Anti-flammable polymers and nanocomposites

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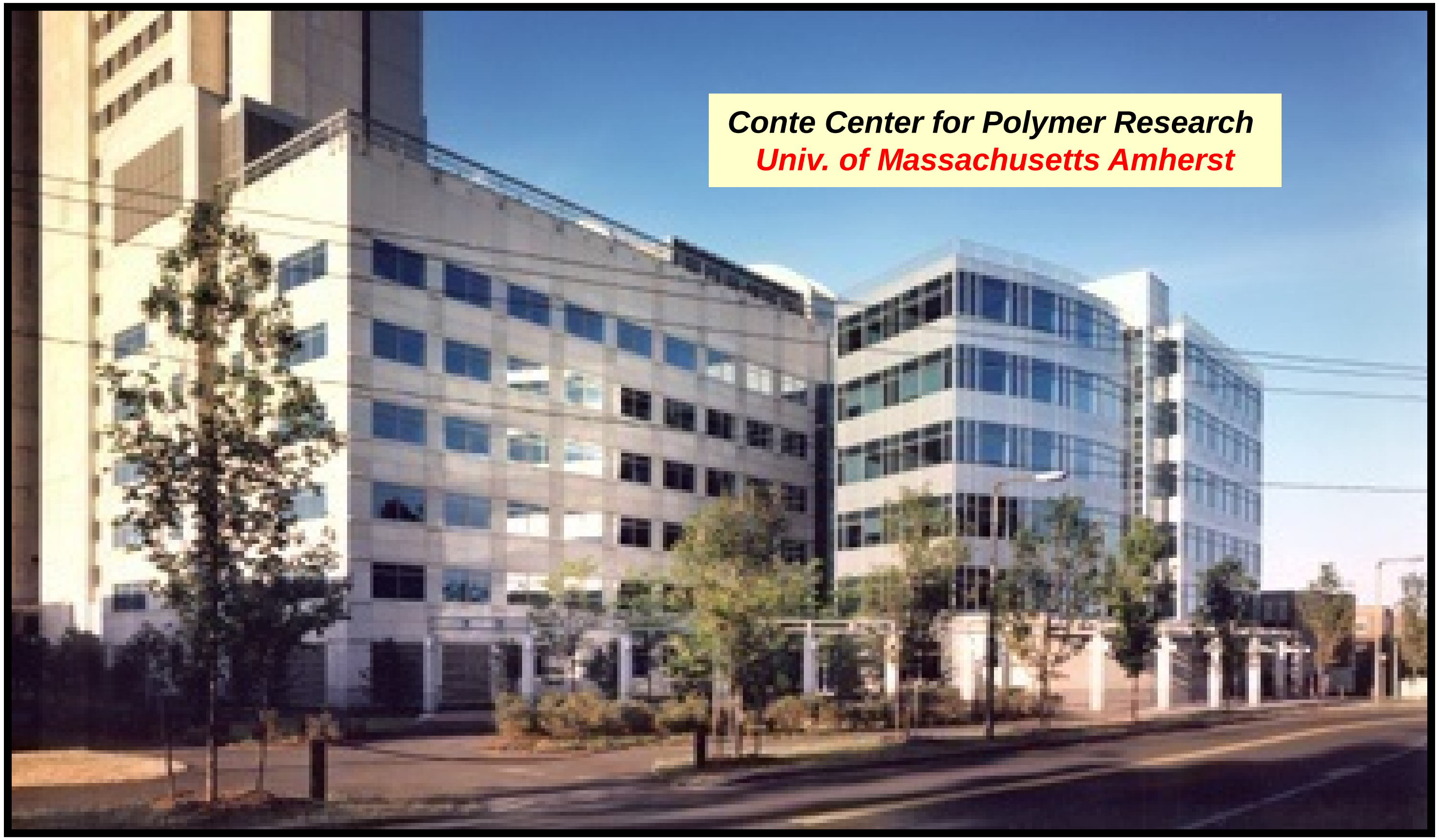

Conte Center for Polymer Research
Univ. of Massachusetts Amherst

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Emrick Group (top-to-bottom)
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Background

Synthetic organic polymers

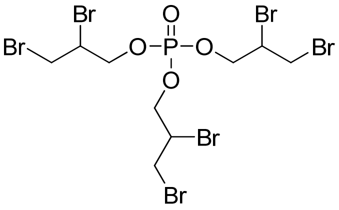
- A mainstay of modern society, used in fabricating textiles, upholstery, construction materials, vehicles, and electronic devices

- Pose a significant threat due to their inherent flammability

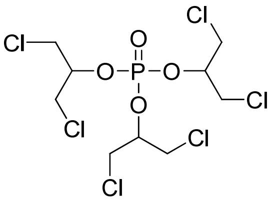
Halogenated flame-retardants (FRs)

- Highly effective for flame-retardation as additives to polymer materials

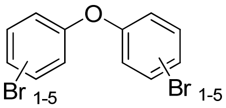
- Face legislative scrutiny, due to health and environmental concerns (particularly related to bioaccumulation and toxicity)



tris(2,3-dibromopropyl)phosphate



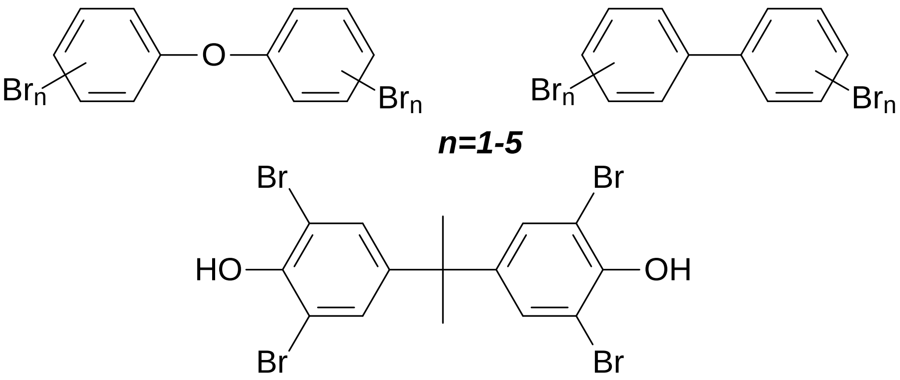
tris(1,3-dichloro-2-propyl)phosphate



polybrominated diphenyl ether **(PBDEs)**

Small molecule flame-retardants

Halogenated



Effective and inexpensive
Used in commodity polymers (polycarbonate, polyurethanes, epoxy ,etc.)

Environmental persistence
Toxicity
Restrictions and legislation

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
Limitation in high-temperature applications

Broader Project Objectives

- Synthesis of novel inherently fire-resistant polymers
- Requirements:
  - High thermal stability
  - Low combustion heat release rate
  - Minimal toxic fume release
  - Environmental friendly (non-halogenated)
  - High char formation
- Polymers with high C/H ratio (aromatic, high degree of unsaturation) show better fire-resistant properties, as the lack of hydrogen fuel leads to facile char formation

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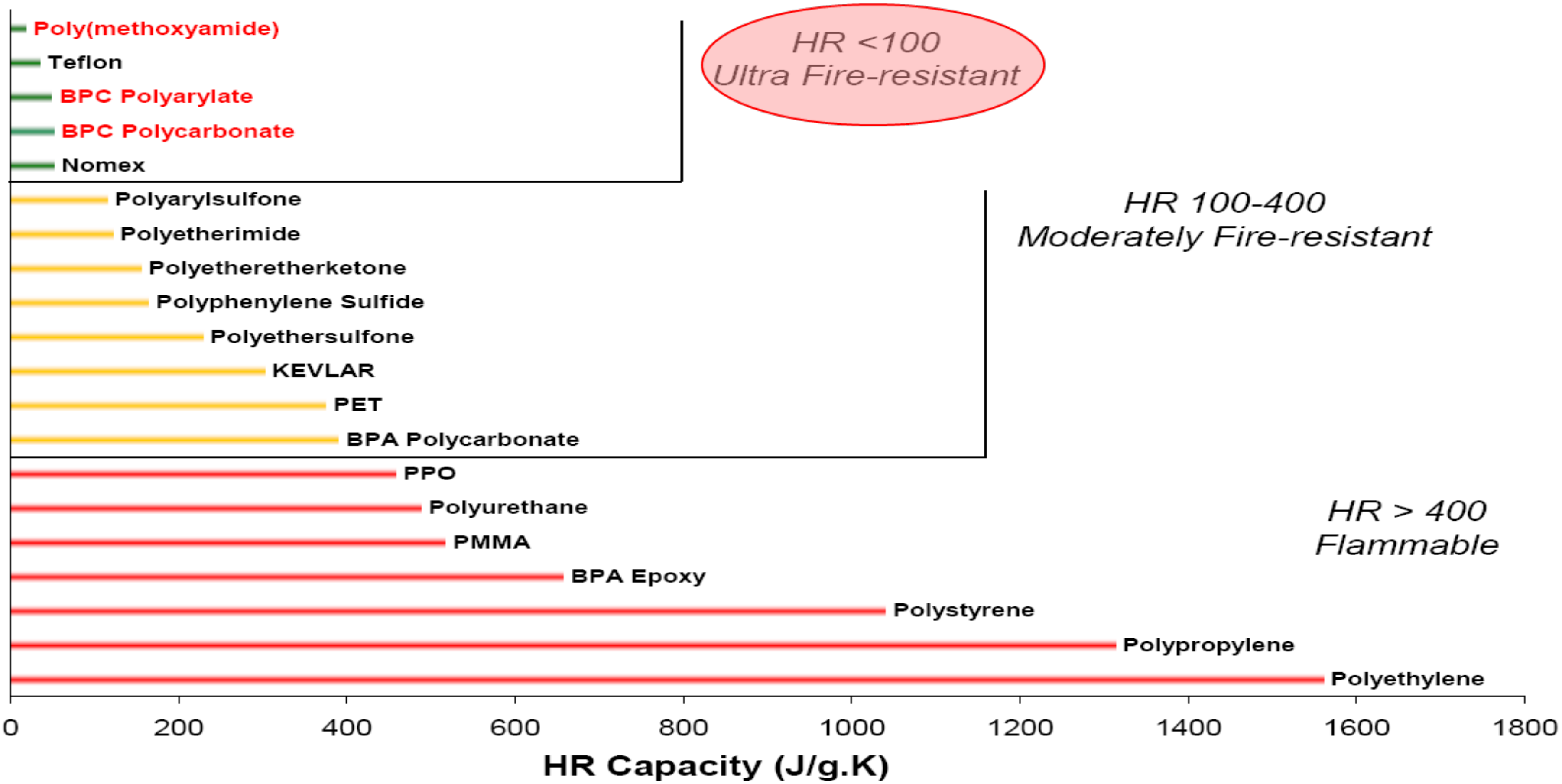
Presentation topics for:
The Sixth Triennial International Fire & Cabin Safety Research Conference
October 27, 2010

1) **Deoxybenzoin-containing polymers (BHDB)**
2) **Bis-phenol triazole (BPT) polymers**

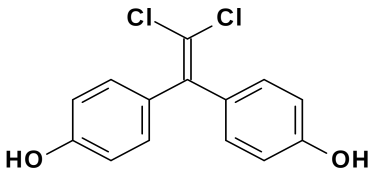
Heat release capacity (HRC) of polymers



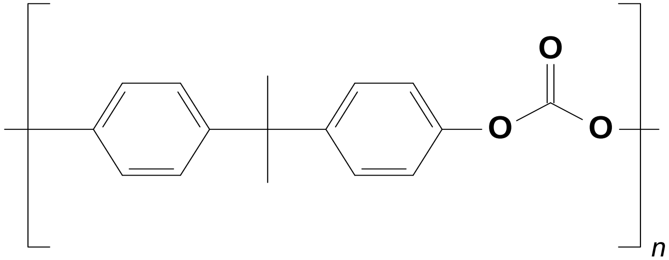
Pyrolysis combustion flow calorimetry (PCFC) enables effective analysis of milligram quantities of novel and known materials!

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

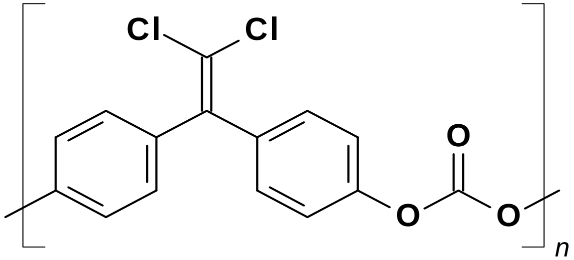
Bisphenol A vs. Bisphenol C



Bisphenol C



Bisphenol A Polycarbonate (Lexan)

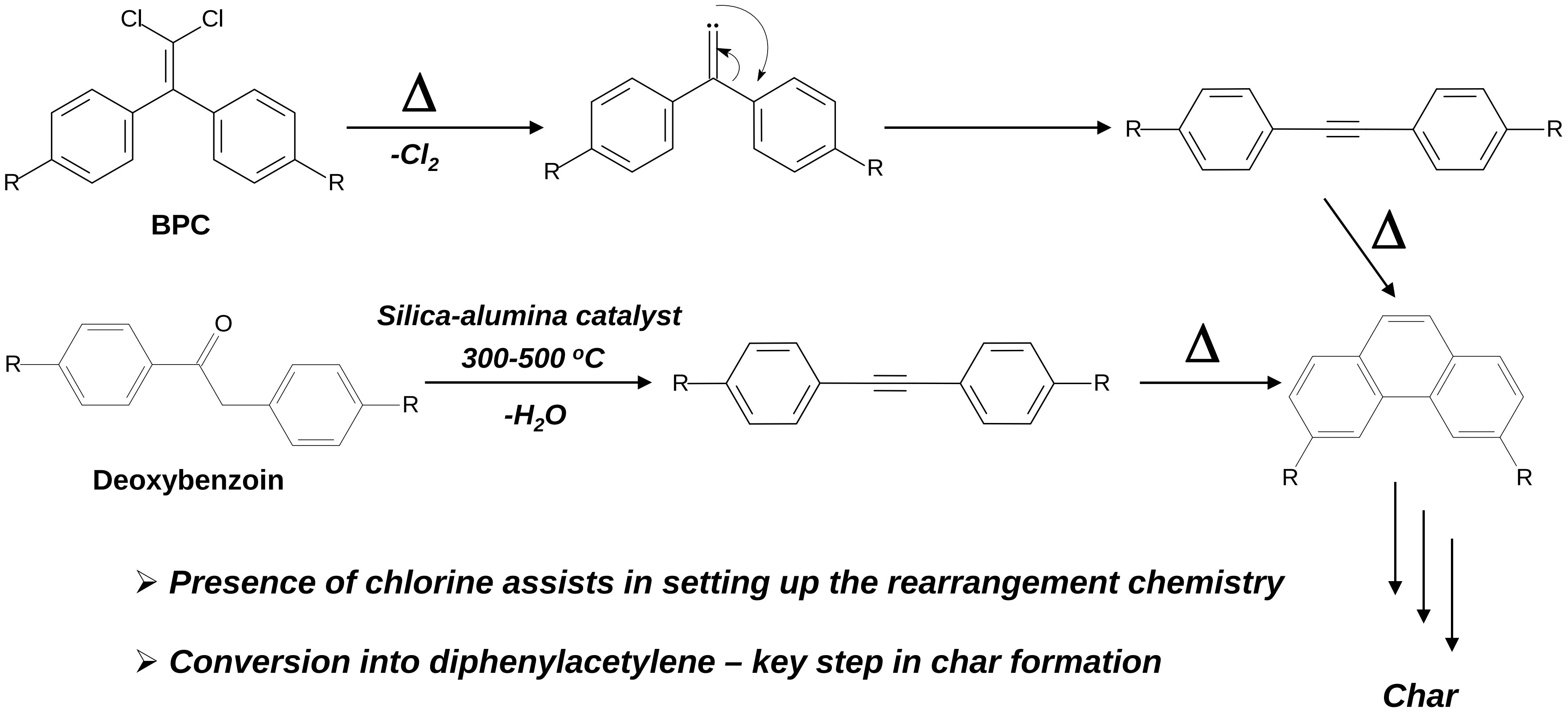


Bisphenol C Polycarbonate

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**

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

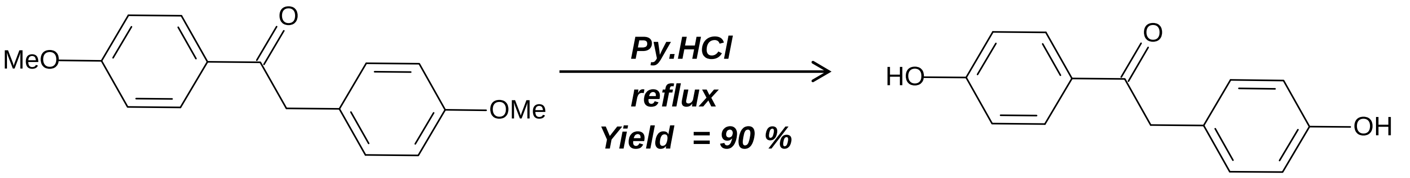
Rationale for observed bis-phenol C charring



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

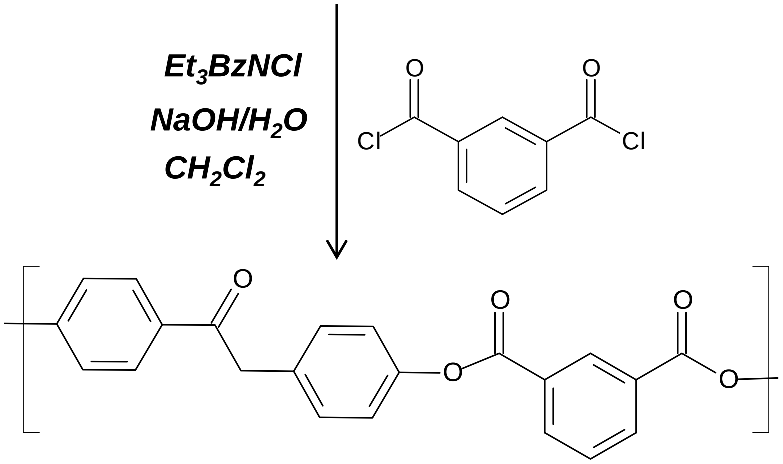
Ramirez, M. L. *Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers. DOT/FAA/AR-00/42.*; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001; Stoliorav, S.I.; Westmoreland, P.R. *Polymer*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

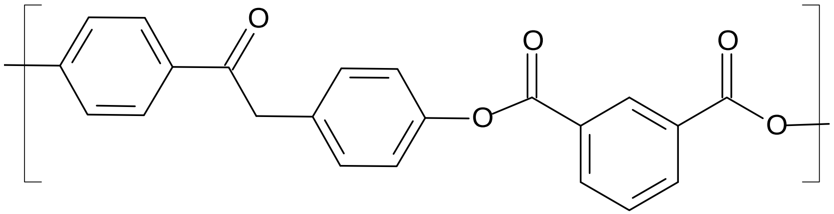


BHDB-Polyarylate

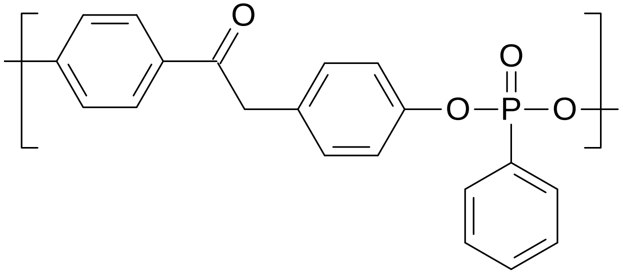
- One step synthesis of monomer in high yields, up to 500 g scale
- Polyarylate: HRC = 65 J/g-K; Char yield = 45%
- Low solubility and low molecular weight (M_w < 5000 g/mol)
- Copolymerization improves processibility

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

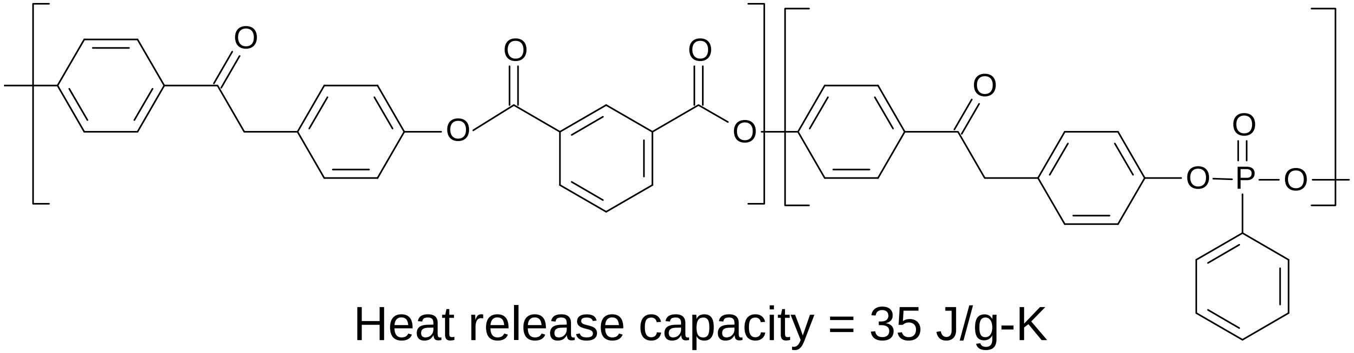
BHDB-based halogen-free polymers are "ultra fire-resistant"



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 %

Macromolecules **2006**, *39*, 3553; *Macromolecules* **2006**, *39*, 5974
J. Polym. Sci. Part A: Polym. Chem. **2007**, *45*, 4573; *Polym. Degrad. Stab.* **2008**
Deoxybenzoin epoxy adhesives: Polymer, 2009

Federal Aviation Administration flammability testing

Predominant charring, no dripping, and lowest flammability (5VA) rating

Reducing flammability of polyurethanes

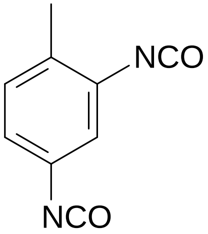
- Polyurethanes from polyols + diisocyanates,
  or polyisocyanates + diols

- Depending on formulation, polyurethanes are obtained with varying hardness and density

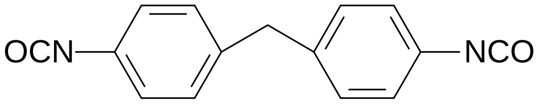
- Polyurethane foams:
  used in mattresses, upholstery, automobile seats, etc.

- Halogenated additives reduce flammability

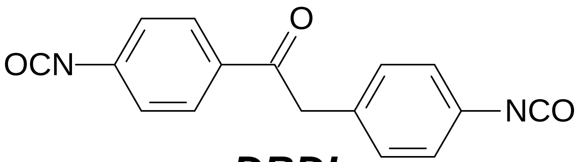
- Objective: prepare non-halogenated low flammable polyurethanes
  with no additives (small molecule or otherwise)



TDI



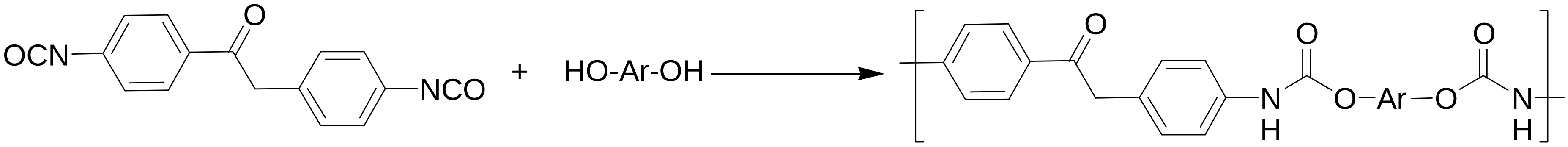
MDI



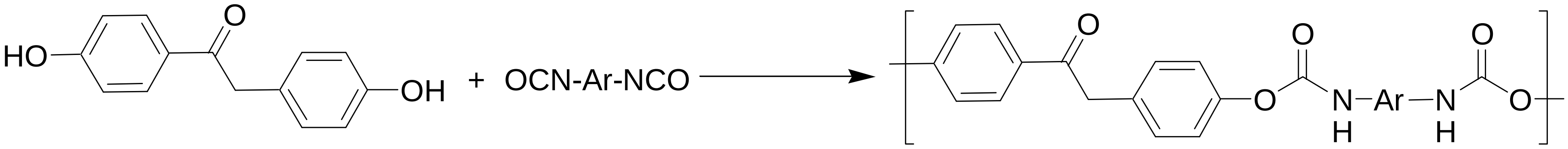
DBDI

Potential options for deoxybenzoin in polyurethanes

1. *Deoxybenzoin for isocyanate formulations*



2. *Deoxybenzoin for hydroxyl formulations*

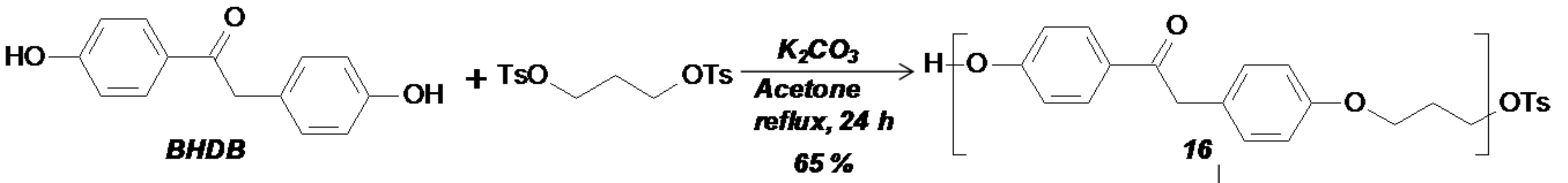


BHDB
(or extended diols)

Journal of Materials Chemistry, 2010

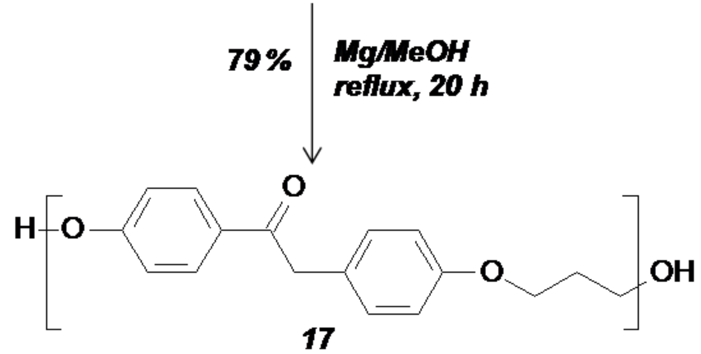
Charring polyurethane foams

Objective: impart flame resistance and charring to foam, while maintaining suitable properties



BHDB

16



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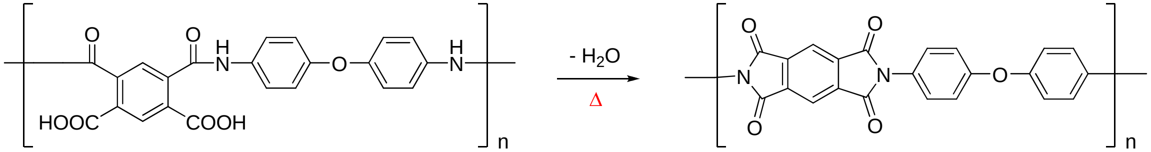
Polymer	Reagents (weight %)				PCFC		TGA
	Polyether polyol	BHDB-oligomer	MDI-prepolymer	Others[a]	HRC (J/g-K)	THR (kJ/g)	Char yield (%)[b]
18	74.9	0	23.1	2.0	476	22.9	0
19	62.6	12.6	22.8	2.0	437	21.1	15
20	53.6	21.6	22.8	1.9	371	19.9	19

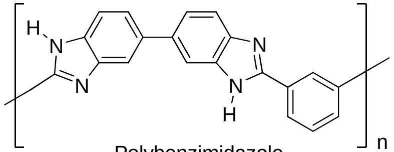
Commercial systems, BHDB, and BPT

Halogen-free ultra low flammability polymers

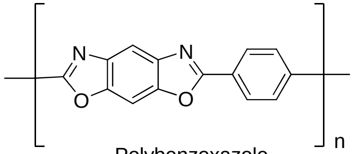


Poly(amic acid)

Polyimide

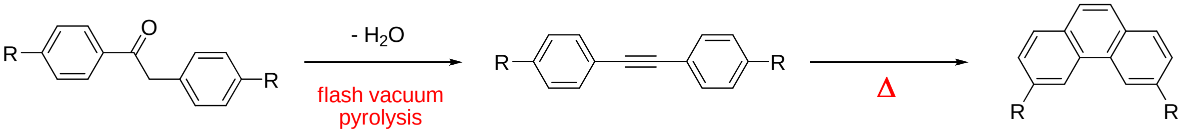


Polybenzimidazole



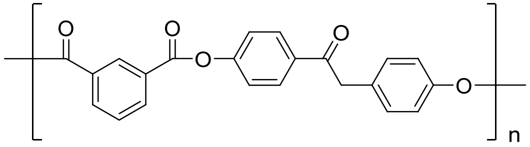
Polybenzoxazole

Thermally induced structural transformation: BHDB and BPT



deoxybenzoin

diphenylacetylene



BHDB polyarylate

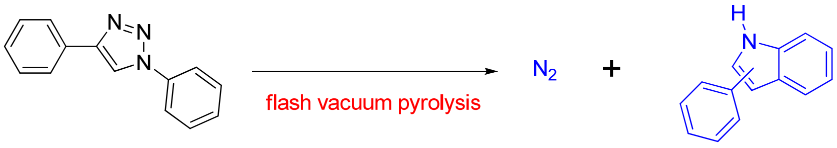
- **K. A. Ellzey *et. al.***
  Macromolecules, 2006, 39, 3553-3558
- **T. Ranganathan *et. al.***
  J. Mater. Chem., 2010, 20, 3681-3687

Heat release properties of BHDB-polyarylate

heat release capacity (HRC): 65 J/(g K);
total heat release (THR): 7.5 kJ/g; char : 45% at 850 ^oC

Bis-phenol triazole (BPT)

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



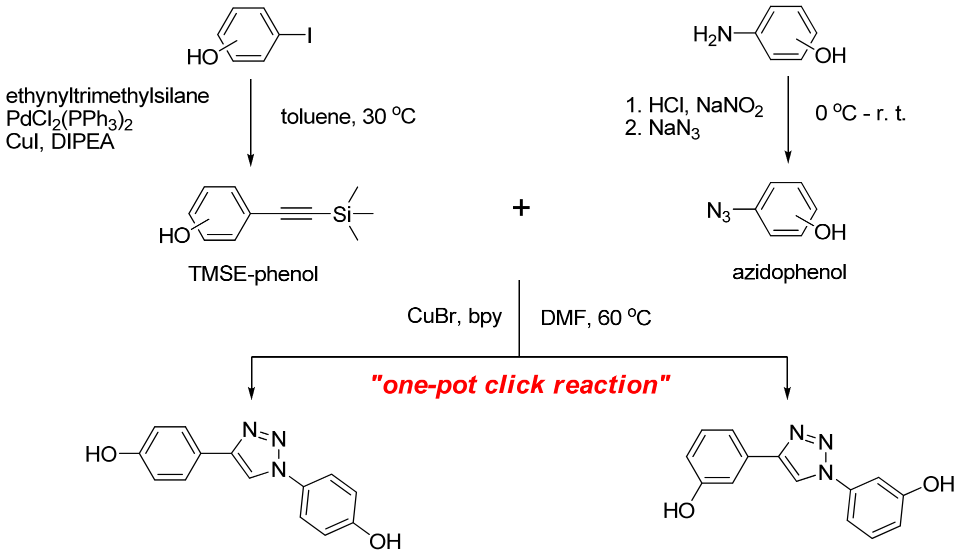
diphenyl-1,2,3-triazole

phenylindoles

Bisphenol-1,2,3-triazoles (BPT)

Synthesis and purification of BPT monomers

Tron and coworkers, ChemMedChem, 2007



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

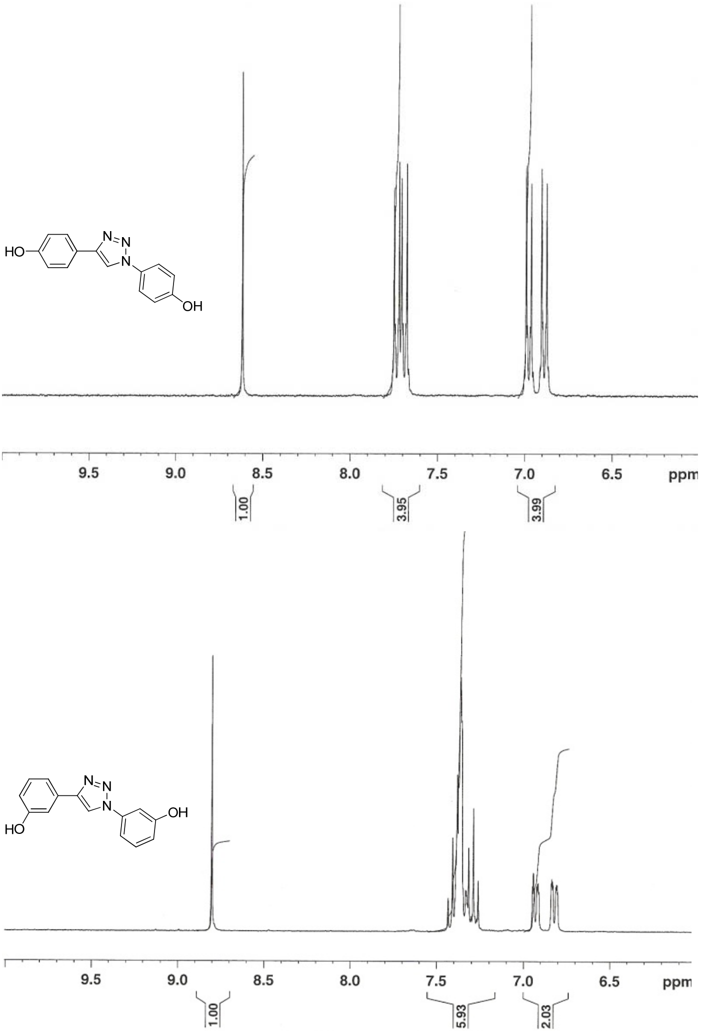
1,4-bis(3-hydroxyphenyl)-1,2,3-triazole
(**3-BPT**, 70% yield)

Purification of BPT monomers

- recrystallized in acetic acid/water

- melting point: 275 °C (4-BPT); 205 °C (3-BPT)

No prior polymerization chemistry reported for BPT

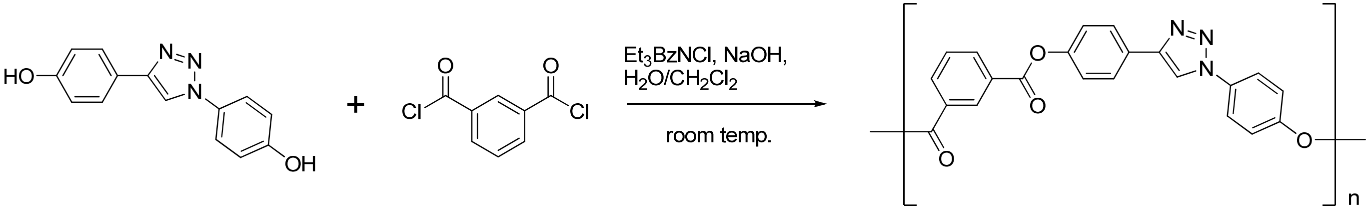


^{1}H NMR spectra of BPT monomers

4-BPT polyarylate

Synthesis of 4-BPT polyarylate

interfacial polymerization



4-BPT

isophthaloyl dichloride

4-BPT polyarylate
(64% yield)

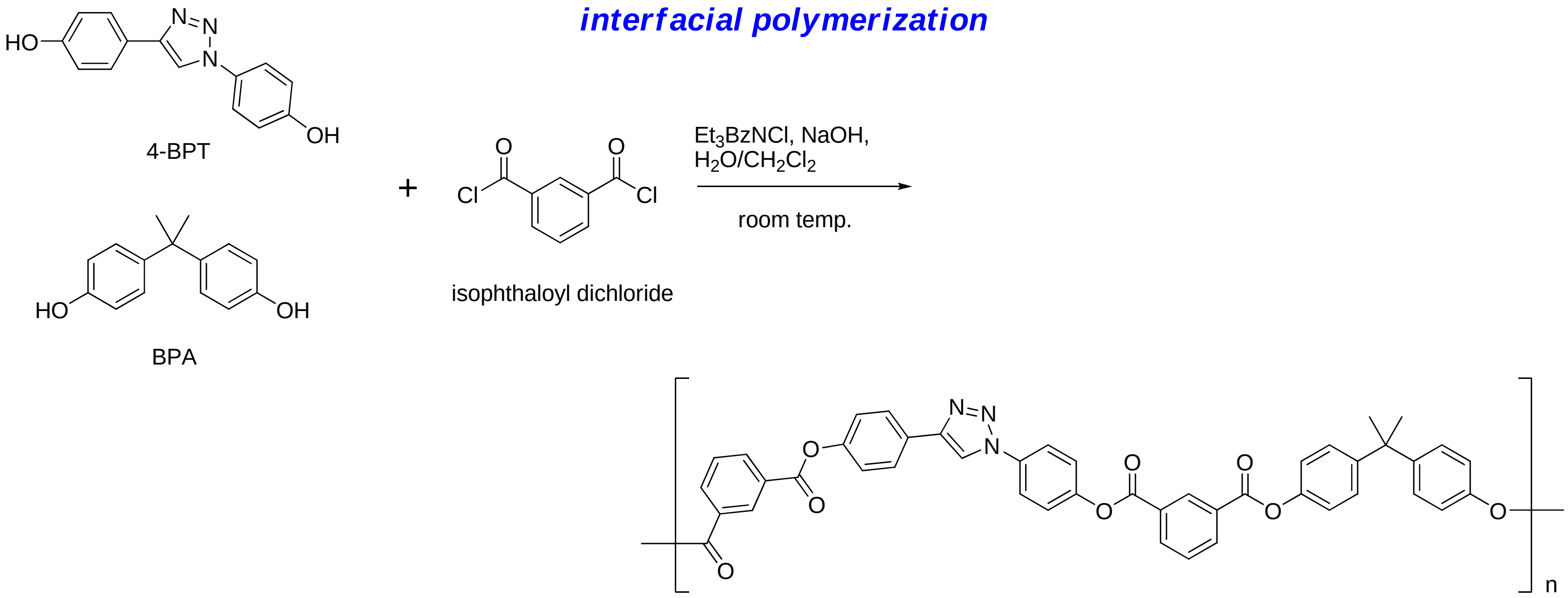
4-BPT polymer is insoluble in common organic solvents such as DMSO, DMF, and NMP

Heat release and char properties of 4-BPT polyarylate compared to bisphenol A (BPA) and other commercial polymers

polymer	***HRC (J/(g K))***	***THR (kJ/g)***	***char (%)***
BPA polyarylate	***456 ± 13***	***17.7 ± 0.5***	***26***
BHDB polyarylate	***65 ± 5***	***7.5 ± 0.2***	***45***
4-BPT polyarylate	***46 ± 5***	***6.8 ± 0.3***	***47***
Kevlar®	***363 ± 2***	***8.8 ± 0.5***	***38***
Nomex®	***99 ± 1***	***6.6 ± 0.2***	***43***

4-BPT/BPA copolyarylate

interfacial polymerization



4-BPT/BPA copolyarylate
50/50 (84% yield)

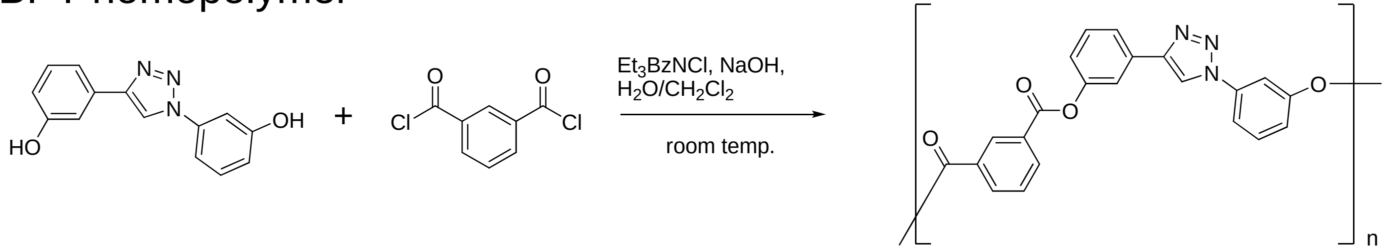
***4-BPT/BPA copolymer is insoluble or partially soluble in common organic solvents**

Heat release and char properties of 4-BPT/BPA copolyarylate

polymer	*HRC (J/(g K))*	*THR (kJ/g)*	*char (%)*
BHDB/BPA 53/47	***148 ± 10***	***12.3 ± 0.5***	***34***
4-BPT/BPA 50/50	***95 ± 4***	***12.0 ± 0.5***	***38***

3-BPT polyarylates

3-BPT homopolymer



Et_3BzNCl, NaOH, H_2O/CH_2Cl_2

room temp.

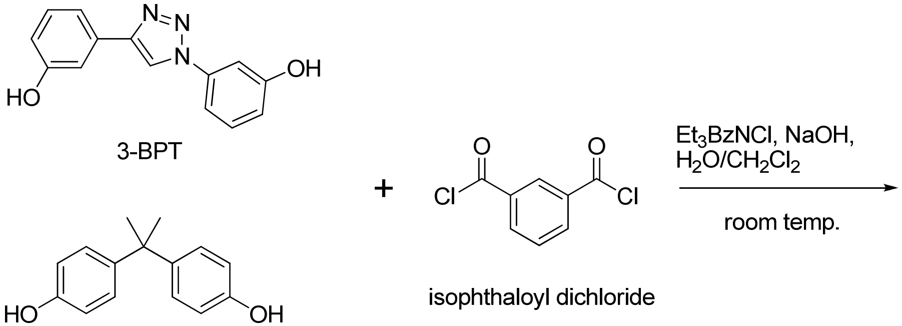
3-BPT

isophthaloyl dichloride

3-BPT polyarylate
(85-90% yield)

meta-structure is more kinked and less rigid

BPT/BPA copolymer



3-BPT

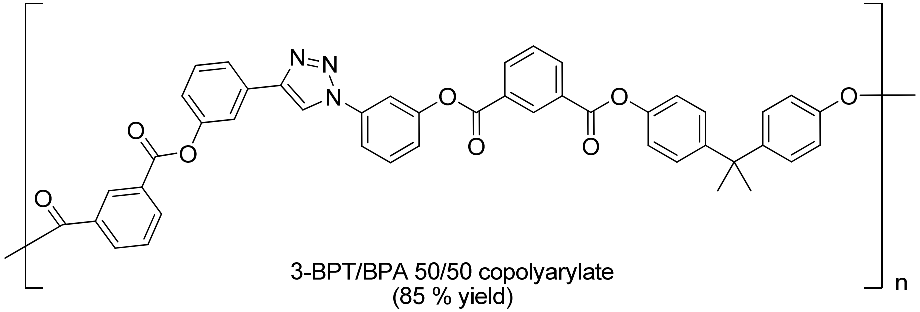
BPA

isophthaloyl dichloride

Et_3BzNCl, NaOH, H_2O/CH_2Cl_2

room temp.

****3-BPT polymer is soluble in NMP, and copolymer is soluble in TCE, DMF, and NMP!***



3-BPT/BPA 50/50 copolyarylate
(85 % yield)

Angewandte Chemie, 2010, in press

3-BPT polyarylates

Estimated molecular weights of 3-BPT polymer and copolymer

polymer	GPC [a]			η_{inh} [b] (dL/g)
	$\overline{Mn}$	$\overline{Mw}$	PDI	
3-BPT polyarylate	10,900	27,600	2.53	0.48
3-BPT/BPA 50/50	7,800	17,900	2.29	0.42

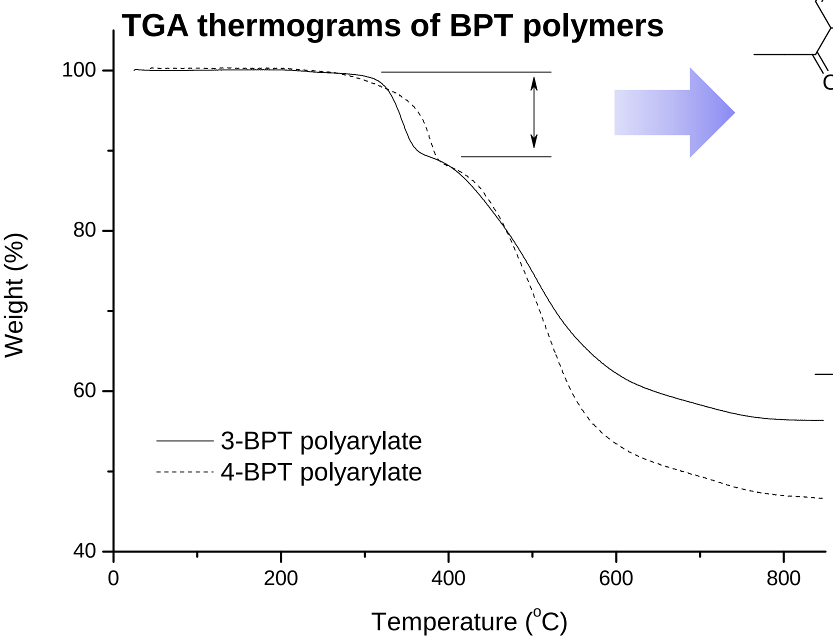
[a] Molecular weights were estimated by size exclusion chromatography in NMP (0.05 M LiCl) at 80 °C. [b] Data were obtained at room temperature.

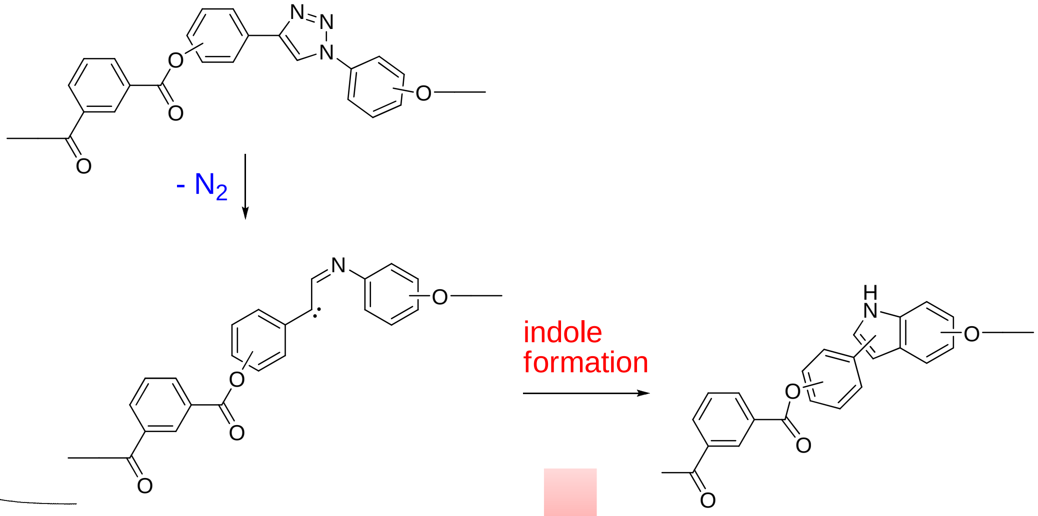
Heat release and char properties of 3-BPT polymers

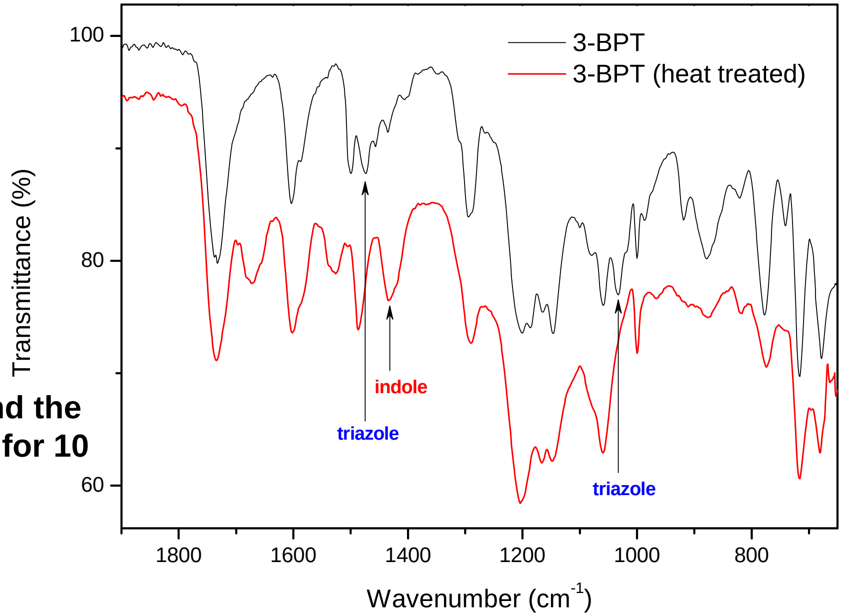
polymer	HRC (J/(g K))	THR (kJ/g)	char (%)
3-BPT/BPA 50/50 [a]	102 ± 5	11.3 ± 0.4	44
4-BPT polyarylate	46 ± 5	6.8 ± 0.3	47
3-BPT polyarylate	23 ± 3	4.6 ± 0.2	56
Kapton®	14	4.0	66

[a] Incorporated ratio was measured in ^1H NMR spectrum.

Thermally induced structural transformation


TGA thermograms of BPT polymers





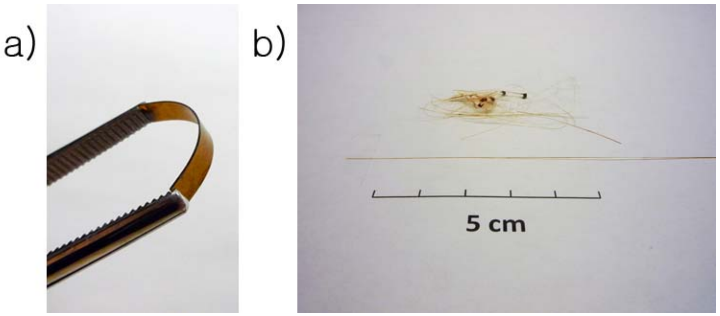
FT-IR spectra of 3-BPT polymer (black), and the same polymer after heating at 350 °C for 10 minutes.

Mechanical properties and flame test on a small sample

Initial tensile test of 3-BPT polymer

- hot pressing at 250 ^{o}C for 10min.
- sample size: 3×0.3×0.025 cm

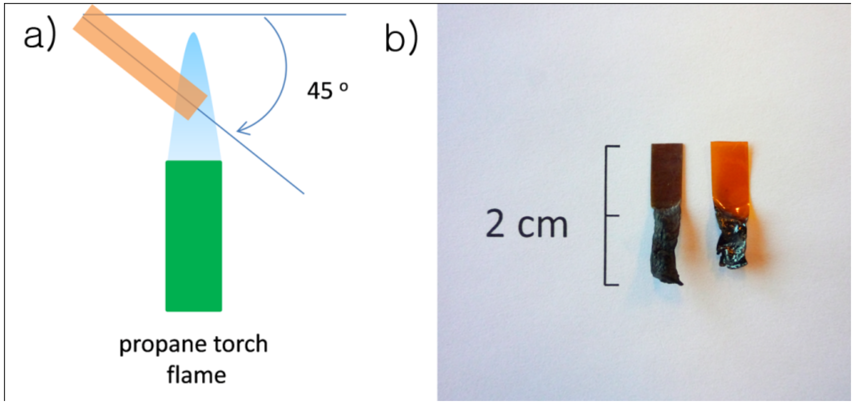
- ultimate strength: 95±25 MPa
  tensile modulus: 2.5±0.3 GPa



a) 3-BPT polymer film formed by hot-pressing;
b) 3-BPT fibers pulled from the melt.

Small-scale flame test

Conducted by placing a sample specimen approximately (2×0.5×0.025) cm in a propane torch flame at a 45 deg angle for 5-10 s and noting the time required for the sample to self-extinguish upon removal from the flame



Films of BPT polymers were seen to be extinguish immediately. (‘self-extinguishing’)

Small-scale flame test configuration; b) samples after the test (left: 3-BPT polyarylate; right: Kapton®.