Hydrogen Atom Transfer Reagents for Polyolefin Upcycling

**Background**

**Industrial Post-Consumer Polyolefin Functionalization**
- Polyolefin recycling via functionalization remains a challenge due to undesirable side reactivity.
- 3º abstraction causes β-sission.
- Increased Mn, decreased MW.

**Previous Work**
- 1º selective
- Transition metal catalyst
- Non-generalizable to other functionality

**General methods for polyolefin upcycling remain a challenge**

**Introduction & Motivation**

**Recent Advances**
- Amidyl radical enables C-H abstraction (N-H BDE = 110 kcal/mol).
- Chain transfer mechanism decouples reagent fragmentation from polymer functionalization.

**This Work**
- Can we...
  - decrease reagent mass loading?
  - vary N-O dissociation temp?
  - modify steric to allow func. of other polyolefins?

<table>
<thead>
<tr>
<th>Reagent</th>
<th>N-O Homolysis Peak Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>104.1</td>
</tr>
<tr>
<td></td>
<td>119.3</td>
</tr>
<tr>
<td></td>
<td>151.2</td>
</tr>
<tr>
<td></td>
<td>177.5</td>
</tr>
</tbody>
</table>

- EWGs lead to electron-poor, destabilized radical: high BDE.
- Electron donors result in loss of homolysis exotherm by DSC.
- Indicates facile tunability of reagent activation temp.

**C–H Functionalization of Polyolefins**

**Chloramides as synthetically facile analogues of HAT reagent**

<table>
<thead>
<tr>
<th>Run</th>
<th>Reagent</th>
<th>Substrate</th>
<th>Initiator</th>
<th>% func.</th>
<th>Mn (kDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2</td>
<td>LLDPE</td>
<td>hv</td>
<td>4</td>
<td>1.97</td>
</tr>
<tr>
<td>b</td>
<td>2</td>
<td>LLDPE</td>
<td>DCP</td>
<td>2</td>
<td>1.63</td>
</tr>
<tr>
<td>c</td>
<td>2</td>
<td>LLDPE</td>
<td>gel</td>
<td>5</td>
<td>1.80</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
<td>LLDPE</td>
<td>gel</td>
<td>5</td>
<td>1.75</td>
</tr>
</tbody>
</table>

**Investigating reagent mass & mechanism**

<table>
<thead>
<tr>
<th>Run</th>
<th>Reagent</th>
<th>Substrate</th>
<th>% func.</th>
<th>Mn (kDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>LLDPE</td>
<td>1%</td>
<td>3.88</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>LLDPE</td>
<td>3%</td>
<td>20</td>
</tr>
</tbody>
</table>

**Tunable Homolysis Temperatures**

- 10% vs. other functionality.
- Generalizable to other functionality.

**Conclusions**

- Benzyl radical intermediate, 2 transition states found.
- Phenyl group likely necessary for intermediate stability.
- Tuning steric and electronics at different sites allows for efficient functionalization of new polyolefin substrates with this reagent.
- Amidyl substituents can be varied while retaining function; however, PhVi moiety is critical to reagent functionality.