Anti-flammable polymers and nanocomposites

Todd Emrick, Polymer Science & Engineering, UMass Amherst

Funding: Federal Aviation Administration, U.S. Army, and the members of the polymer flammability industrial consortium (Cluster F) at the University of Massachusetts Amherst
Acknowledgements

Emrick Group (top-to-bottom)
C.C. Chang
Beth Cooper, Yunxia Hu, Katrina Kratz, Samantha McRae, Caroline Miesch, Delphine Chan-Seng
Zak Page, Brent Hammer, Cheol Hee Lee, Xiangji Chen, Matt Rozin, B. Ryu, Sangram Parelkar
(not pictured: P.K. Sudeep, Irem Kosif, Jimmy Lawrence, Emily Pentzer)
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)

![Types of FRs](image1.png)
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

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! 

Bisphenol A vs. Bisphenol C

Bisphenol A Polycarbonate (Lexan)

Bisphenol C Polycarbonate

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Bisphenol A</th>
<th>Bisphenol C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (°C)</td>
<td>152</td>
<td>168</td>
</tr>
<tr>
<td>Flex Modulus (ksi)</td>
<td>336</td>
<td>376</td>
</tr>
<tr>
<td>Flex Strength (psi)</td>
<td>16,300</td>
<td>16,200</td>
</tr>
<tr>
<td>Tensile Yield Strain (%)</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>NBS Smoke (Dm)</td>
<td>165</td>
<td>75</td>
</tr>
<tr>
<td>Oxygen Index (%)</td>
<td>26</td>
<td>56</td>
</tr>
<tr>
<td>HR Capacity (J/g.k)</td>
<td>390</td>
<td>29</td>
</tr>
</tbody>
</table>

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

- 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

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 %
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)
Potential options for deoxybenzoin in polyurethanes

1. Deoxybenzoin for isocyanate formulations

$$\text{OCN-} \begin{array}{c} \text{NCO} \\ \text{NCO} \end{array} + \text{HO-Ar-OH} \rightarrow \begin{array}{c} \text{OCN-Ar-NCO} \\ \text{NH} \end{array}$$

2. Deoxybenzoin for hydroxyl formulations

BHDB (or extended diols)

$$\text{BHDB} + \text{OCN-Ar-NCO} \rightarrow \begin{array}{c} \text{BHDB} \\ \text{OCN-Ar-NCO} \end{array}$$

Journal of Materials Chemistry, 2010
Charring polyurethane foams

**Objective:** impart flame resistance and charring to foam, while maintaining suitable properties
Commercial systems, BHDB, and BPT

**Halogen-free ultra low flammability polymers**

- Poly(amic acid)
- Polybenzimidazole
- Polybenzoxazole

**Thermally induced structural transformation: BHDB and BPT**

- Deoxybenzoin diphenylacetylene
  - 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 °C

**Bis-phenol triazole (BPT)**


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

**Synthesis and purification of BPT monomers**

*Tron and coworkers, ChemMedChem, 2007*

\[ \text{Bisphenol-I} \xrightarrow{\text{CuI, DIPEA}} \text{TMSE-phenol} \]

\[ \text{R} \xrightarrow{\text{H}_2\text{N-phenol}} \text{azidophenol} \]

\[ \text{CuBr, bpy} \xrightarrow{\text{DMF, 60 }^\circ\text{C}} \text{one-pot click reaction} \]

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)

**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

\[ ^1\text{H NMR spectra of BPT monomers} \]
4-BPT polyarylate

Synthesis of 4-BPT polyarylate

*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

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

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

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

<table>
<thead>
<tr>
<th>polymer</th>
<th>HRC (J/(g K))</th>
<th>THR (kJ/g)</th>
<th>char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHDB/BPA 53/47</td>
<td>148 ± 10</td>
<td>12.3 ± 0.5</td>
<td>34</td>
</tr>
<tr>
<td>4-BPT/BPA 50/50</td>
<td>95 ± 4</td>
<td>12.0 ± 0.5</td>
<td>38</td>
</tr>
</tbody>
</table>
3-BPT polyarylates

3-BPT homopolymer

3-BPT is soluble in NMP, and copolymer is soluble in TCE, DMF, and NMP.

BPT/BPA copolymer

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

Angewandte Chemie, 2010, in press
# 3-BPT Polyarylates

Estimated molecular weights of 3-BPT polymer and copolymer

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>PDI</th>
<th>$\eta_{inh}^b$ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-BPT polyarylate</td>
<td>10,900</td>
<td>27,600</td>
<td>2.53</td>
<td>0.48</td>
</tr>
<tr>
<td>3-BPT/BPA 50/50</td>
<td>7,800</td>
<td>17,900</td>
<td>2.29</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th>polymer</th>
<th>HRC (J/(g K))</th>
<th>THR (kJ/g)</th>
<th>char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-BPT/BPA 50/50</td>
<td>102 ± 5</td>
<td>11.3 ± 0.4</td>
<td>44</td>
</tr>
<tr>
<td>4-BPT polyarylate</td>
<td>46 ± 5</td>
<td>6.8 ± 0.3</td>
<td>47</td>
</tr>
<tr>
<td>3-BPT polyarylate</td>
<td>23 ± 3</td>
<td>4.6 ± 0.2</td>
<td>56</td>
</tr>
<tr>
<td>Kapton®</td>
<td>14</td>
<td>4.0</td>
<td>66</td>
</tr>
</tbody>
</table>

*a Incorporated ratio was measured in $^1$H 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 °C for 10min.
- sample size: 3×0.3×0.025 cm
- ultimate strength: 95±25 MPa
tensile modulus: 2.5±0.3 GPa

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')