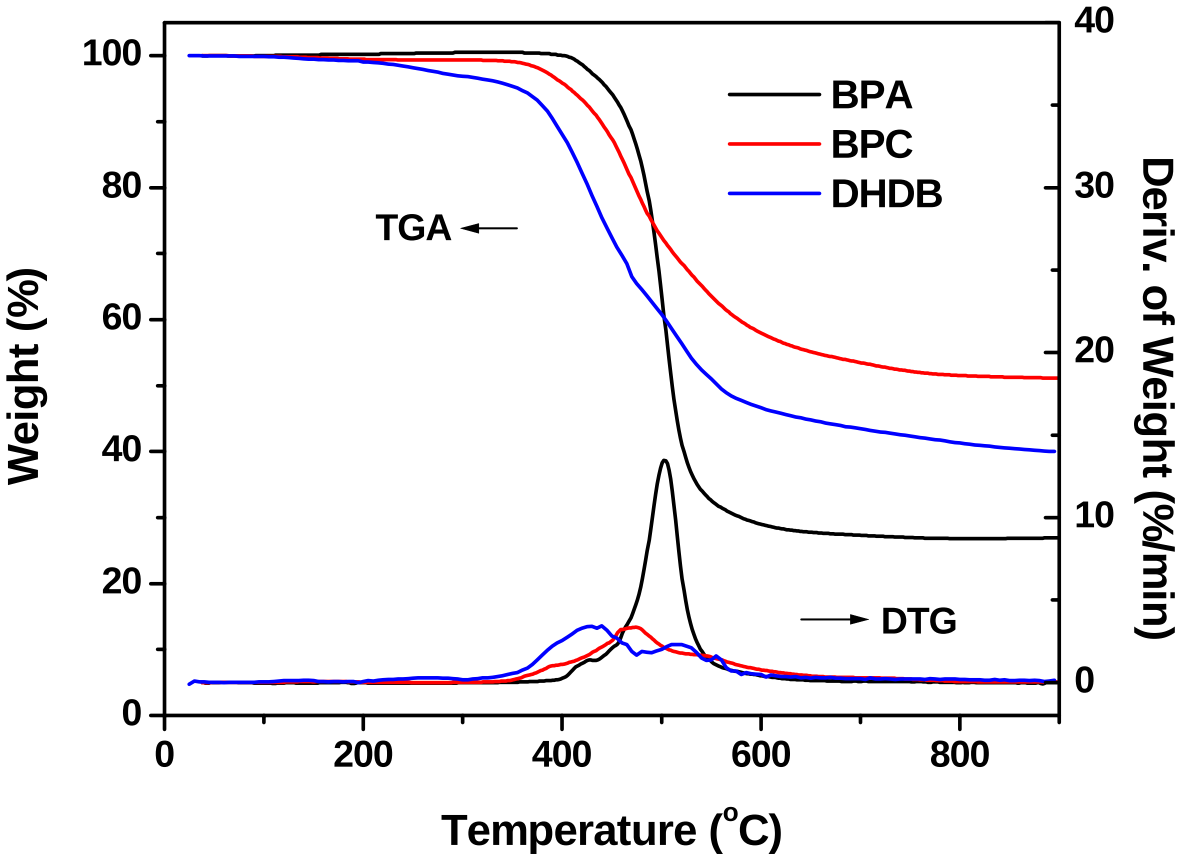
BPC vs. BHDB polymers

non-halogenated BHDB vs. chlorinated bis-phenol C

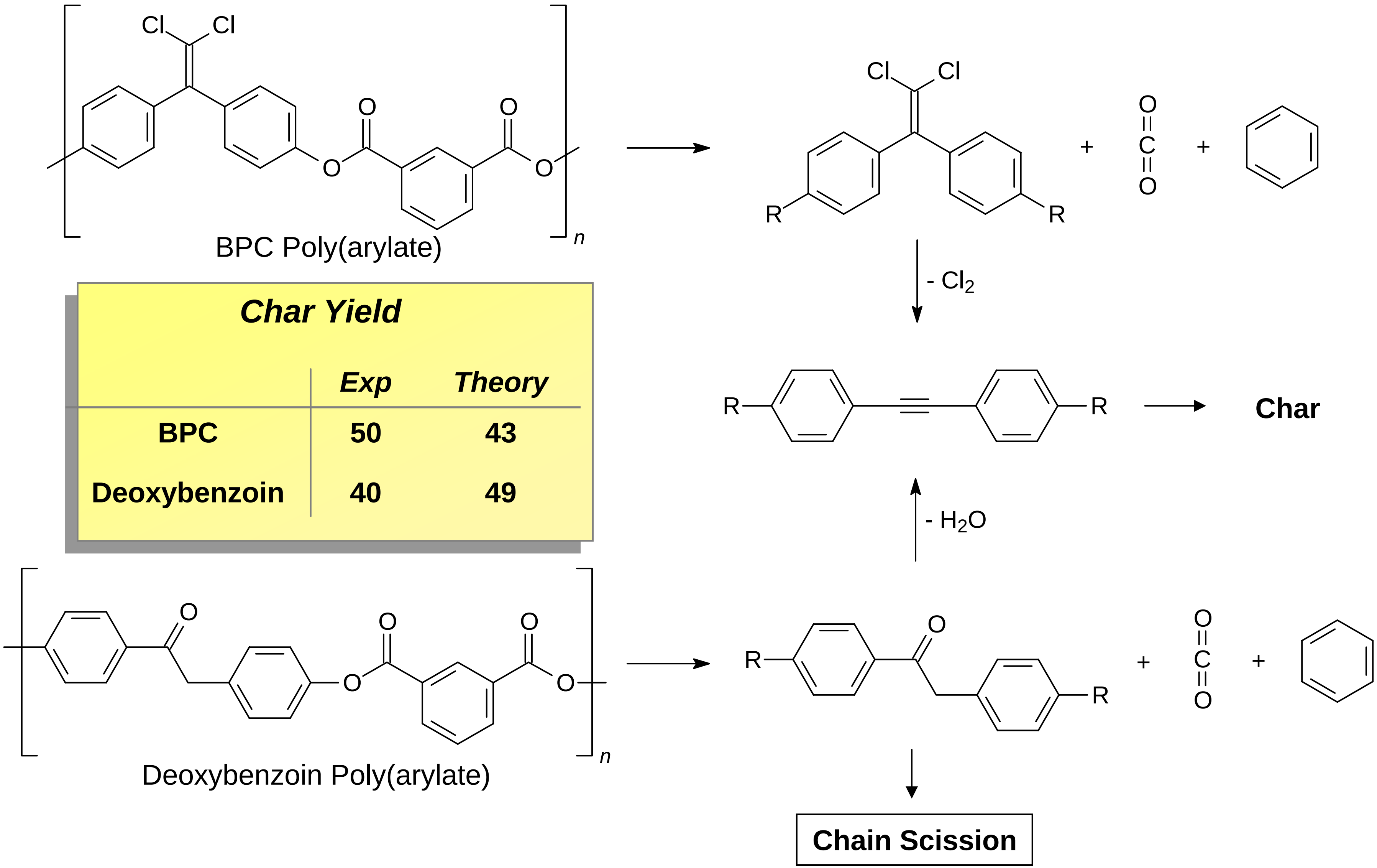


Deoxybenzoin/BPC/BPA Polyarylate Comparison

Bisphenol	Char Yield (%)	HR Capacity (J/g.K)	Total HR (kJ/g)
BPC	50	29	3.0
BHDB	40	81	10.6
BPA	22	459	19.1



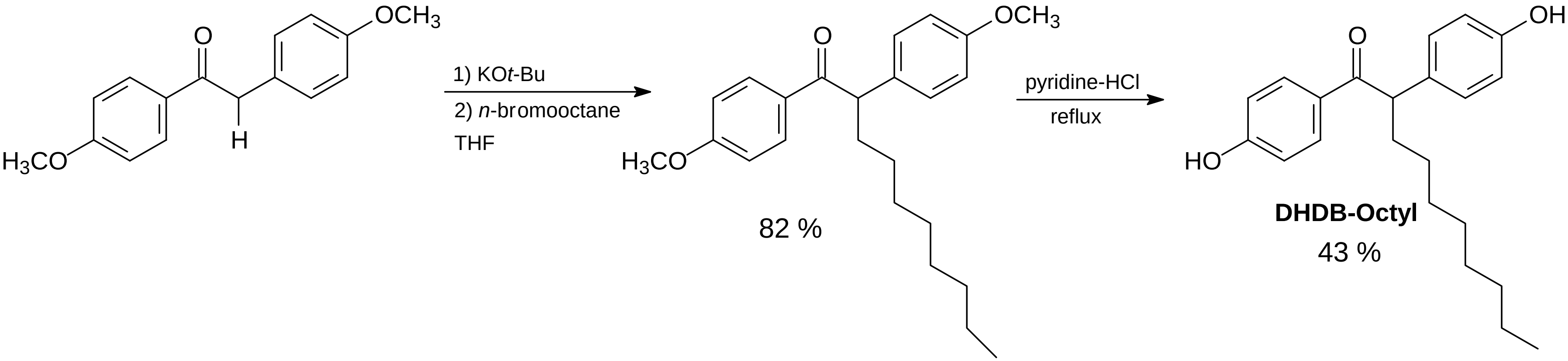
BPC and Deoxybenzoin Char Formation



Char Yield

	Exp	***Theory***
BPC	**50**	**43**
Deoxybenzoin	**40**	**49**

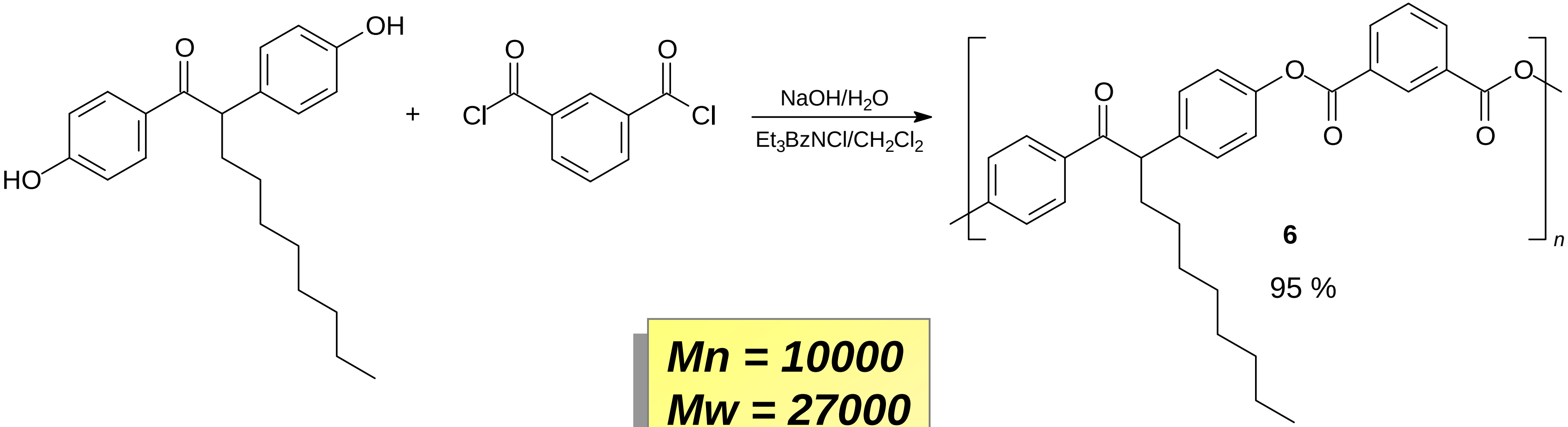
n-octyl Substituted BHDB Polyarylates



82 %

DHDB-Octyl

43 %



6

95 %

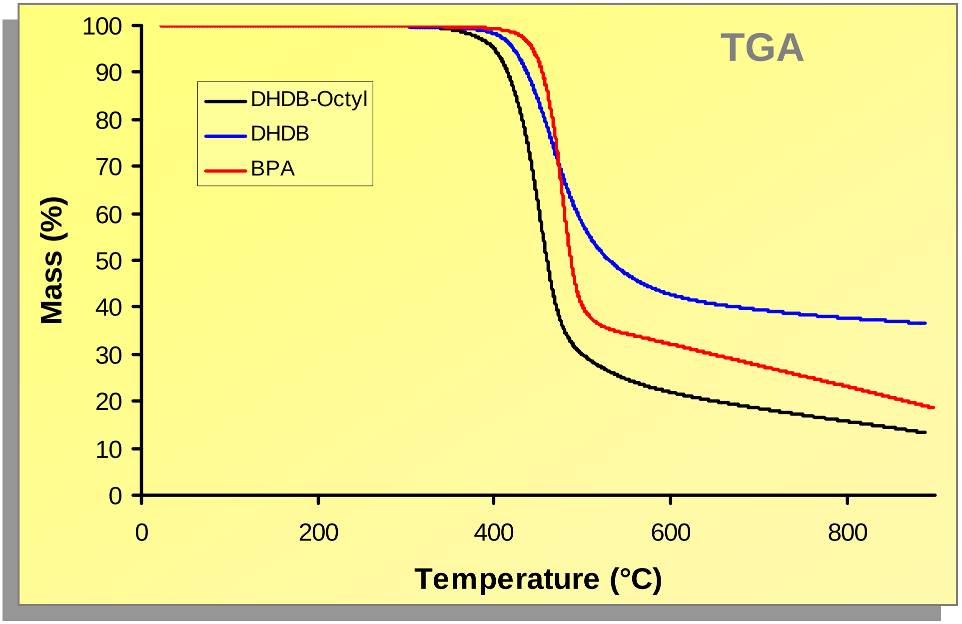
Mn = 10000

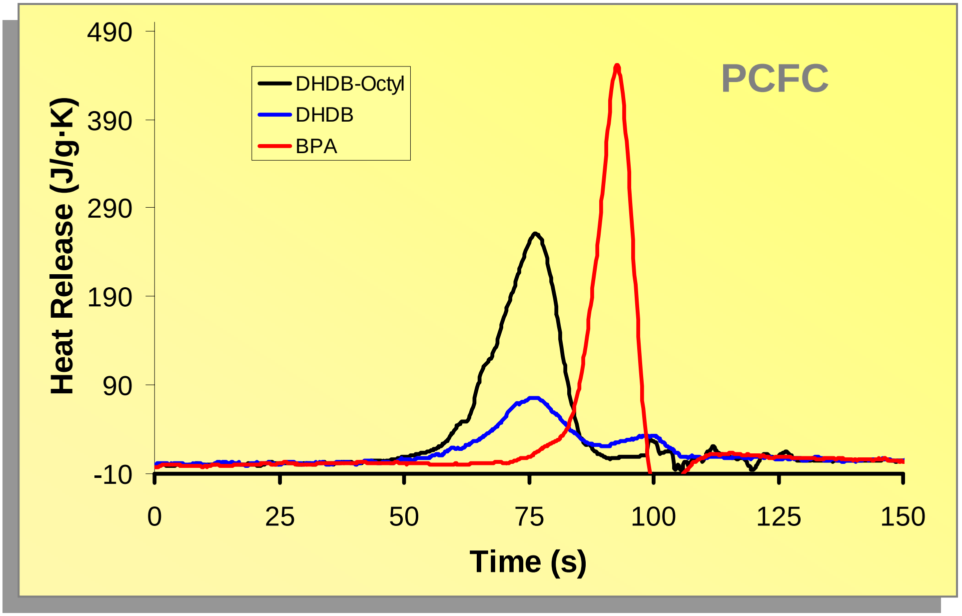
Mw = 27000

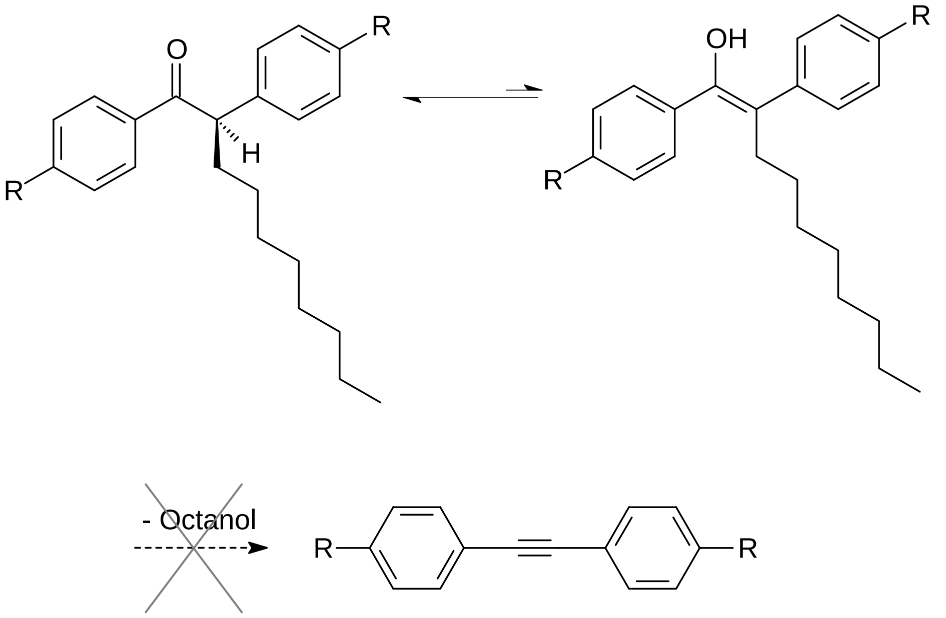
PDI = 2.7

Soluble Polyarylates

Properties of n-octyl polyarylate derivatives



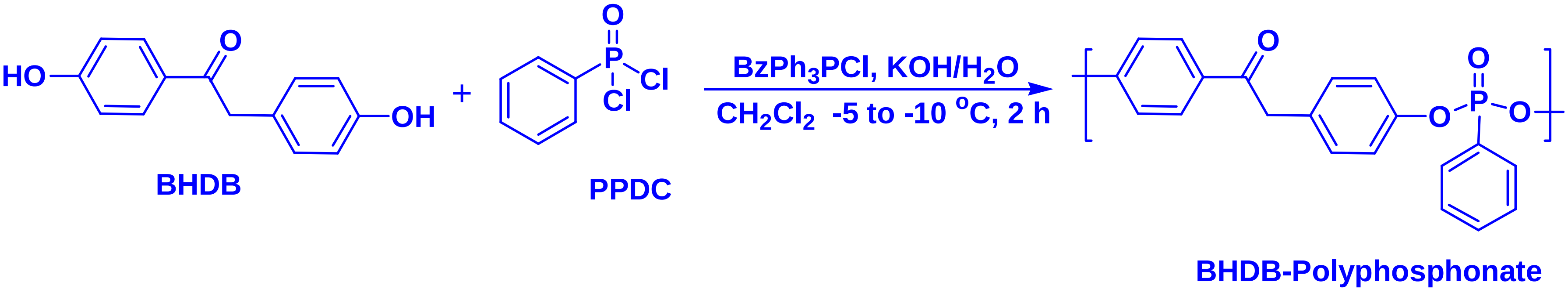




17.5% char yield

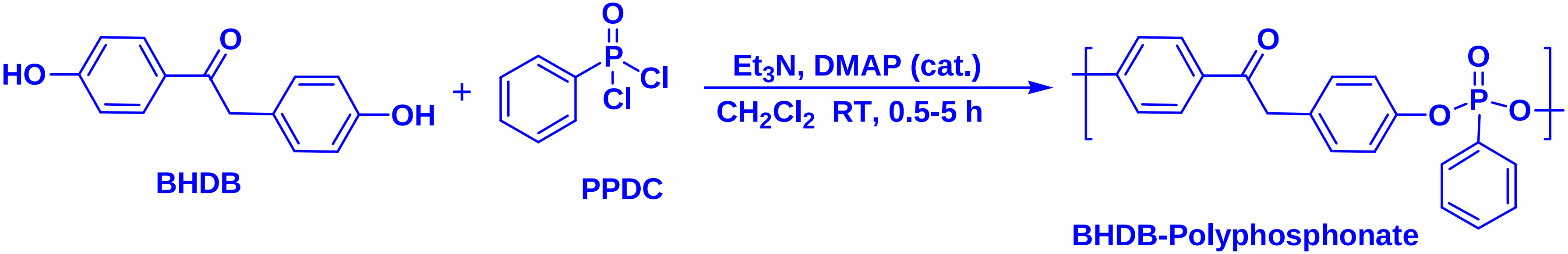
Polymer	HR Capacity (J/g·K)^{a}	Total HR (kJ/g)^{a}	Char Yield (%)^{b}
BHDB	81	10.6	40.0
BHDB-Octyl	284	20.1	17.5
BPA	459	19.1	18.6

Synthesis of BHDB polyphosphonates by interfacial polymerization



- Soluble in most of common organic solvents like dichloromethane, chloroform, THF, DMSO, DMF etc.
- ^{31}P NMR: δ 12.7 ppm (-O-*P*O-O)
  Three overlapping peaks
  (H-H, T-T and H-T regioisomers)
- FT-IR: 1681 (ν_{CO}), 1269 ($\nu_{P=O}$), 1193 ($\nu_{P\text{-}O\text{-}C}$)
- GPC (DMF): M_w=22,300 (PDI=2.6)

BHDB Polyphosphonates by solution polycondensation



End-capping reagent	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

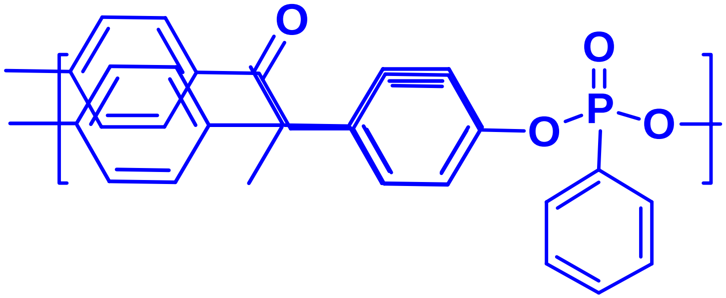
[a] Reactions were continued for another hour after the addition of end- capping agents;
[b] DMF as eluent against polystyrene standards; [c] Without catalyst.

- 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

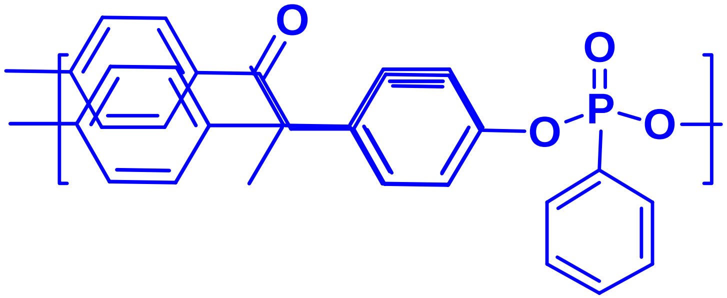
Typical values for BHDB polyphosphonates

- Heat Release Capacity = 80-100 J/g-K
- Char yield = ~50%
- Decomposition temperature = 340-360 ^{o}C (5% weight loss)
- Glass transition temperature = 100-110 ^{o}C

BHDB as a drop-in replacement for BPA

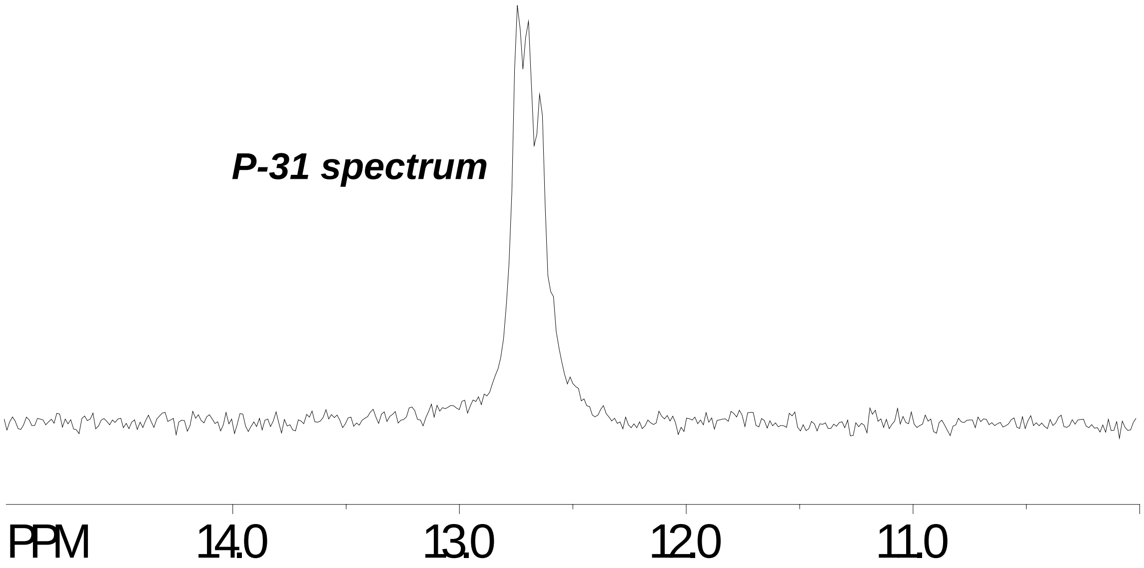


Heat Release Capacity = 480 J/g.K
Heat Release Capacity ~ 300-700 J/g.K
Char yield = 15%
Char yield = 30%



Heat Release Capacity = 480 J/g.K
Heat Release Capacity ~ 300-700 J/g.K
Char yield = 15%
Char yield = 30%

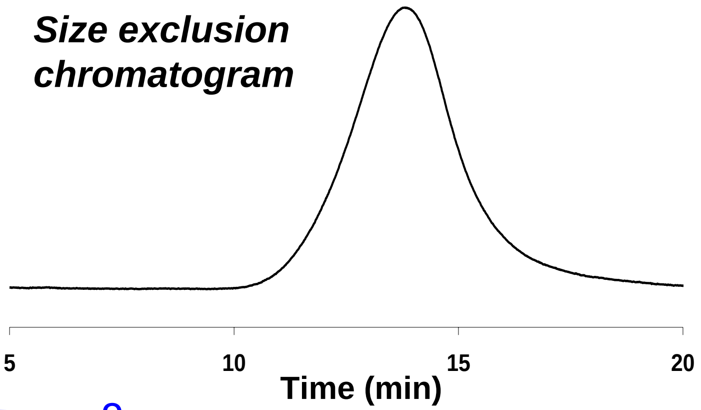
BHDB polyphosphonates

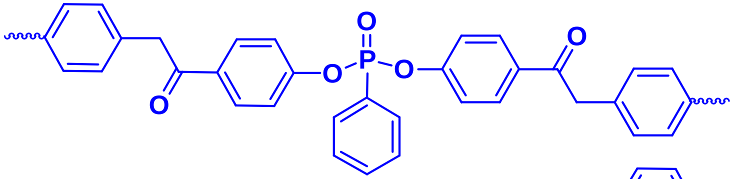


P-31 spectrum

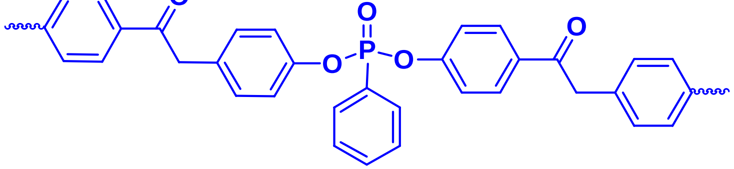
Size exclusion chromatogram

M_w = 54,600; M_n = 24,100
PDI = 2.3

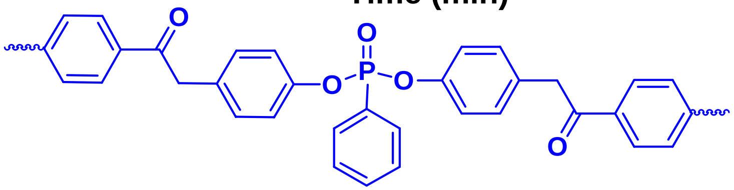




12.8 ppm (H-H)



12.7 ppm (H-T)



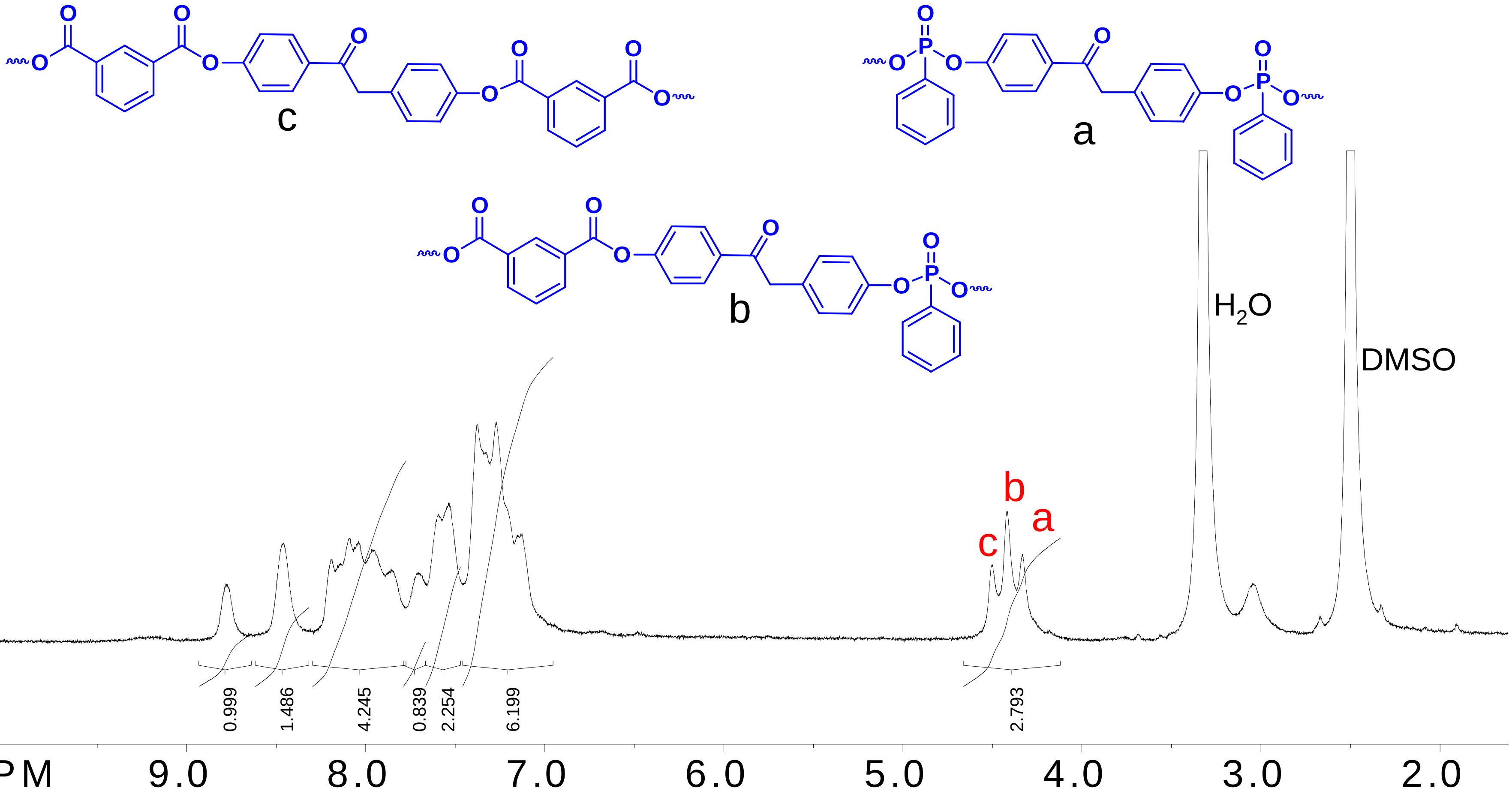
12.6 ppm (T-T)

Heat release capacity 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

^{1}H NMR spectrum of BHDB poly(phosphonate-arylate) copolymers



Molecular weight characterization: phosphonate-arylate copolymers

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

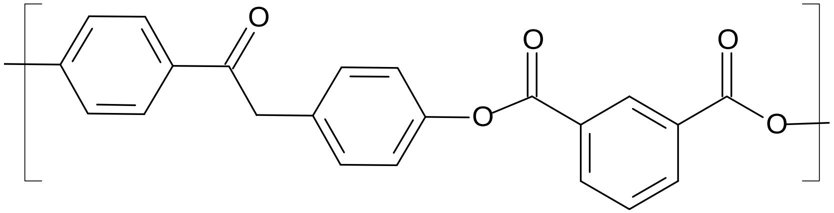
[a] Calculated from ^{1}H NMR spectroscopy; [b] Using DMF as eluent, against polystyrene standards

Thermal/Heat Release Data

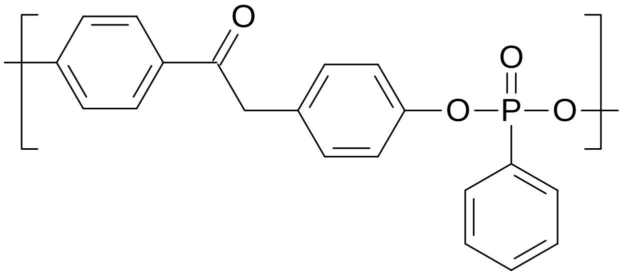
Isophthaloyl chloride: PPDC (molar ratios)	PCFC	TGA		DSC
	Heat release capacity (J/g-K)	5% Weight loss temperature (°C)	Char yield at 800 °C (%)	Glass transition temperature (°C)
100:0	65	340	45	157
77:23	48	346	50	142
57:43	41	383	56	133
46:54	36	367	54	131
39:61	40	390	57	124
23:77	59	394	55	110
0:100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

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

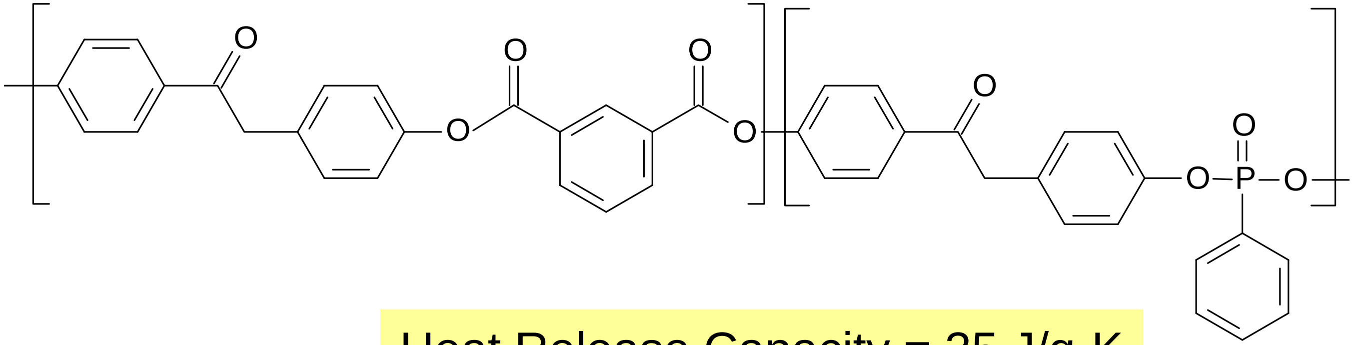
Summary of BHDB-containing polymers with low heat release capacity values



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 %

Molecular weight change at high temperature

Sample preparation
BHDB & BPA polyarylate **(MW: 100K)**
Phosphonate: Arylate (50:50)
Drying: vacuum oven at 120 °C
Heating under air at 150 °C or 180 °C

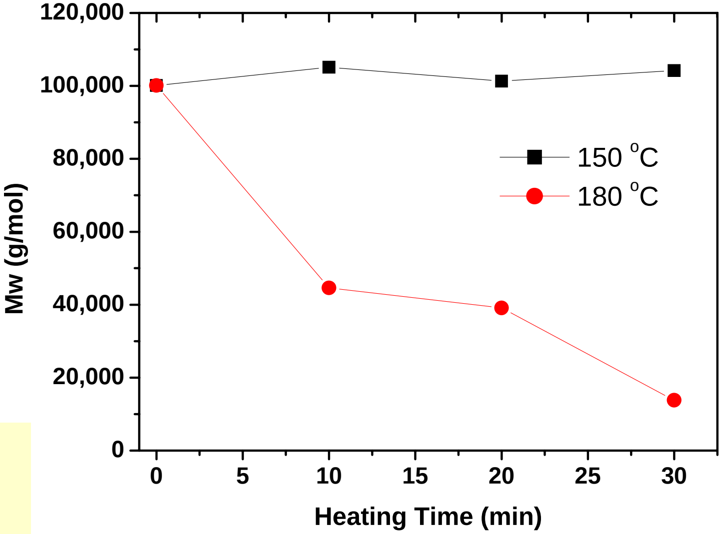
Results
BHDB poly(arylate-co-phosphonate)
show temperature sensitivity (150 vs 180 °C)

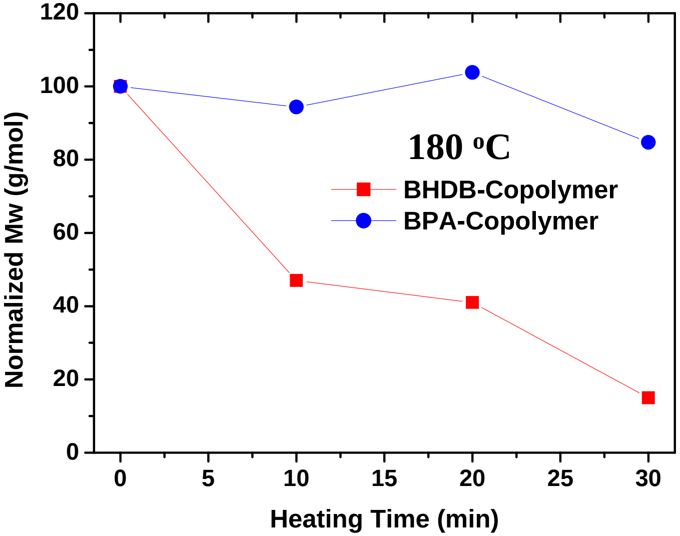
BPA polyarylates are stable at high temperature (180 °C)

BPA poly(phosphonate-co-arylate) (T_g: 137 °C)

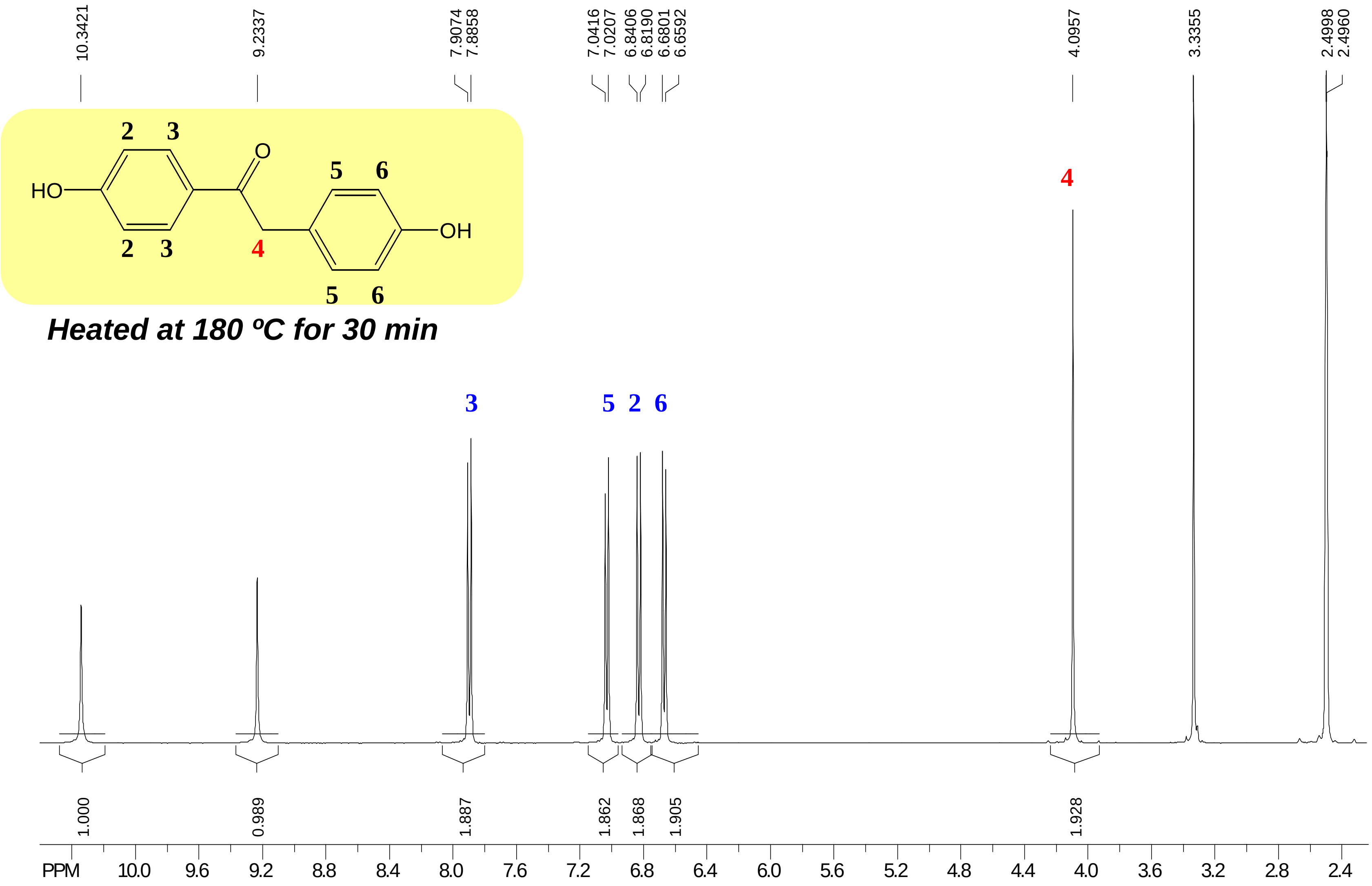
BHDB poly(phosphonate-co-arylate) (T_g: 130 °C)

BHDB poly(phosphonate-co-arylate)



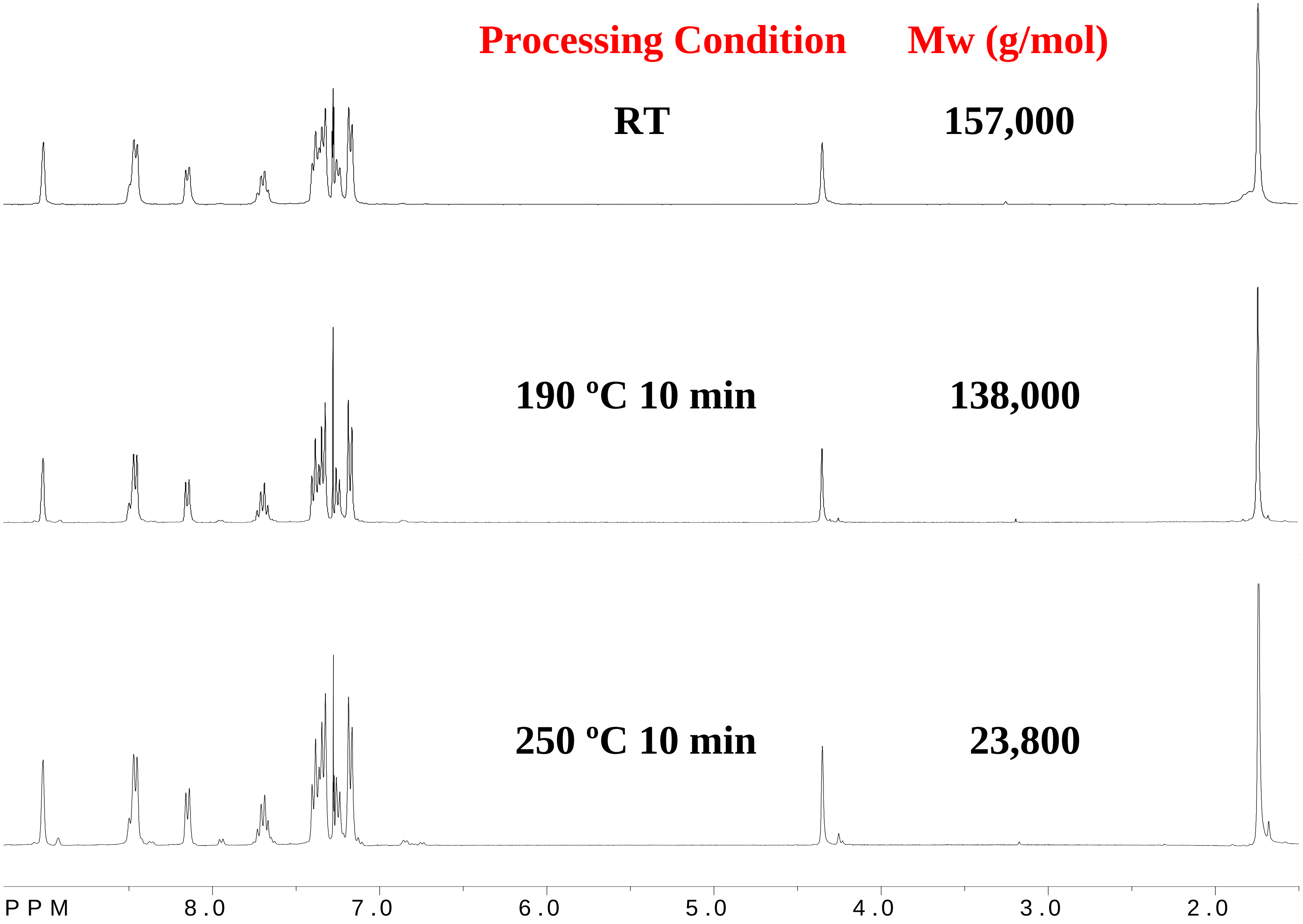


^{1}H-NMR Spectrum of BHDB



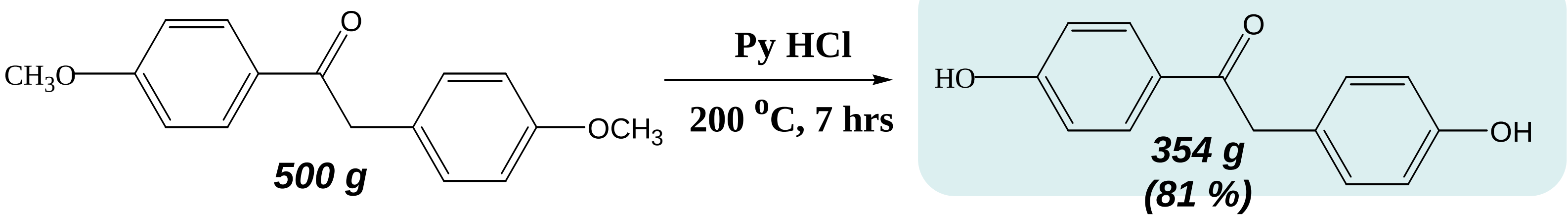
Heated at 180 ºC for 30 min

BHDB-co-BPA (45:56) Polyarylates



Processing Condition	Mw (g/mol)
RT	157,000
190 ºC 10 min	138,000
250 ºC 10 min	23,800

High molecular weight BHDB polyarylates prepared by solution polymerization

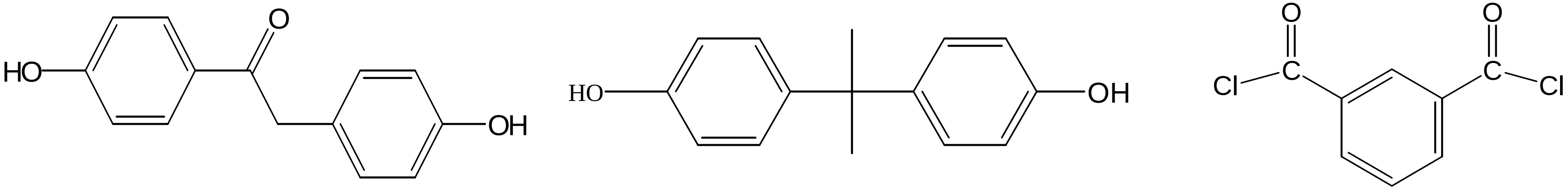


500 g

Py HCl

200 ^{o}C, 7 hrs

354 g (81 %)



Interfacial Polymerization BzPh$_3$PCl

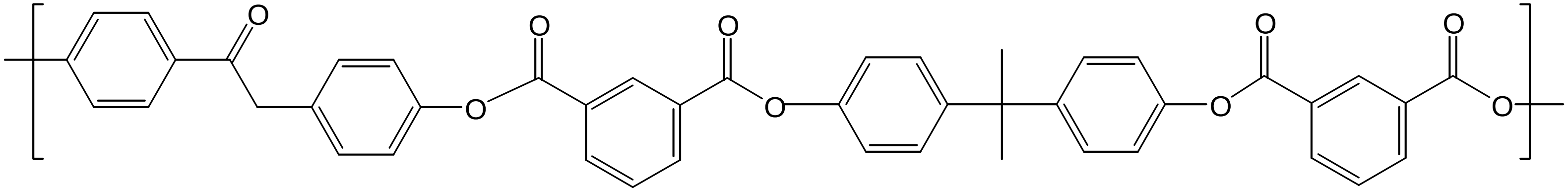
Mw: 3K ~ 20 K KOH, DCM

DMAP (Cat.)

TEA, DCM

Solution polymerization

Mw: 100K ~ 157K



Synthesis of BHDB-BPA Polyarylates

Monomer	BHDB: BPA (mol %) Feed	BHDB: BPA (mol %) Incorporated[a]	Yield (%)	Solvent (mL) 1g/BHDB/BPA	GPC[b]		
					M_w (g/mol)	M_n (g/mol)	PDI
BPA	0:100	0:100	74	40	168,600	86,400	1.95
BHDB-BPA	20:80	26:74	74	90	103,600	47,000	2.21
BHDB-BPA	40:60	35:65	66	90	108,500	44,800	2.42
BHDB-BPA	50:50	42:58	79	90	139,700	46,100	3.03
BHDB-BPA	60:40	60:40	73	90	102,000	42,500	2.40
BHDB-BPA	70:30	69:31	81	90	99,300	37,200	2.67
BHDB-BPA	80:20	insoluble	68	75	Insoluble		
BHDB-BPA	85:15		72	90			
BHDB-BPA	90:10		51	85			
BHDB	100:0	100:0	68	60			

[a] ^{1}H-NMR [a]$CHCl_3$ [b]GPC (Flow rate: 0.8 mL/min, PS std, 30 ^{o}C)

Thermal Properties: DSC & TGA

Monomer	BHDB: BPA (mol %) Feed	BHDB: BPA (mol %) Incorporated	T_g (°C) 1st Run (DSC)	T_g (°C) 2nd Run (DSC)	5 wt % loss TGA
BPA	0:100	0:100	178	171	457
BHDB-BPA	20:80	26:74	178	179	430
BHDB-BPA	40:60	35:65	171	172	406
BHDB-BPA	50:50	42:58	172	172	408
BHDB-BPA	60:40	60:40	168	168	407
BHDB-BPA	70:30	69:31	166 (240)	159	409
BHDB-BPA	80:20	insoluble	171 (251)	163	402
BHDB-BPA	85:15		166 (278)	164	406
BHDB-BPA	90:10		143 (287)	164	395
BHDB	100:0	100:0	174 (308)	163 (290)	390

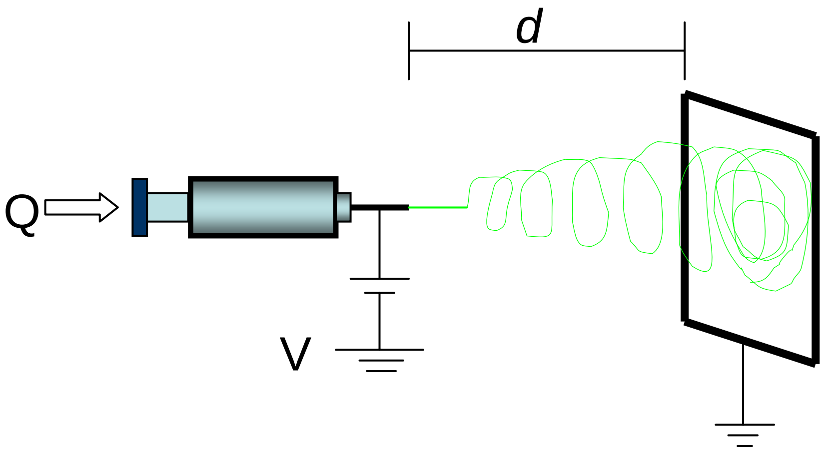
Heating rate of DSC & TGA: 10 °C/min under N_2

HRC and Char Yield

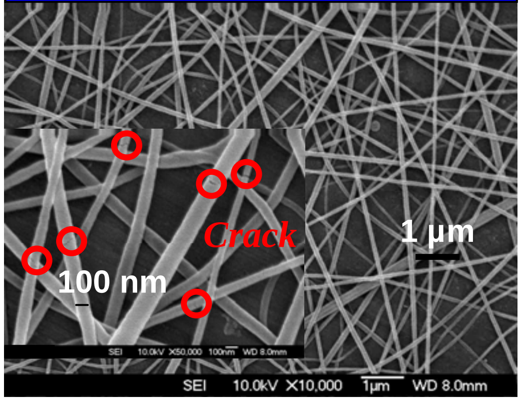
Monomer	BHDB: BPA (mol %) Feed	BHDB: BPA (mol %) Incorporated	HRC (J/g K)	Char yield (%) PCFC	Char yield (%) TGA
BPA	**0:100**	**0:100**	**360 (SD 19.3)**	**28.1 (SD 1.7)**	**29**
BHDB-BPA	**20:80**	**26:74**	**205 (SD 7.9)**	**33.1 (SD 3.1)**	**31.7**
BHDB-BPA	**40:60**	**35:65**	**148 (SD. 1.3)**	**36.1 (SD 1.6)**	**35.9**
BHDB-BPA	**50:50**	**42:58**	**(125 ~ 135)**	**(35 ~ 40)**	**35.6**
BHDB-BPA	**60:40**	**60:40**	**114 (SD 2.1)**	**39.7 (SD 2.9)**	**40.2**
BHDB-BPA	**70:30**	**69:31**	**99 (SD 6.0)**	**37.4 (SD 1.9)**	**40.8**
BHDB-BPA	**80:20**	**insoluble**	**86 (SD 1.8)**	**42.8 (SD 3.2)**	**44.5**
BHDB-BPA	**85:15**		**87 (SD 4.6)**	**42.6 (SD 1.6)**	**44.3**
BHDB-BPA	**90:10**		**84 (SD 2.5)**	**43.1 (SD 1.1)**	**43.3**
BHDB	**100:0**	**100:0**	**73 (SD 2.4)**	**45.3 (SD 2.4)**	**42**

Electrospun Nanofibers with BHDB polymers

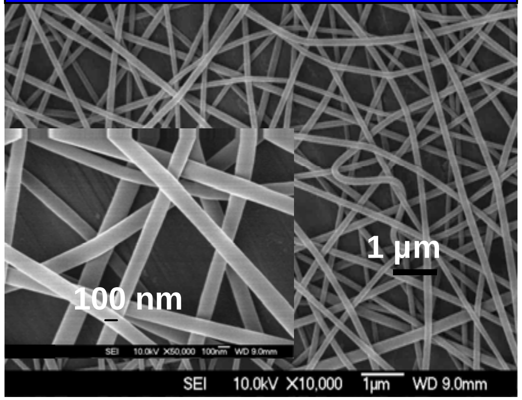
- Polymer : BHDB-polyphosphonate
- Molecular Weight: **44,700** (PDI = 3.28)
- Voltage (**V**) : **10 kV**, Solvent : **DMF**
- Flow Rate (**Q**): **0.06 ~ 0.18 mL/sec.**
- Polymer concentration (**C**): **55 ~ 70 wt %**
- Distance (***d***) between needle and target:**12 cm**



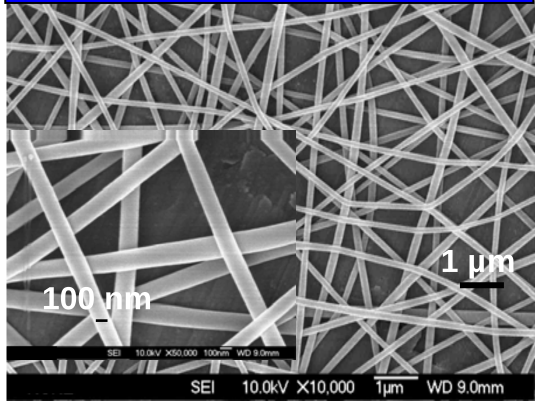
C = 55 wt %, Q = 0.060 mL/s



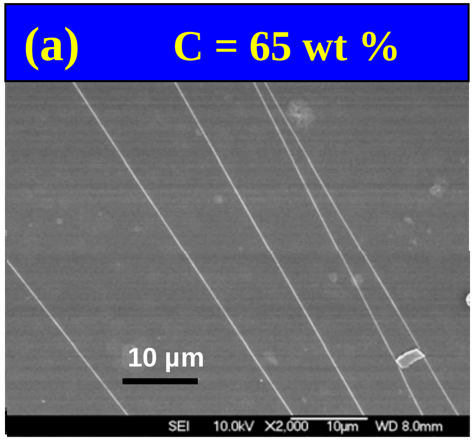
C = 65 wt %, Q = 0.180 mL/s

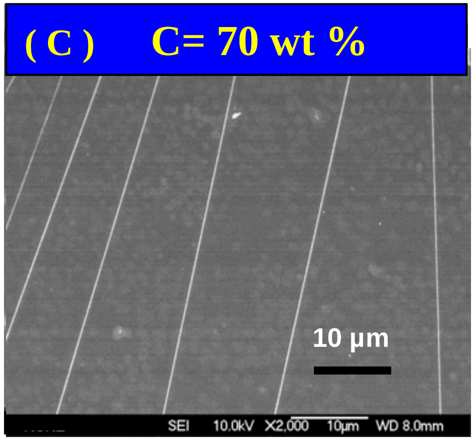


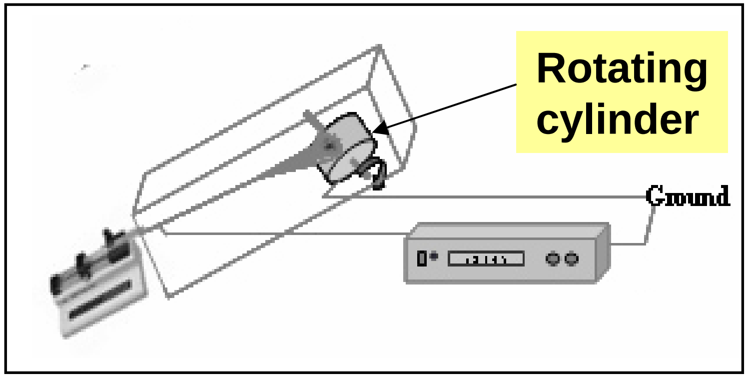
C = 70 wt %, Q = 0.180 mL/s



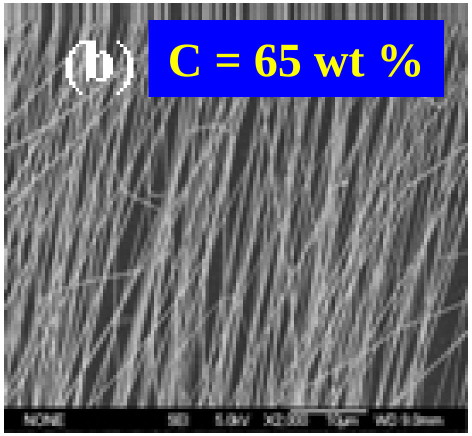
Oriented Electrospun Nanofibers

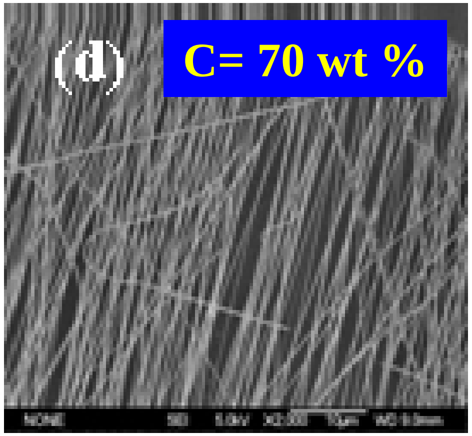






Rotating speed : **9.8 m/sec**





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

Properties of Electrospun Nanofibers

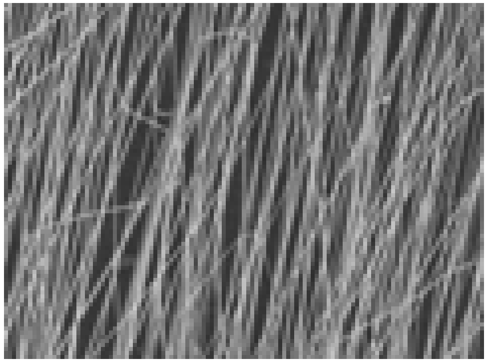
Heat Release Capacity (HRC)

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**

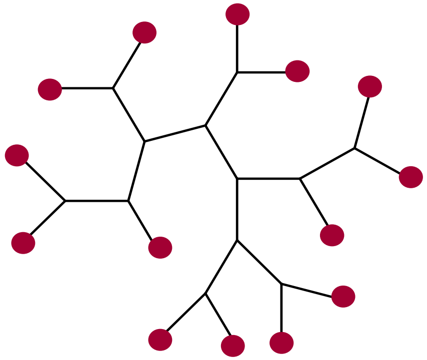
1) **Undrawn fiber (U)**
2) **50 % drawn fiber (D)**

density: 0.77 g/cm^3, diameter: 588 ± 87 nm

Farris and coworkers

Hyperbranched non-flammable additives and coatings

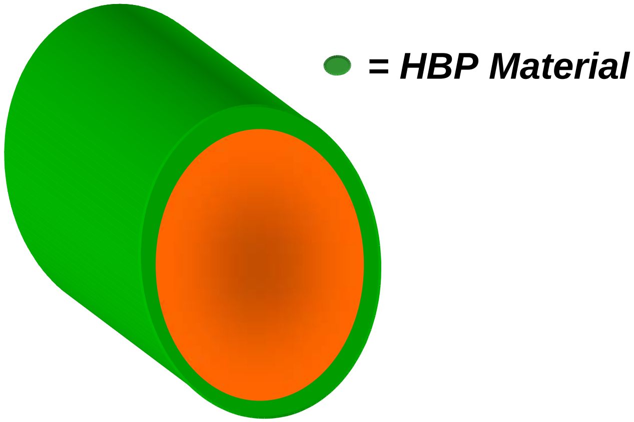
Hyperbranched polymers have been shown to migrate to polymer surfaces during co-extrusion processes



5% HBP

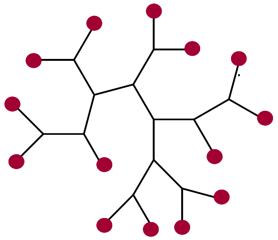
Co-extrusion with polymer of interest (polyethylene, polypropylene, polystyrene, etc…)

→



Fiber cross-section showing HBP coating on polymer surface

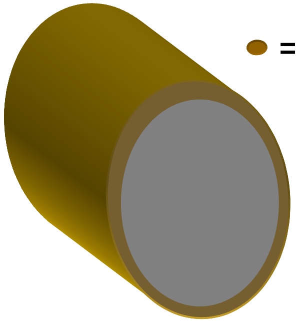
Hyperbranched non-flammable additives and coatings



Hyperbranched Polymer (HBP)

Extrusion

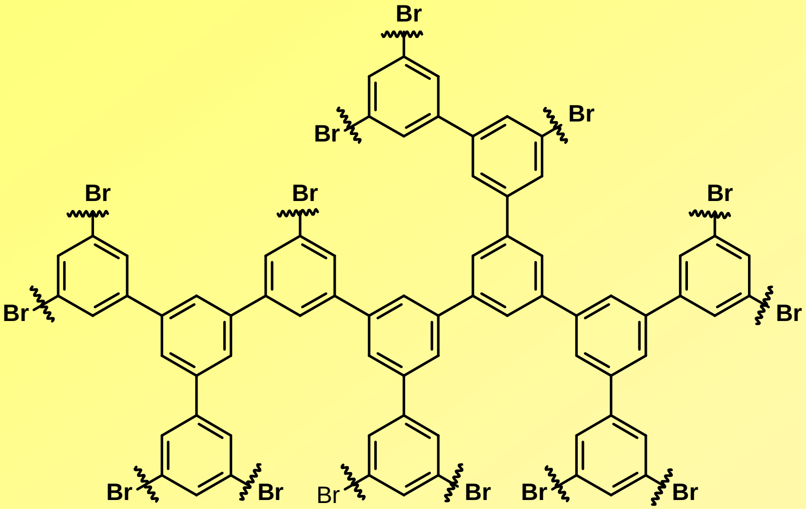
Bulk Polymer



● = HBP Material

Fiber Cross-Section showing
HBP coating on surface

May be used to deliver functionality to surface



Hyperbranched Polyphenylene
(HBPP-Br)

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

Bromide replacement

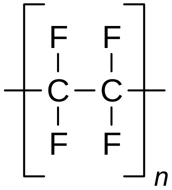
Variety of hyperbranched polyphenylenes (e.g., for low flammability adhesives)

Webster & Kim, J. Am. Chem. Soc. 1990

Inherently Fire-resistant Polymers

- **Replace hydrogen with another atom**
  - *Teflon*
  - *Poly(vinyl chloride)*
- **Increase aromaticity**
- **Add heteroatoms.**
  - *Polyetherimides*

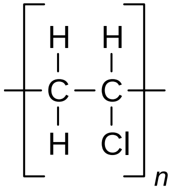
Increase C-H ratio



$$-\!\left[CF_2-CF_2\right]_n\!-$$

Teflon

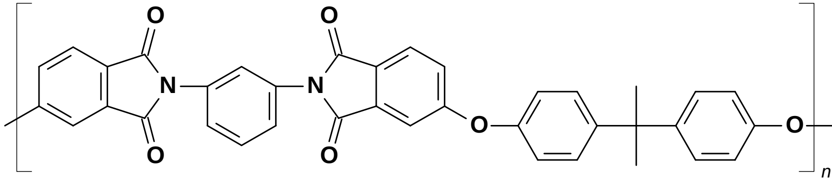
Char Yield = 0 %
HR Cap = 35 J/g·K



$$-\!\left[CH_2-CHCl\right]_n\!-$$

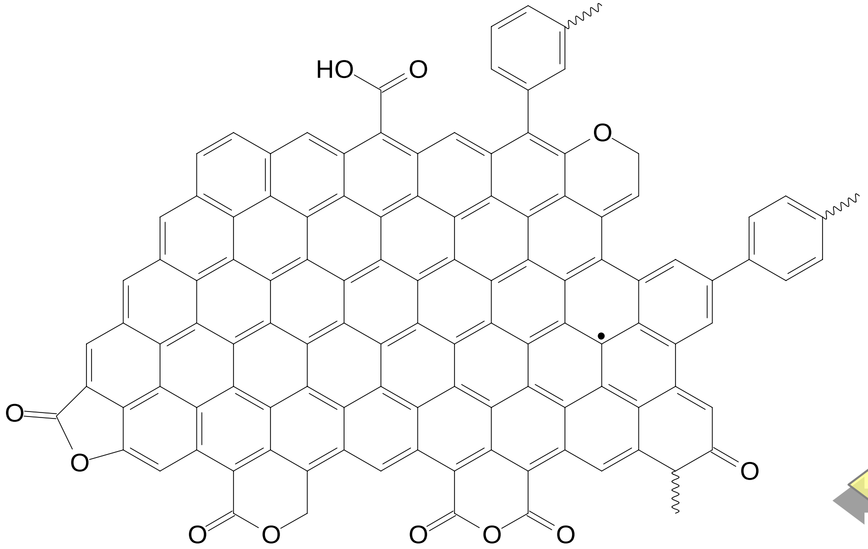
Poly(vinyl chloride)

Char Yield = 15 %
HR Cap = 138 J/g·K



Ultem (polyetherimide)

Char Yield = 49 %
HR Capacity = 121 J/g·K



Char