Advances in Low Flammability Non-halogenated Polymers

The 7th Triennial International Fire and Cabin Safety Research Conference
December 2 – 5, 2013 Philadelphia, PA

Investment in Research to Enhance Safety in a Changing World

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Conte Center for Polymer Research
UMass Amherst

***Funding:* Federal Aviation Administration, BASF, Army, and consortium member companies at UMass Amherst**

Acknowledgements

Emrick research group   UMass Amherst   Summer 2013

Presentation Topics

I. Polymer flammability: a persistent problem with plastics

II. BHDB-polymers
A new molecule for anti-flammable polymers
(and, a potential bisphenol A replacement)

III. Non-flammable adhesive materials:
BEDB, BPT, and more

Materials design criteria:

1. Inherently non-flammable polymers – design polymers to char instead of burn
2. Practical advantage: no flame retardants needed (major cost benefit)

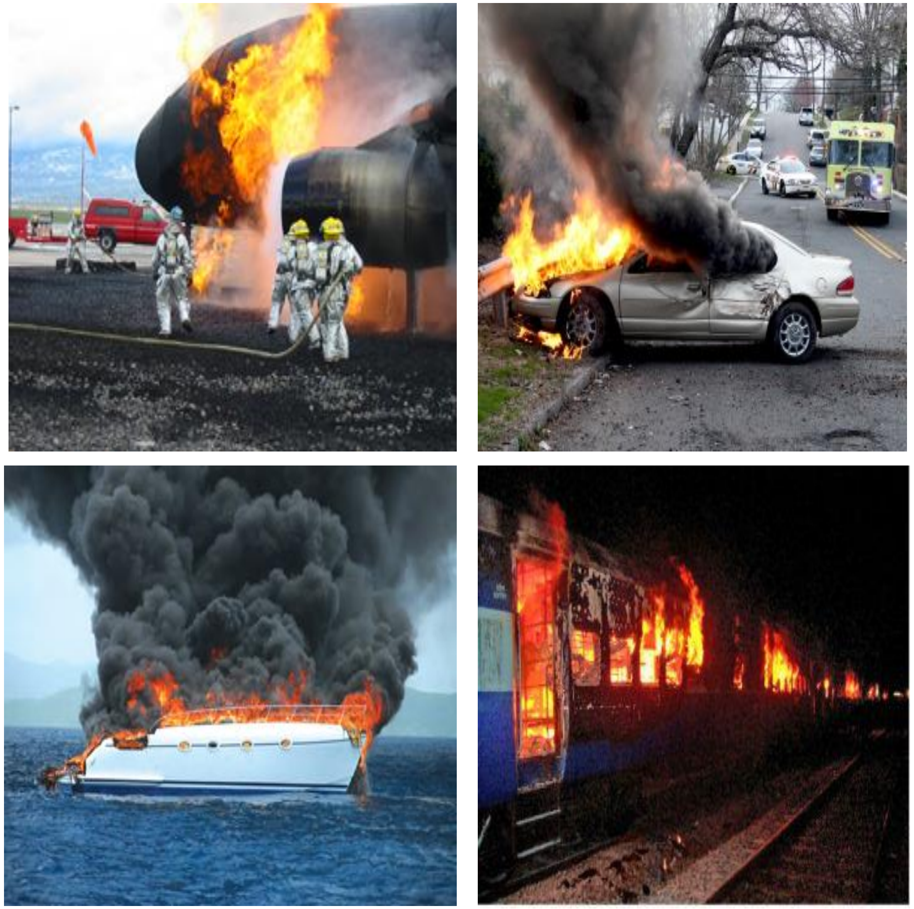
Background: burning plastics and polymer foams

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

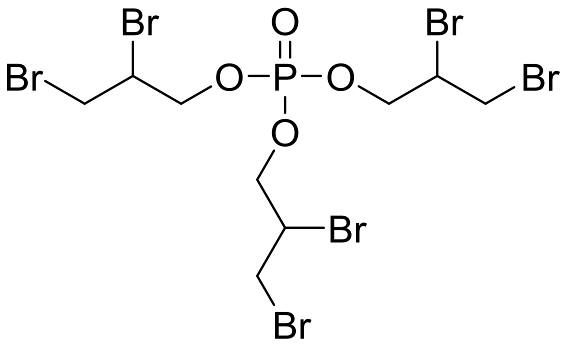
How advanced plastics saved lives on Asiana Flight 214

Plastics Today July 2013

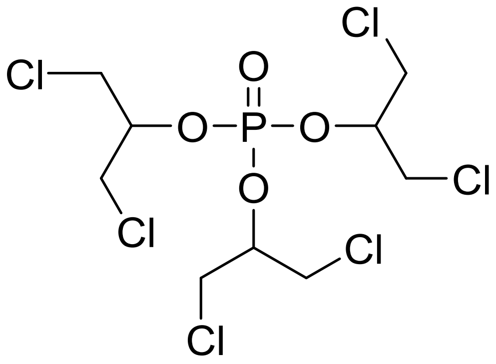
Halogenated flame retardants (HFRs)

HFRs have demonstrated effectiveness for suppressing flammability when used as additives in polymer materials

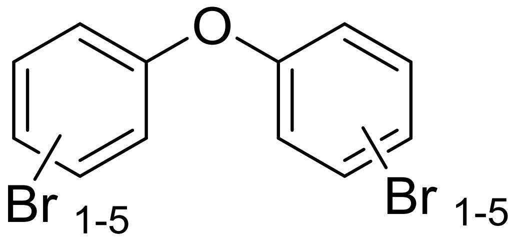
HFRs face legislative scrutiny due to their health and environmental concerns (bioaccumulation and toxicity)



Tris(2,3-dibromopropyl) phosphate



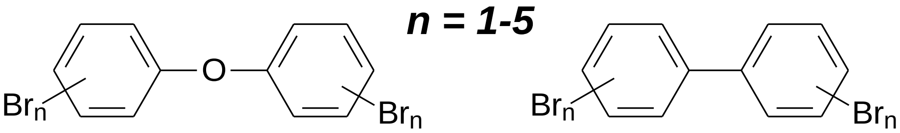
Tris(1,3-dichloro-2-propyl) phosphate

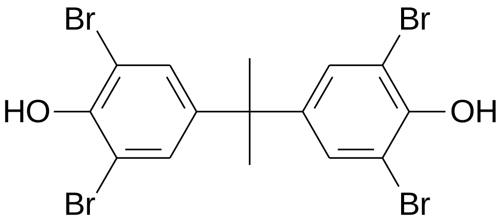


Polybrominated diphenyl ether (PBDEs)

Small molecule flame-retardants

Halogenated aromatics





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

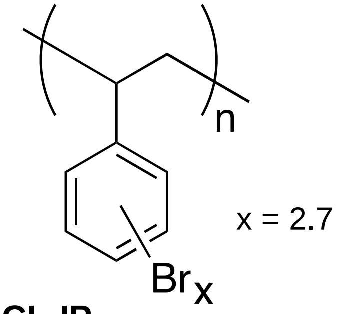
Phosphorus, nitrogen, and silicon-based inorganics

Environmentally-friendly
Used in commodity polymers

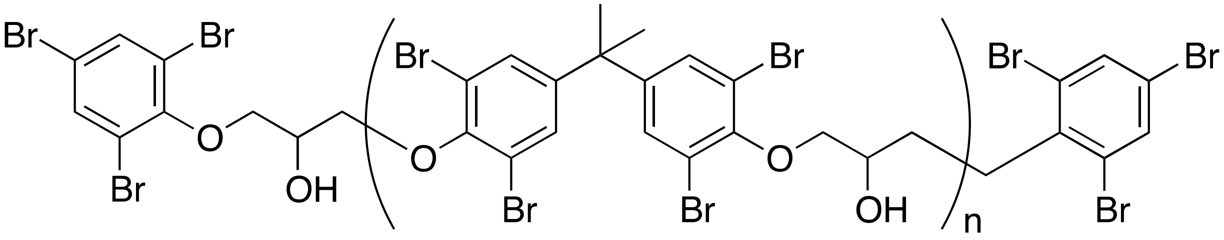
High loading needed for FR activity
Negative impact on mechanical properties of host polymer materials
Limitations in high-temperature applications

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

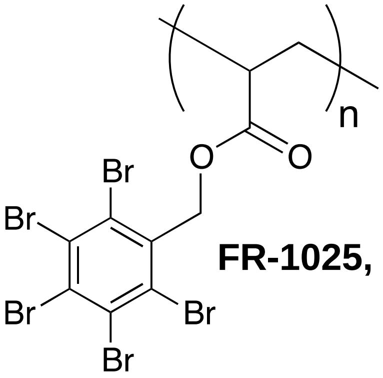
Brominated Flame Retardant Polymers



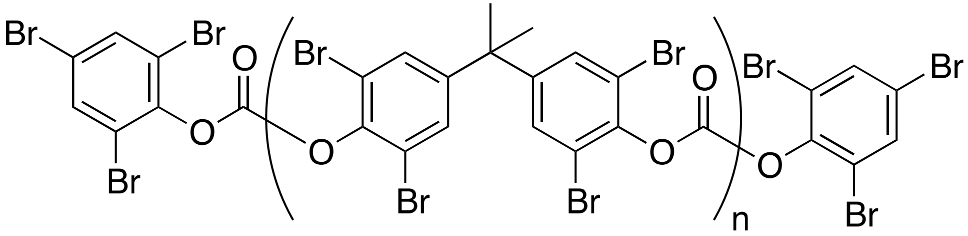
FR-803P, ICL-IP
SAYTEX® HP-310, Albemarle



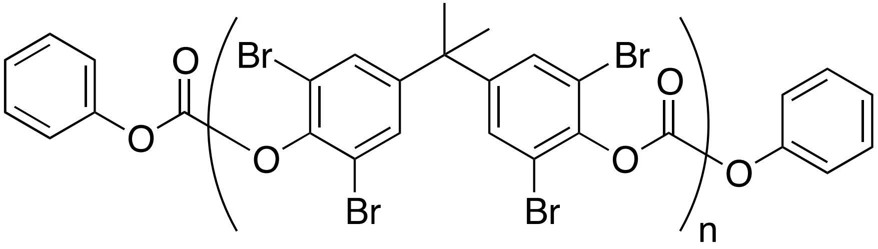
F-3100, F-3014, F-3020, ICL-IP



FR-1025, ICL-IP



BC-58™, Chemtura



BC-52™, Chemtura

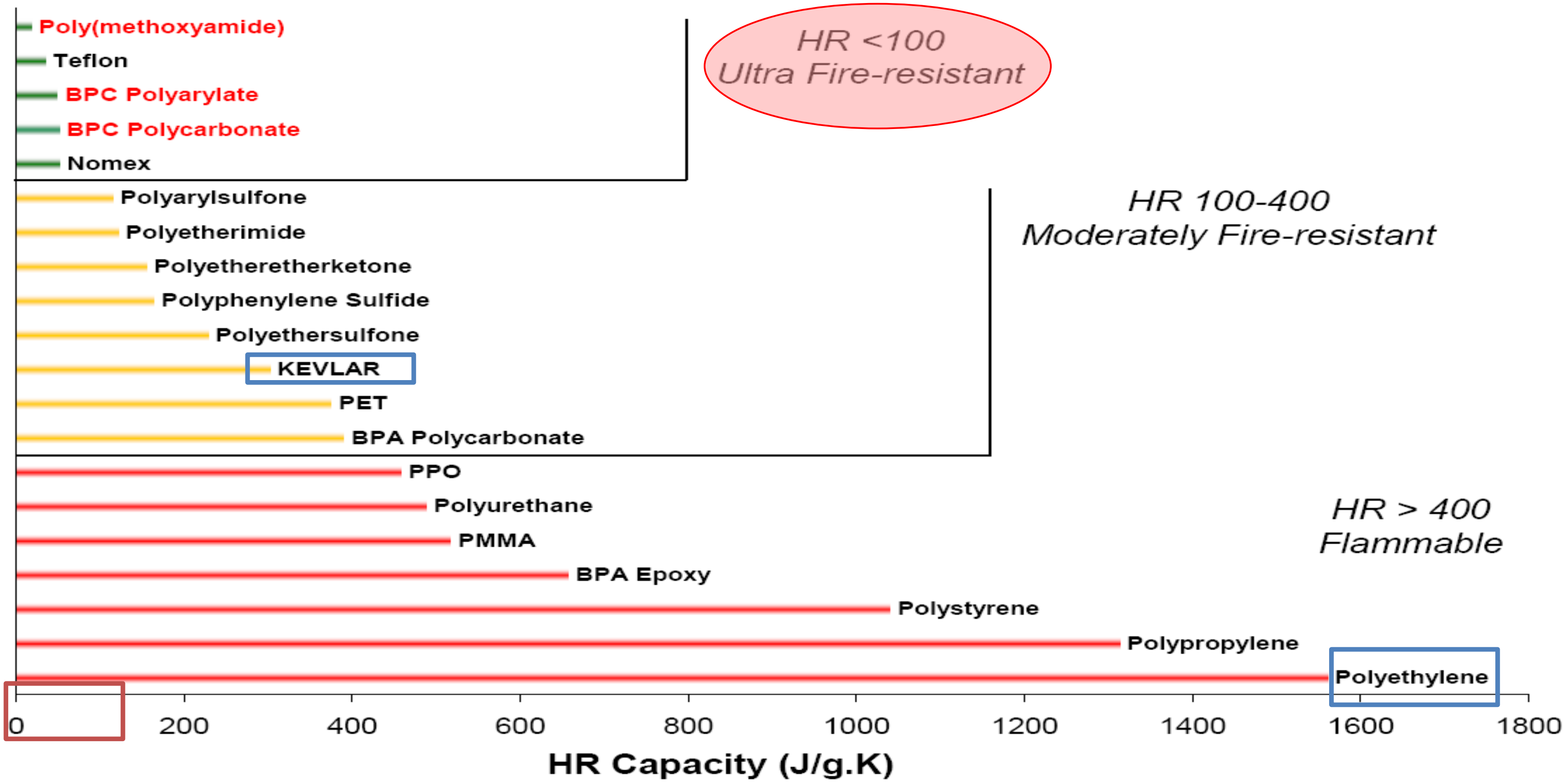
Thermoplastic additives

Thermal stability

Bloom-free

Suitable for extrusion and injection molding

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

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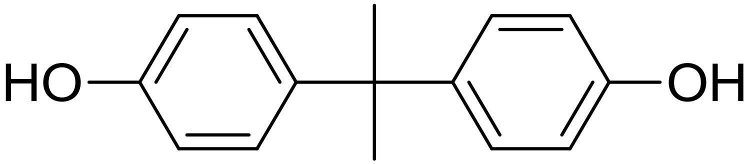
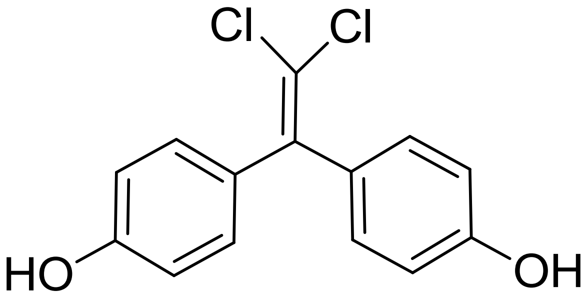
Bisphenolic monomers

Well-known structures:

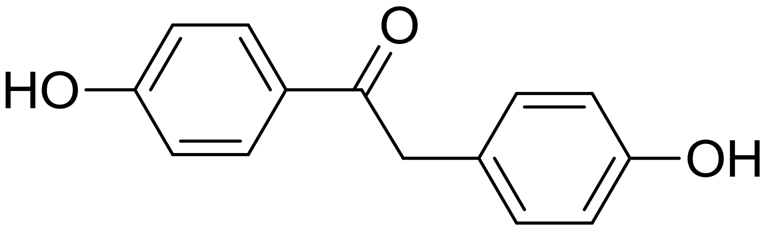


Bis-phenol A (BPA)

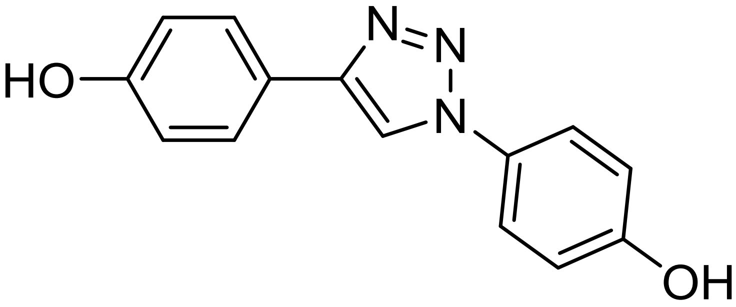


Bis-phenol C (BPC)

New molecules:

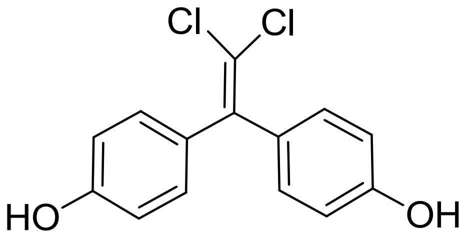


Bis-hydroxydeoxybenzoin (BHDB)

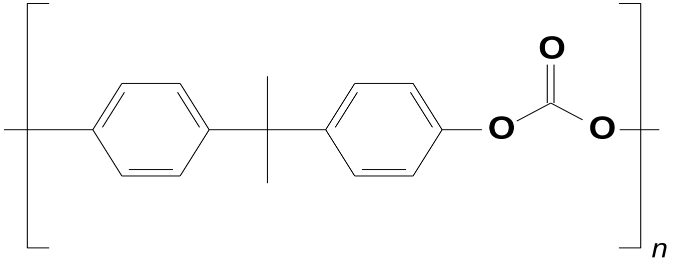


Bis-phenol triazole (BPT)

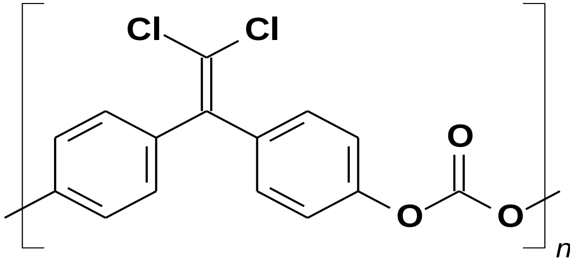
BPA vs. BPC



Bisphenol C



BPA Polycarbonate (Lexan)

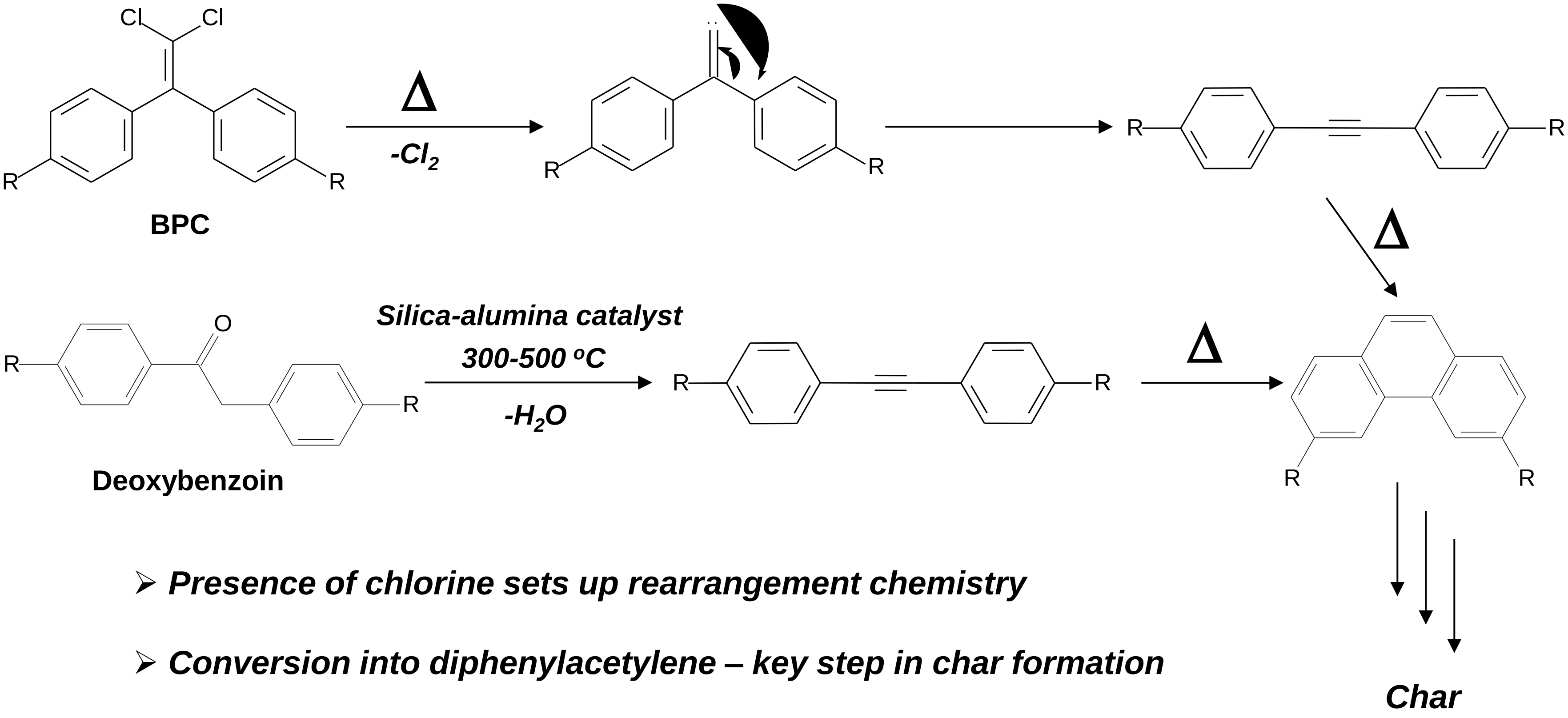


BPC Polycarbonate

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**

J. Polym. Sci. Part A: Polym. Chem. Ed. **1980**, *18*, 579; *J. Appl. Polym. Sci.* **2003**, *87*, 548

BPC and BHDB: common pathways towards char formation?

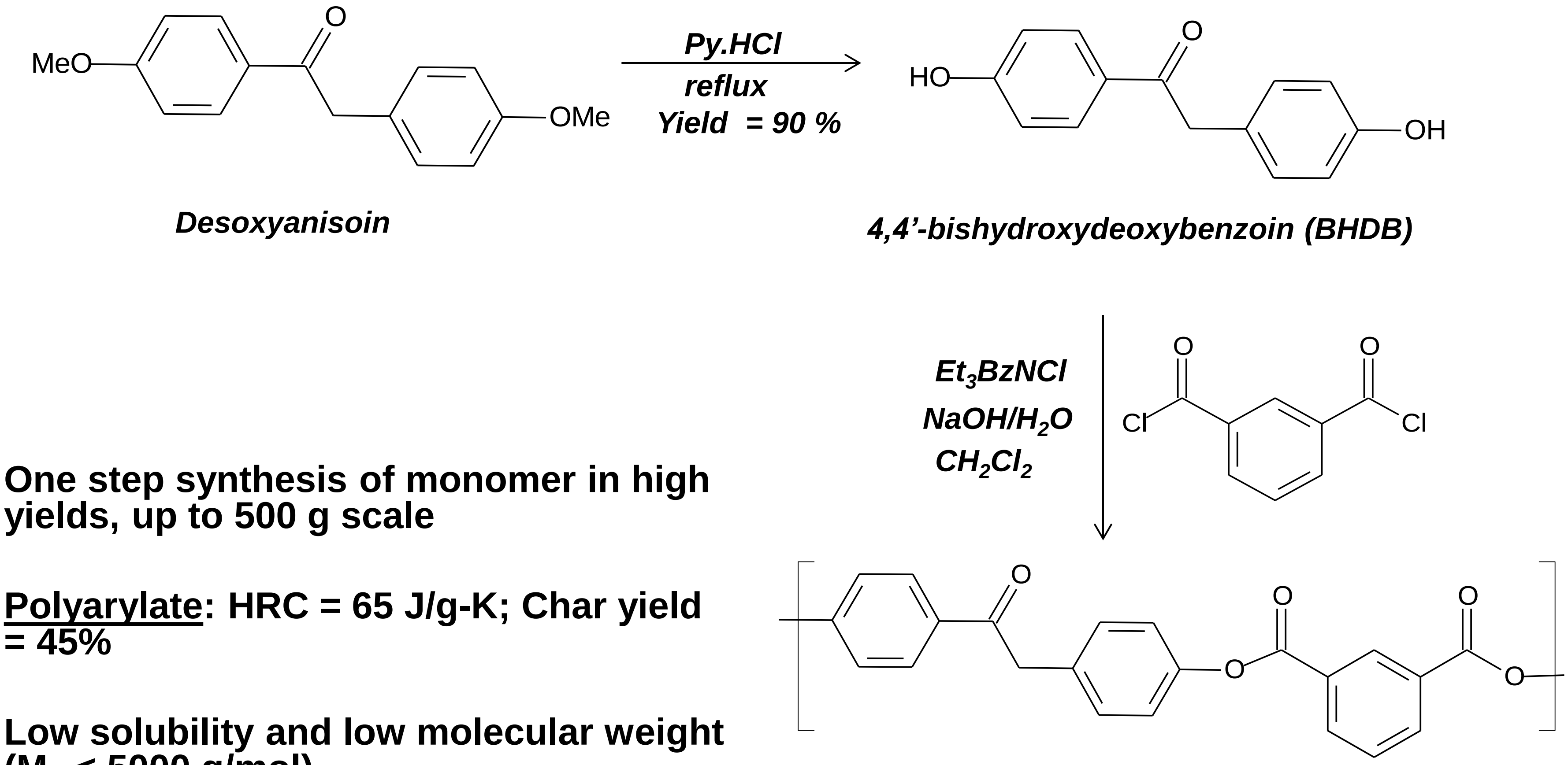


- ➢ ***Presence of chlorine sets up rearrangement chemistry***
- ➢ ***Conversion into diphenylacetylene – key step in char formation***
- ➢ ***Deoxybenzoin conversion to diphenylacetylene at high temperatures***

No prior reports of polymerization chemistry using BHDB

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

BHDB preparation from desoxyanisoin, and integration into polyarylates



Desoxyanisoin

4,4'-bishydroxydeoxybenzoin (BHDB)

BHDB-Polyarylate

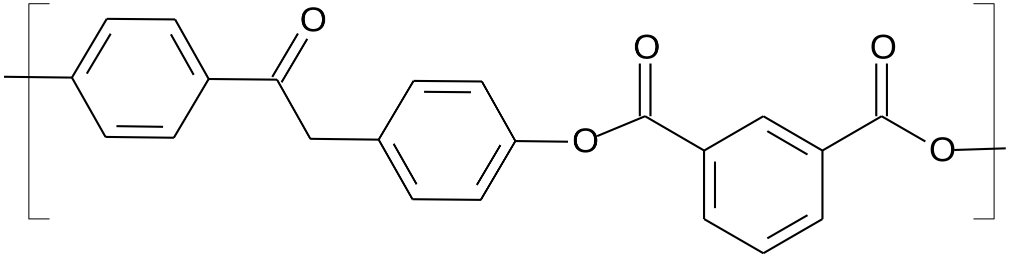
- **One step synthesis of monomer in high yields, up to 500 g scale**
- **Polyarylate: HRC = 65 J/g-K; Char yield = 45%**
- **Low solubility and low molecular weight (M_w < 5000 g/mol)**

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

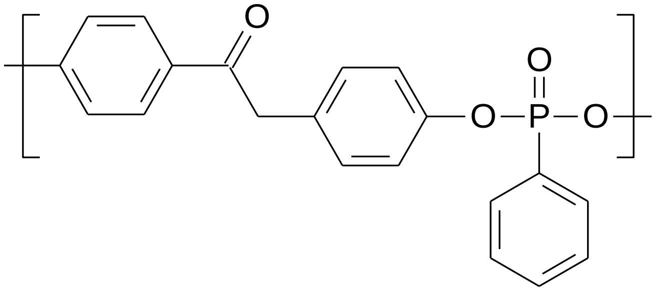
BHDB polymers:
halogen free, ultra-low heat release, high char yield

Synthesized structures: polyesters, polyphosphonates, polyurethanes, polycarbonates, epoxy polymers, cyanate esters,….

Heat release capacity = 65 J/g-K
Char yield = 45 %



Heat release capacity = 80 J/g-K
Char yield = 52 %



UL-94 results
- Predominant charring
- No flame spread
- No dripping
- V-0 and 5VA ratings

(from microcalorimetry data analysis, sample had a 96% probability of achieving V-0)

Macromolecules 2006, 39, 3553; Macromolecules 2006, 39, 5974; J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 4573; Polym. Degrad. Stab. 2008; Polymer 2009; Journal of Materials Chemistry 2010; Angewandte Chemie 2011; Green Chemistry 2013

4 awarded patents (2008-2013)

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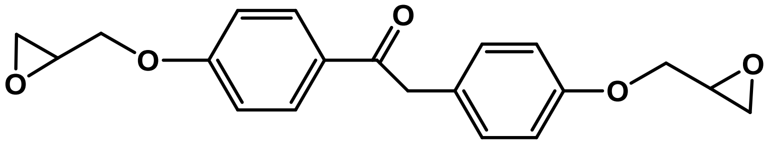
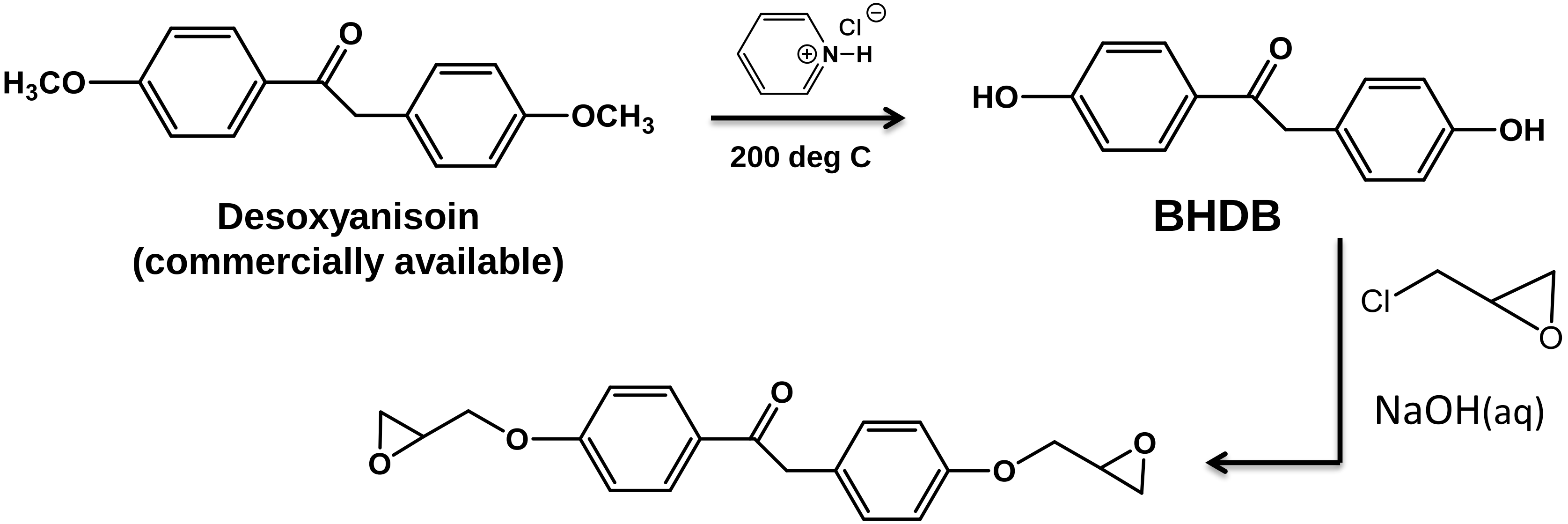
Deoxybenzoin-based epoxy resins



Bis-epoxydeoxybenzoin (BEDB), or
Deoxybenzoin diglycidyl ether (DB-DGE)



Desoxyanisoin
(commercially available)

BHDB

BEDB

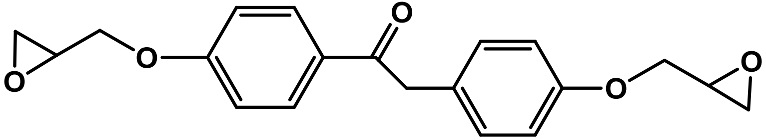
BEDB: Easily prepared at 100 gram scale
Would be trivial to scale to kilogram levels

Polymer 2009 p767

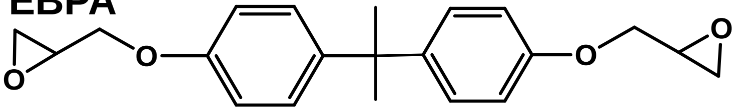
Cured BEDB resins: thermal and mechanical properties

Epoxies

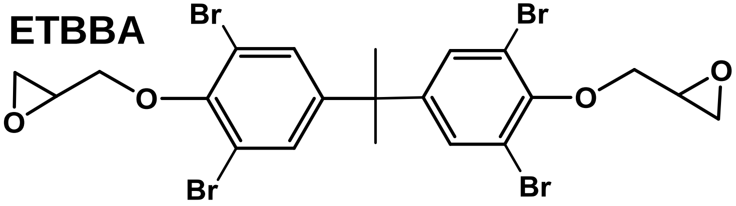
BEDB



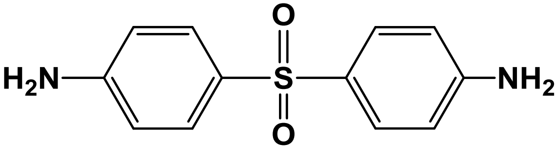
EBPA



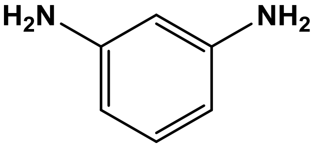
ETBBA



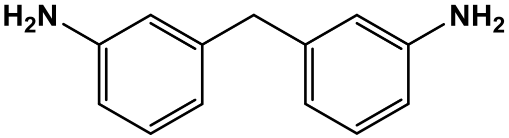
Amines (25 examples)



DDS



PDA



DDM

Curing conditions:
Mix epoxies with amines at 60-130 C

Cure in DSC instrument, then measure Tg

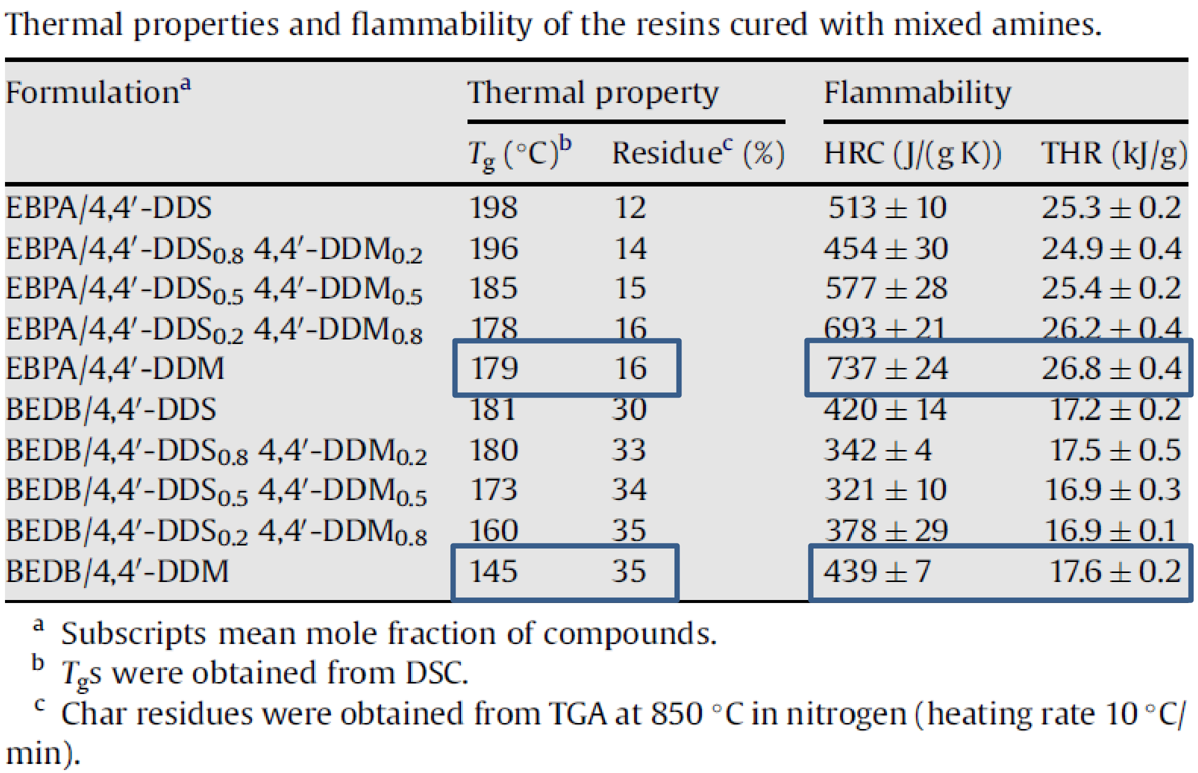
DDM example: Tg and decomposition

BEDB-DDM Tg: 145 C; dec: 354 C
EBPA-DDM Tg: 179 C; dec: 372 C
ETBBA-DDM Tg: 192 C; dec: 274 C

- BEDB gives lower Tg epoxy resins
- Decomposition not complicated by liberation of HBr, and effect on carbon monoxide, as for brominated epoxy resins

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.

BPA

BEDB

Formulation[a]	Thermal property		Flammability	
	T_g (°C)[b]	Residue[c] (%)	HRC (J/(g K))	THR (kJ/g)
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
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 / heating rate

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

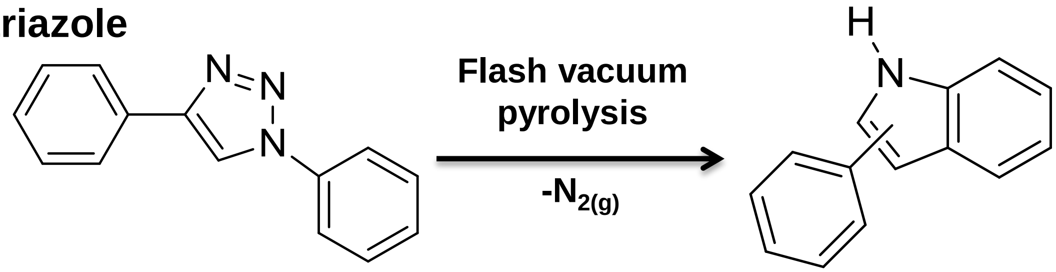
ASTM D 1002 protocol EBPA/DDS: 11.0 MPa; EBPA/DDM: 9.2 MPa

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

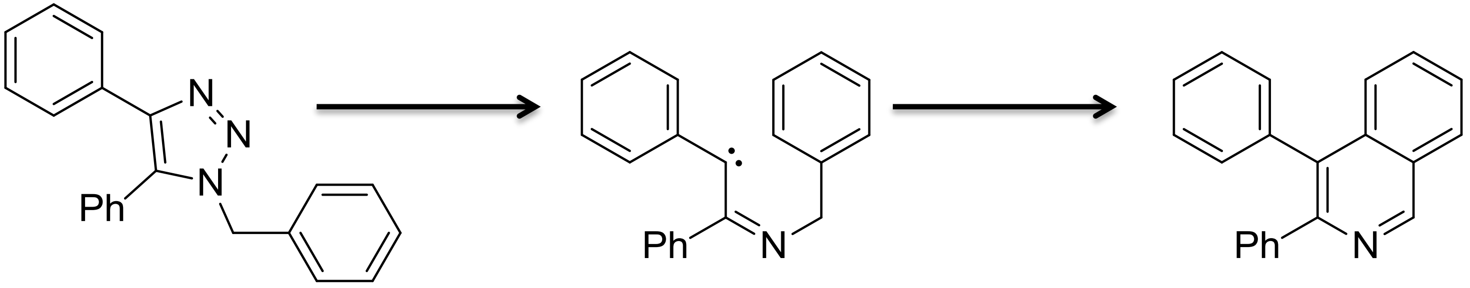
Aromatic triazoles: thermal decomposition mechanisms

Gilchrist *et. al. J. Chem. Soc. Perkin Trans. 1, 1975, pp 1-8*

Diphenyl-1,2,3-triazole



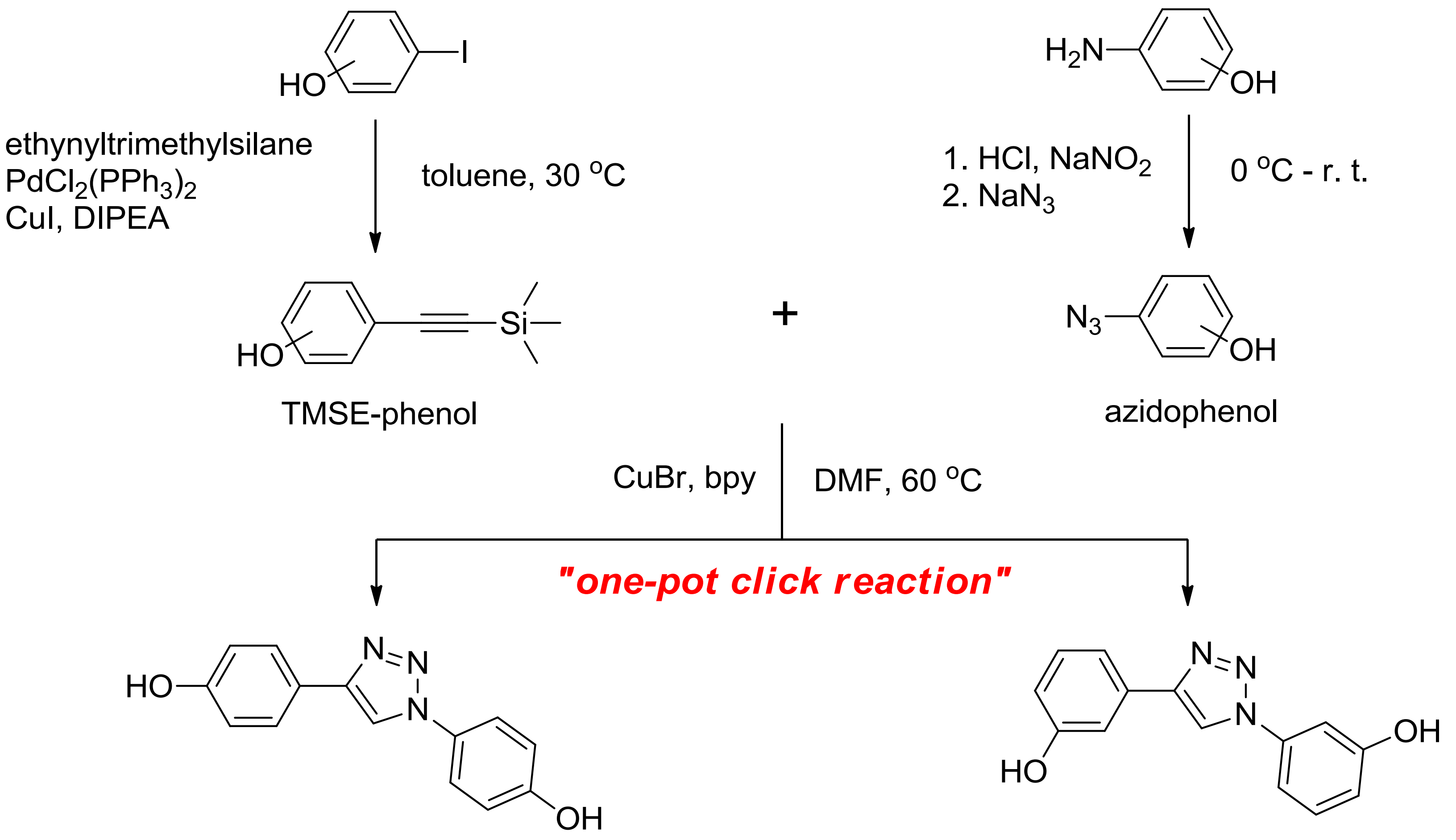
Benzyl benzotriazoles



Isoquinoline product

Objective:
Synthesize BPT-containing monomers and test their polymerization chemistry and thermal properties

BPT-monomer syntheses



ethynyltrimethylsilane
$PdCl_2(PPh_3)_2$
CuI, DIPEA

toluene, 30 °C

1. HCl, $NaNO_2$
2. NaN_3

0 °C - r. t.

TMSE-phenol

azidophenol

CuBr, bpy

DMF, 60 °C

"one-pot click reaction"

1,4-bis(4-hydroxyphenyl)-1,2,3-triazole
(**4-BPT**, 60% yield)

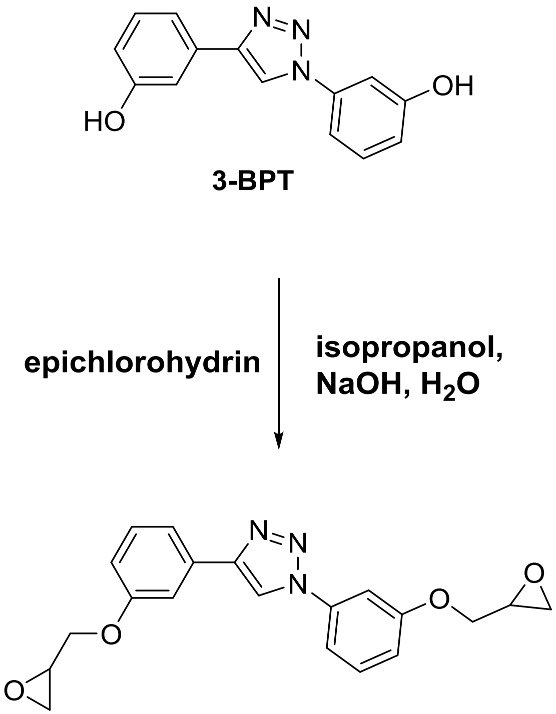
1,4-bis(3-hydroxyphenyl)-1,2,3-triazole
(**3-BPT**, 70% yield)

Monomers recrystallized from acetic acid/water
Melting points: 275 C (4-BPT); 205 C (3-BPT)

No prior reports of polymerization chemistry using BPTs

BPT epoxy resins

Synthesis of BPT diglycidyl ethers

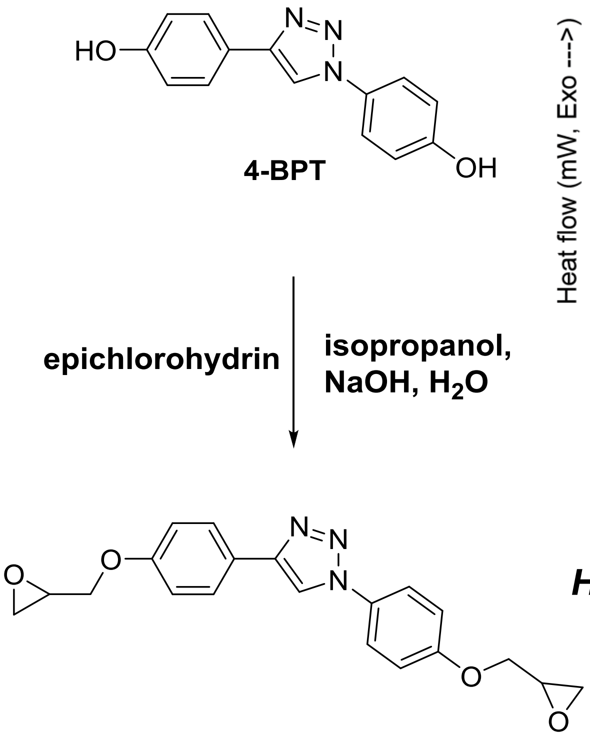


3-BPT

epichlorohydrin

isopropanol, NaOH, H_2O

diglycidyl ether of 3-BPT
(**3-DGE-BPT**, 82% yield)



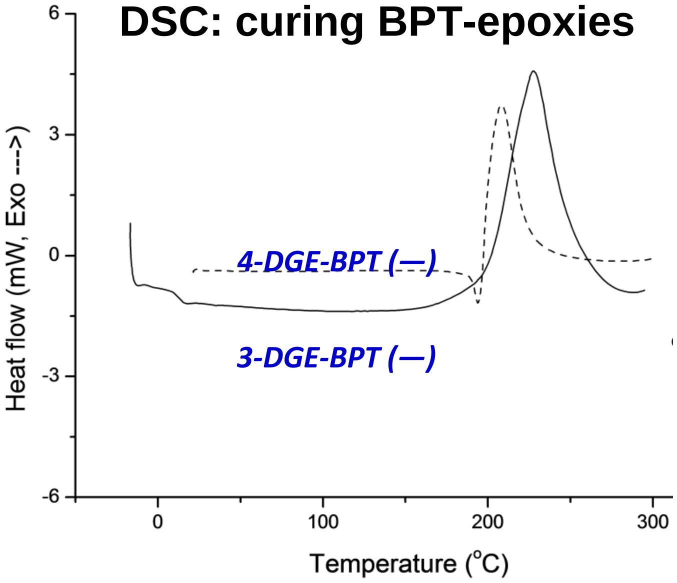
4-BPT

epichlorohydrin

isopropanol, NaOH, H_2O

diglycidyl ether of 4-BPT
(**4-DGE-BPT**, 62% yield)

DSC: curing BPT-epoxies

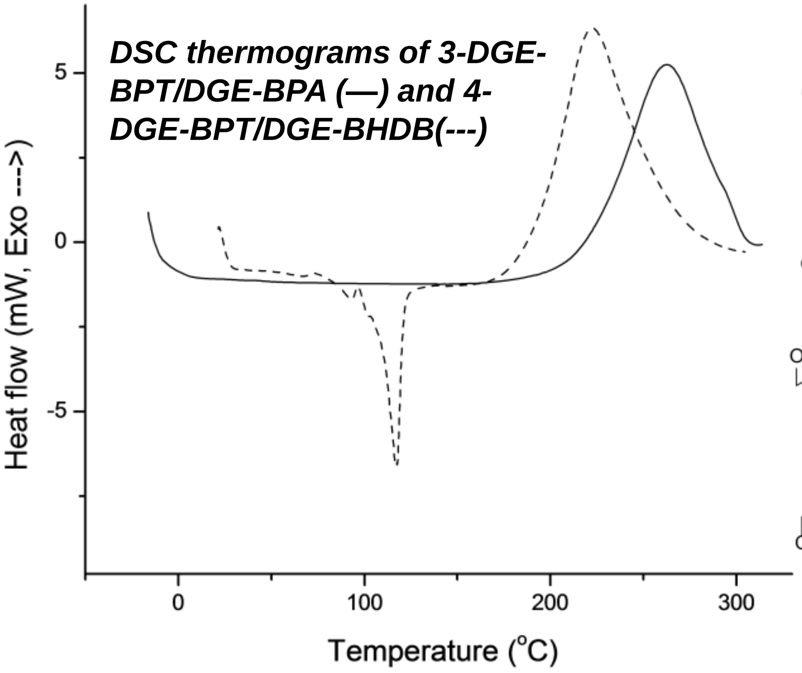


High resolution mass spectroscopy
EI mode:
$[M\text{-}N_2]^+$ 337.13 m/z observed

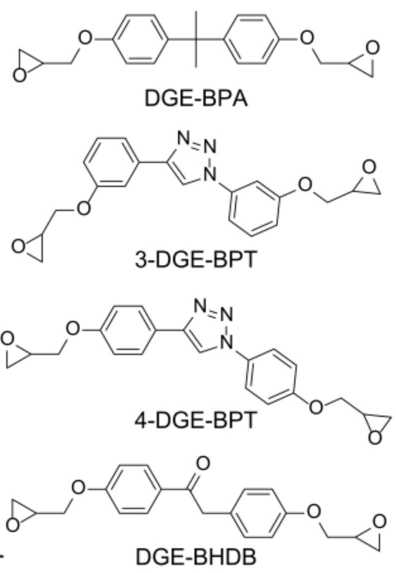
FAB mode
3-DGE-BPT $[M+H]^+$: 366.1462 m/z
4-DGE-BPT $[M+H]^+$: 366.1426 m/z observed
(calculated : 366.1454 m/z)

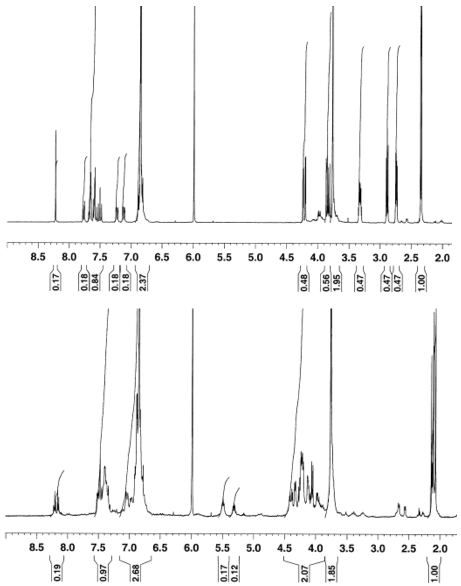
Macromolecules 2011

BPT epoxy resins are self-curing

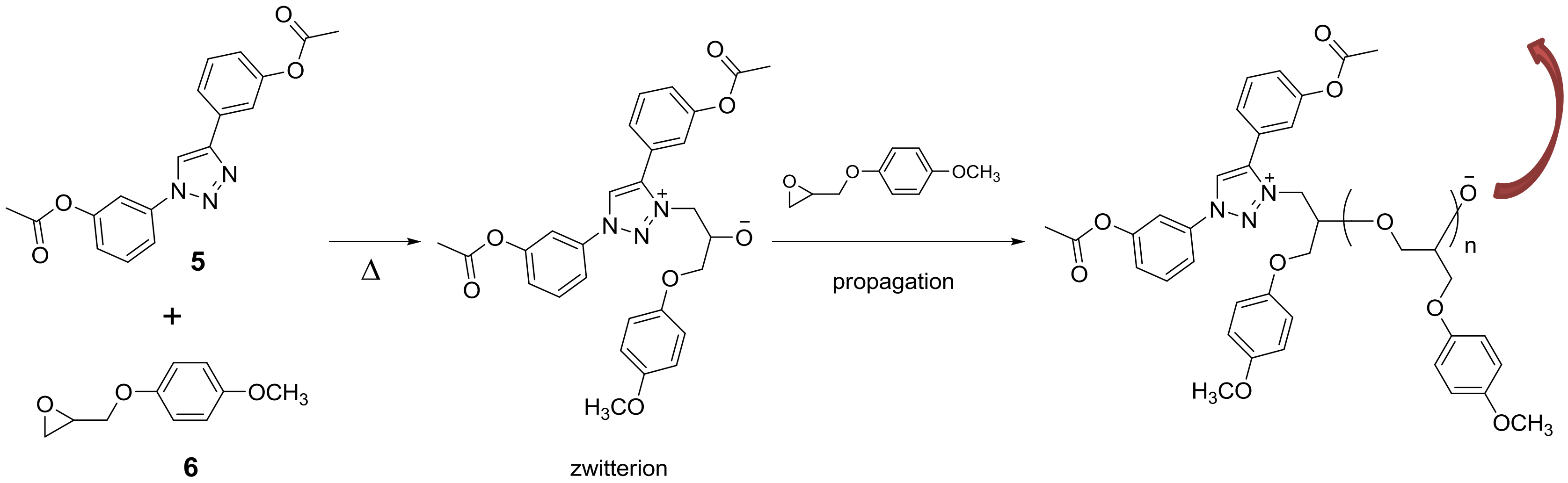


DSC thermograms of 3-DGE-BPT/DGE-BPA (—) and 4-DGE-BPT/DGE-BHDB(---)





^{1}H-NMR spectra of the mixtures
(top: before reaction; bottom: after reaction)



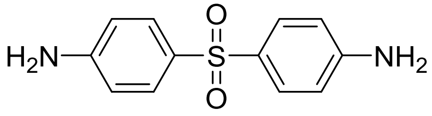
BPT epoxy resins

Heat release and char properties of cured resins

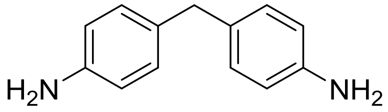
Entry	composition (w/w)	HRC (J/(g K))	THR (kJ/g)	char (%)
1	DGE-BPA/DDS [a]	513 ± 10	25.3 ± 0.2	12
2	DGE-BPA/3-DGE-BPT (1/1)	408 ± 10	16.9 ± 0.2	26
3	DGE-BHDB/DDS [a]	420 ±14	17.2 ± 0.2	30
4	DGE-BHDB/DDM [a]	439 ± 7	17.6 ± 0.2	35
5	DGE-BHDB/4-DGE-BPT (4/1)	265 ± 5	16.6 ± 0.4	35
6	DGE-BHDB/3-DGE-BPT (1/1)	222 ± 5	12.5 ± 0.2	43
7	3-DGE-BPT (self-cured)	200 ± 7	10.9 ± 0.3	45

[a] Equivalent amount of aromatic diamine was used.

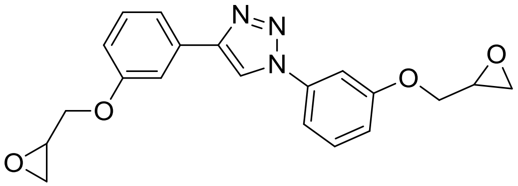
DDS

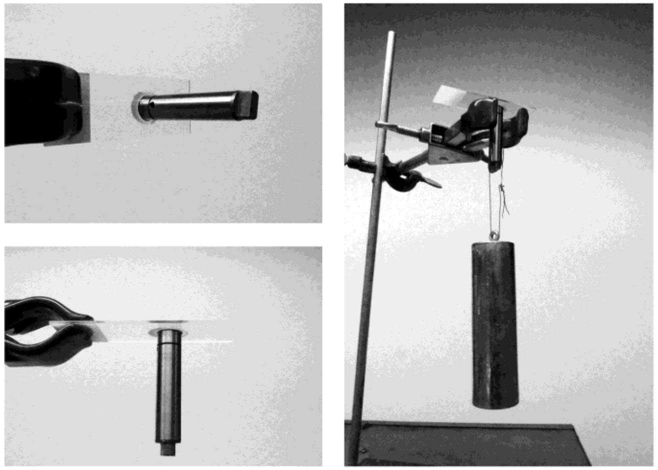


DDM



Adhesion demonstration using 3-DGE-BPT resin (a) before loading additional weight and (b) after loading 700 g weight)





a) b)

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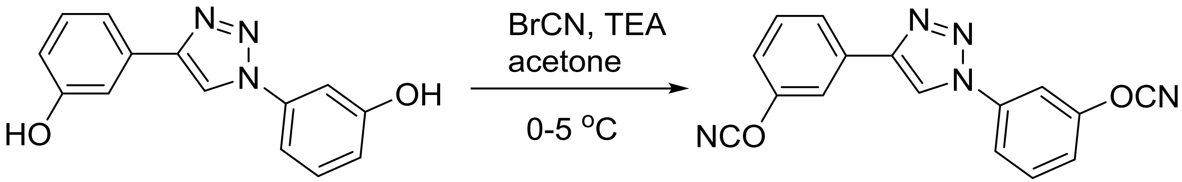
BPT cyanate ester

Synthesis



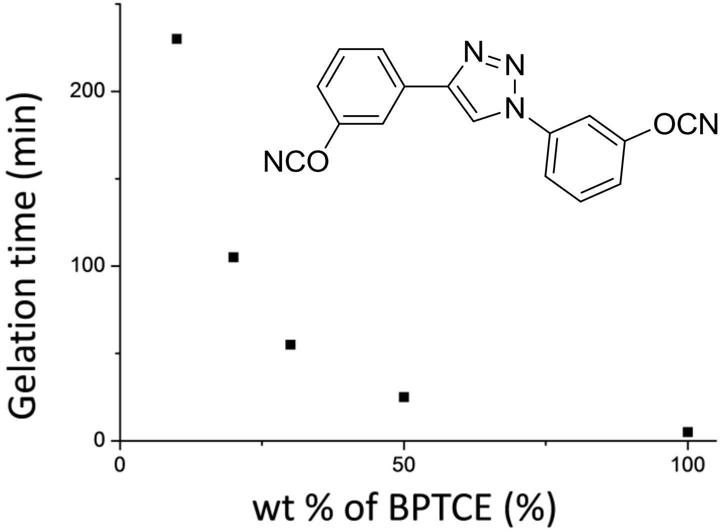
3-BPT

dicyanate ester of 3-BPT
(3-BPTCE, 90% yield)

High resolution mass spectroscopy
FAB mode 3-BPTCE $[M+H]^+$: 304.0822 m/z (cald: 304.0834 m/z)
EI mode $[M-N_2]^+$: 275.1 m/z
Melting point: 155-160 °C

Curing by cyclization to triazines

Gelation times were measured by using a magnetic stir bar (1 cm) in a 100 mg of sample at 170 °C, noting the time required for a mixture stirring initially at 200 rpm to stop completely



(in blends with BPA-CE)

composition (w/w)	*Gel. time (min)*
BPACE	*a*
BPACE/BPTCE (9/1)	*230*
BPACE/BPTCE (8/2)	*105*
BPACE/BPTCE (7/3)	*55*
BPACE/BPTCE (5/5)	*25*
BPTCE	*5*

[a] **BPACE did not show evidence of curing over 360 min.**

BPT cyanate ester

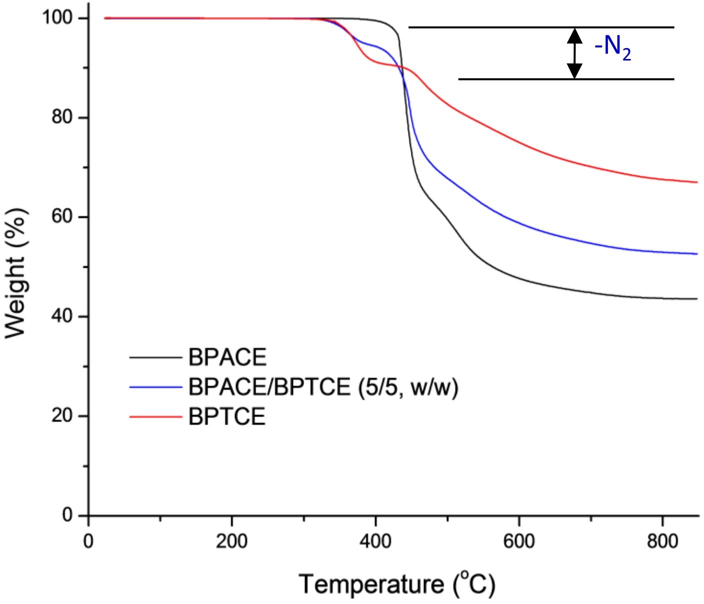
Heat release and char properties of the BPT/BPA cyanate ester blends

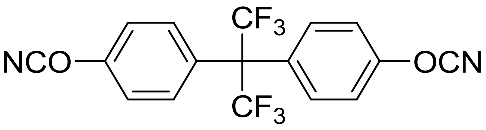
Sample preparation

1. **homogeneous mixture (BPACE/BPTCE = 9/1, 2/8, 3/7, and 5/5, w/w) at 170 °C**
2. **curing at 170 °C for 4 h, and 4 h at 240 °C**
3. **post-curing at 280 °C for 1 h**

composition (w/w)	HRC (J/(g K))	THR (kJ/g)	char (%)
BPACE	**332 ± 10**	**14.5 ± 0.2**	**44**
BPACE/BPTCE (9/1)	**285 ± 14**	**13.4 ± 0.3**	**44**
BPACE/BPTCE (8/2)	**280 ± 15**	**12.5 ± 0.2**	**46**
BPACE/BPTCE (7/3)	**261 ± 12**	**11.2 ± 0.4**	**48**
BPACE/BPTCE (5/5)	**200 ± 15**	**9.2 ± 0.2**	**53**
BPTCE	**10 ± 2**	**2.0 ± 0.2**	**67**

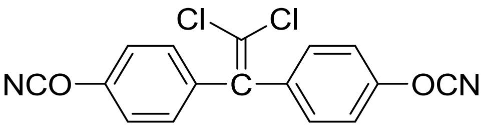
TGA thermograms of cured blends





HRC : 62 J/(g K)
THR : 4.6 kJ/g
Char : 43%

hexafluorobisphenol A CE



HRC : 24 J/(g K)
THR : 4.2 kJ/g
Char : 53%

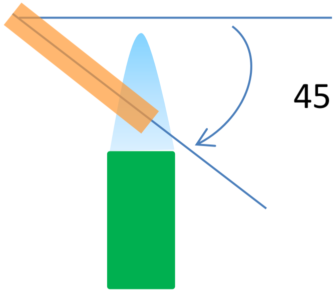
bisphenol C CE

Lyon, R. E. et al *Fire Mater*. 2006, *30*, 89-106

BPT cyanate ester

Small scale flame tests

Specimen (1 × 0.35 × 0.1) cm placed in a propane torch flame at a 45 ° angle for 3 s, noting time required for the sample to self-extinguish upon removal from the flame



propane torch flame

(a)
BPACE/BPTCE 9/1

(b)
BPACE/BPTCE 9/1

(c)
BPTCE

(d)
BPTCE

(e)

composition (w/w)	flame test
BPACE	> 5 s burn
BPACE/BPTCE (9/1)	> 5 s burn
BPACE/BPTCE (8/2)	> 5 s burn
BPACE/BPTCE (7/3)	> 5 s burn
BPACE/BPTCE (5/5)	1-2 s burn
BPTCE	extinguished immediately

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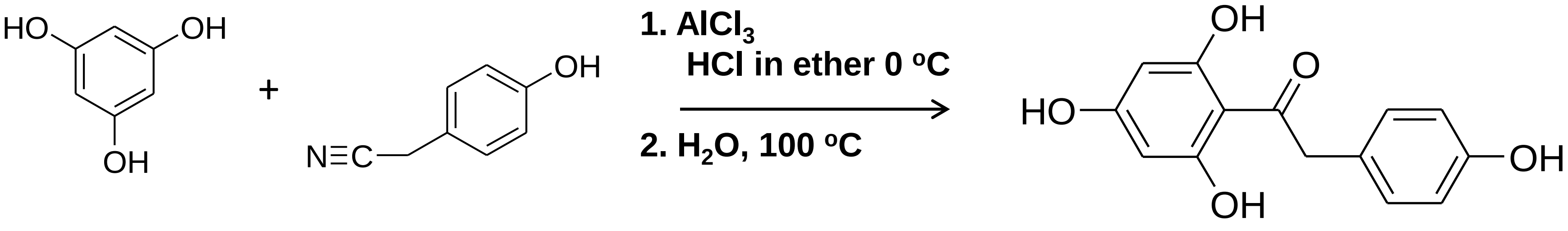
Tetrahydroxydeoxybenzoin (THDB)
A new multifunctional compound for anti-flammable materials

Houben-Hoesch conditions



1. $AlCl_3$
HCl in ether 0 ^oC

2. H_2O, 100 ^oC

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

86% yield on 10 g scale
Pale yellow powder