Bio-based 1,5-Pentanediol: A new renewable monomer for the coatings industry

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C4-C6 Diols Market and End-use

$1B/yr Global Market
8% CAGR

1,5-Pentanediol (1,5-PDO) $6000/ton
1,6-Hexanediol (1,6-HDO) $3000-4700/ton

1,5-PDO 1,6-HDO

Polyesters
Polycarbonates
Acrylates

Renewable 1,5-PDO

Adipic Acid

Co-
monomer

Paints

Coatings

Plastics

Adhesives
1,5-PENTANEDIOL PRODUCTION
1,5-PDO is currently produced from dicarboxylic acid as byproduct in caprolactam production.
Large amounts of low-cost furfural are available

- Technology commercialized since 1942
- Possible biomass feedstocks include corn stover, bagasse, and wood but primarily made from corn cobs today
- 604 kiloton market with 4.3% CAGR

Furfural synthesized from five-carbon (C5) hemicellulose fraction of biomass
Process combines biomass fractionation with chemical production

- >80% of the initial wood converted to products:
  1. High purity cellulose
  2. Furfural
  3. High purity lignin
  4. Acetic acid
  5. Formic acid
  6. Levulinic acid

- >$500 revenues per MT of wood

- High biomass loading 20-30 wt%
Furfural to 1,5-PDO Reaction Scheme

High yields demonstrated for each step in continuous flow reactors:

- **Step 1:** Furfural Hydrogenation (commercially established process)
- **Step 2:** THFA Dehydration
- **Step 3:** DHP Hydration
- **Step 4:** 2-HY-THP Hydrogenation

>85% overall 1,5-PDO yield from furfural

1) Data from Nakagawa et. al.
2) Chemicals from Biomass: Combining Ring-Opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural, 2017. ChemSusChem 10, 1351-1355
Key Technological Advantages

- Highly stable catalysts in flow reactors
- Clean process – no byproducts (only wastewater treatment)
- Water solvent (or no solvent) for every reaction step
- No liquid recycle streams
- Thermochemical conversion (vs. biological)
1,5-PENTANEDIOL IN COATINGS
1,6-Hexanediol Applications

"Polyesters" MM lbs.
- Cast Elastomers: 50 lbs.
- TPU's: 34 lbs.
- "Coatings": 40 lbs.
  - SB Liquid
  - PUD's
  - Synthetic Leather

"Polyurethanes" MM lbs.
- "Coatings": 40 lbs.
  - Sat Polyester: 53 lbs.
  - Polyester Powder: 53 lbs.
    (incl some PU Powder)

"Adhesives" MM lbs.
- Polyester: 37 lbs.
- PU: 20 lbs.

"Acrylates" MM lbs.
- Monomer: 75 lbs.
  (Mainly HDODA)
1,5-Pentanediol used as monomer in several polymer groups

**Focus of presentation:**

- Polyester Polyols
- Polycarbonate Polyols
- UV-Cure Diacrylates
Polyester Polyols: Diol-adipates show odd-even effect

<table>
<thead>
<tr>
<th>Diol</th>
<th>MW (g/mol)</th>
<th>OH number (mg KOH/g)</th>
<th>Acid number</th>
<th>Viscosity (cP)</th>
<th>Glass transition (°C)</th>
<th>Melting transition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-ethanediol (EG)</td>
<td>2114</td>
<td>52.8</td>
<td>0.53</td>
<td>1334</td>
<td>-46.9</td>
<td>48.0</td>
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<tr>
<td>1,3-propanediol (1,3-PrDO)</td>
<td>2029</td>
<td>55.3</td>
<td>0.36</td>
<td>1471</td>
<td>-59.7</td>
<td>39.7</td>
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<tr>
<td>1,4-butanediol (1,4-BDO)</td>
<td>2110</td>
<td>53.2</td>
<td>0.61</td>
<td>1482</td>
<td>-53.7</td>
<td>53.3</td>
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<tr>
<td>1,5-pentanediol (1,5-PDO)</td>
<td>2188</td>
<td>51.3</td>
<td>1.24</td>
<td>1316</td>
<td>-61.8</td>
<td>38.6</td>
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<tr>
<td>1,6-hexanediol (1,6-HDO)</td>
<td>1961</td>
<td>57.3</td>
<td>0.26</td>
<td>1100</td>
<td>none</td>
<td>51.8</td>
</tr>
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</table>

Source: DuPont Tate & Lyle BioProducts
Polyester Polyols: Diol-furanoates show odd-even effect

Polyester Polyol = Linear Diol + Furandicarboxylic acid (FDCA)

100% renewable resin!!!

Source: Bikiaris, DN et al. “New poly(pentylene furanoate) and poly(heptylene furanoate) sustainable polyesters from diols with odd methylene groups” Materials Letters. 178 (2016) 64-47
Polyester Polyols: Hardness/crystallinity increased with reformulation

Polyester Polyol = 1,5-Pentanediol + Succinic acid + Furandicarboxylic acid (FDCA)

Sources:
Lomeli-Rodriguez et al. “Synthesis and Characterization of Renewable Polyester Coil Coatings from Biomass-Derived Isosorbide, FDCA, 1,5-Pentanediol, Succinic Acid, and 1,3-Propanediol.” Polymers. 10 (2018) 600
Polyester Polyols: Hardness/crystallinity increased with reformulation

"The consideration of **bioderived 1,5-pentanediol as a main building block** opens the possibility toward the development of **flexible coatings but with better hardness than currently used diols, such as 1,6-hexanediol**, enhanced by the presence of FDCA…"

Sources:
Lomeli-Rodriguez et al. “Synthesis and Characterization of Renewable Polyester Coil Coatings from Biomass-Derived Isosorbide, FDCA, 1,5-Pentanediol, Succinic Acid, and 1,3-Propanediol.” *Polymers*. 10 (2018) 600
Polycarbonate Polyols (PCPs) used in coatings and polyurethane dispersions

- **Adhesives**
- **Elastomers**
- **Car Interior**
- **Coatings**
- **Synthetic Leather**
- **Flooring**
Renewable polycarbonate diol for enhanced polyurethane applications

- **Monomer #1:** Dimethyl carbonate
  - Produced from methanol and CO via oxycarbonylation

- **Monomer #2:** 1,5-Pentanediol (1,5-PDO)
  - Produced from furfural via Pyran’s technology

- **Polymer:** Polycarbonate polyol
**Polycarbonate Polyols (PCPs)** provide value-added properties over Polyesters & Polyethers

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<td>Heat Stability:</td>
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<td>Cost:</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
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* Data summarized from Asahi Kasei (http://www.asahi-kasei.co.jp/pcdlhp/en/technical_data.html) and Ube Industries (“Polycarbonates Eternacoll”) Technical Guides
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<td>Oil-based 1,5-PDO</td>
<td>Oil-based 3MPDO</td>
<td>Oil-based 1,6-HDO</td>
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<td>Price:</td>
<td>$6000/ton</td>
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<td>$4500/ton</td>
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<td>Renewable 1,5-PDO</td>
<td></td>
<td>&lt;$3000/ton</td>
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Polycarbonate Polyols made from 1,5-pentanediol are “greener” and more easily processed

- 1,5-Pentanediol-based PCPs currently available on the market:

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<tr>
<th>Polycarbonate Polyol Type</th>
<th>MW (g/mol)</th>
<th>OH Value (mg KOH/g)</th>
<th>Acid Value (mg KOH/g)</th>
<th>Viscosity (cps @ 75 °C)</th>
<th>Melting Range (°C)</th>
<th>Appearance</th>
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<td>HDO Homopolymer</td>
<td>2000</td>
<td>51-61</td>
<td>&lt;0.1</td>
<td>1900-2600</td>
<td>36-50</td>
<td>Solid</td>
</tr>
<tr>
<td>PDO:HDO Co-polymer</td>
<td>2000</td>
<td>51-64</td>
<td>&lt;0.1</td>
<td>1600-3400</td>
<td>N/A</td>
<td>Liquid</td>
</tr>
</tbody>
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- PCPs made via 1:1 ratio of 1,5-pentanediol:1,6-hexanediol (PDO:HDO) marketed as value add-over HDO homopolymer due to liquid-phase properties
  - Facile processability
  - Improved flexibility and softness
  - Lower VOCs
  - Pyran’s 1,5-PDO: Renewably-sourced and <30% cost of HDO

UV-Cure Acrylates: 1,5-PDO substitutes for hexanediol diacrylate

- **Example chemistry:**

  - **Acrylated Oligomer**
    - *Epoxy acrylate*
    - ![Acrylated Oligomer](image)
    - 30-60%

  - **Acrylic monomer**
    - *Hexanediol diacrylate (HDODA)*
    - ![Acrylic monomer](image)
    - 20-60%

  - **Photo-initiator**
    - *Benzophenone*
    - ![Photo-initiator](image)
    - 3-5%

  - ...plus flow and other additives: 2-4%

- HDODA a “reactive diluent”: does not contribute much to coating end-properties
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- **Hypothesis:** 1,5-PDO can substitute 1,6-HDO in HDODA with little effect on properties or need for reformulation
Summary

- Pyran has proprietary process to produce renewable 1,5-pentanediol (1,5-PDO)

- 1,5-PDO replaces oil-based 1,6-hexanediol at 30% lower costs with enhanced properties in polyester and polycarbonate polyols

- Low-cost 1,5-PDO enables breakthrough in polycarbonate polyols as higher-quality replacement to polyesters/ethers
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