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

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C4-C6 Diols Market and End-use

Pyran

biomass

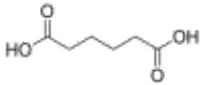
$1B/yr Global Market
8% CAGR

1,5-PDO
1,6-HDO

Polyesters
Polycarbonates
Acrylates

Co-monomer

Adipic Acid



Paints

Coatings

Plastics

Adhesives

1,5-Pentanediol (1,5-PDO)

$6000/ton → **$2500-3000/ton**

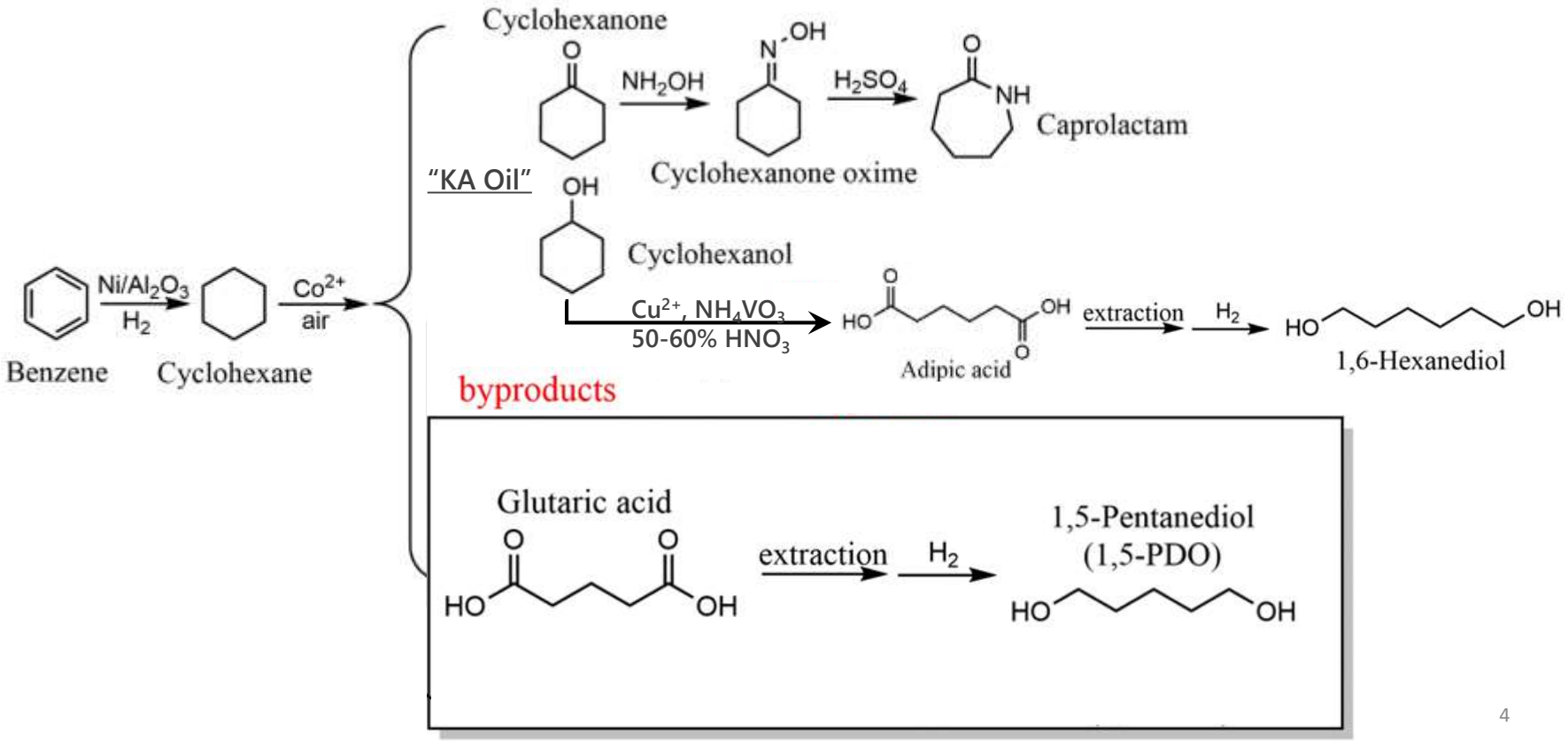
Renewable 1,5-PDO

1,6-Hexanediol (1,6-HDO)

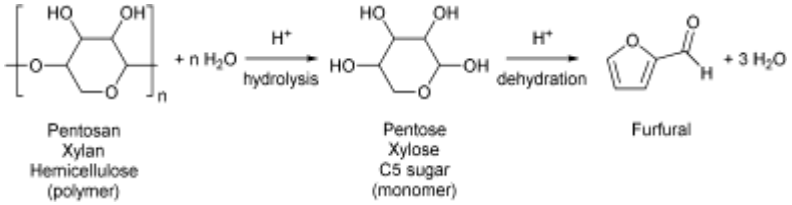
$3000-4700/ton

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



Furfural synthesized from five-carbon (C5) hemicellulose fraction of biomass

- 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

Source: IHS Chemical Report-Furfural, 2016

GlucanBio

- Process combines biomass fractionation with chemical production

- >80% of the initial wood converted to products:

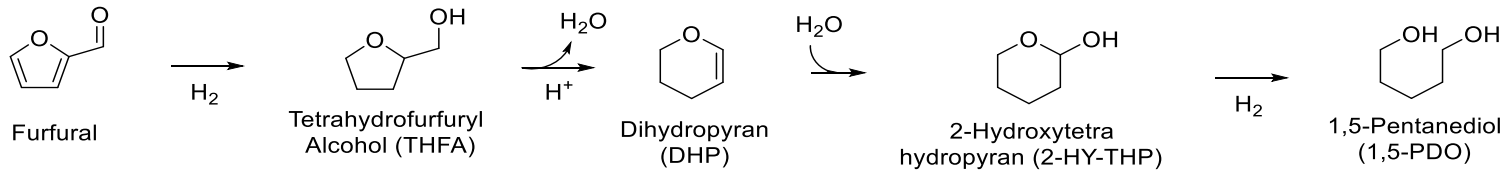
1. High purity cellulose
2. Furfural
3. High purity lignin
4. Acetic acid
5. Formic acid
6. Levulinic acid

- >$500 revenues per MT of wood

- **High biomass loading 20-30 wt%**

D.M. Alonso et al. Science Advances 3 (5), e1603301

Furfural to 1,5-PDO Reaction Scheme



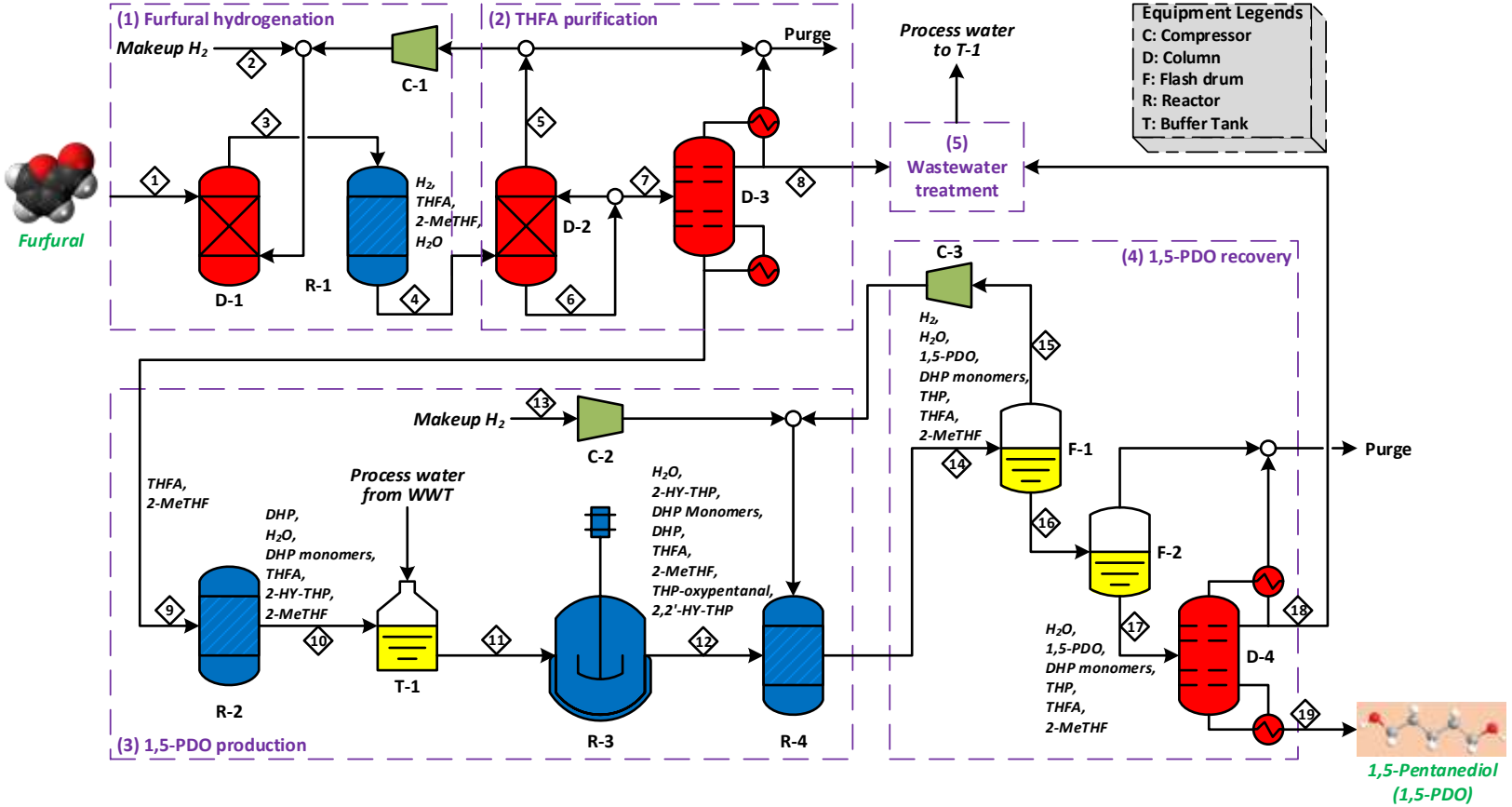
High yields demonstrated for each step in continuous flow reactors:

- **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
3) Conversion of Furfural to 1,5-Pentanediol: Process Synthesis and Analysis, 2017. *ACS Sustainable Chemistry & Engineering* 5, 4699-4706.

Process Flow Diagram

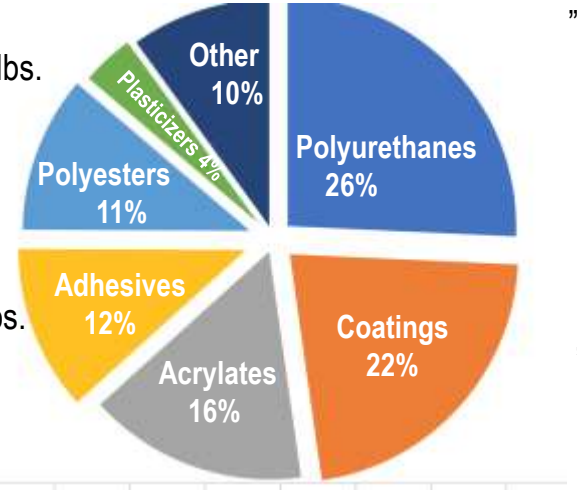


Key Technological Advantages

- 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.
Powder Coating. Resins	42
Resins	12
Coatings, others	

"Adhesives"	MM lbs.
Polyester	37
PU	20

"Acrylates"	MM lbs.
Monomer (Mainly HDODA)	75

"Polyurethanes"	MM lbs.
Cast Elastomers	50
TPU's	34
"Coatings"	40

- SB Liquid
- PUD's
- Synthetic Leather

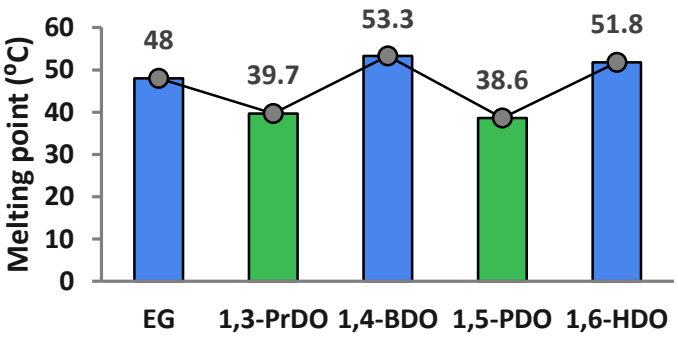
"Coatings"	MM lbs.
Sat Polyester	53
Polyester Powder (incl some PU Powder)	53

1,5-Pentanediol used as monomer in several polymer groups

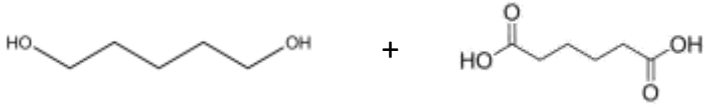
Focus of presentation:

- Polyester Polyols
- Polycarbonate Polyols
- UV-Cure Diacrylates

Polyester Polyols:
Diol-adipates show odd-even effect



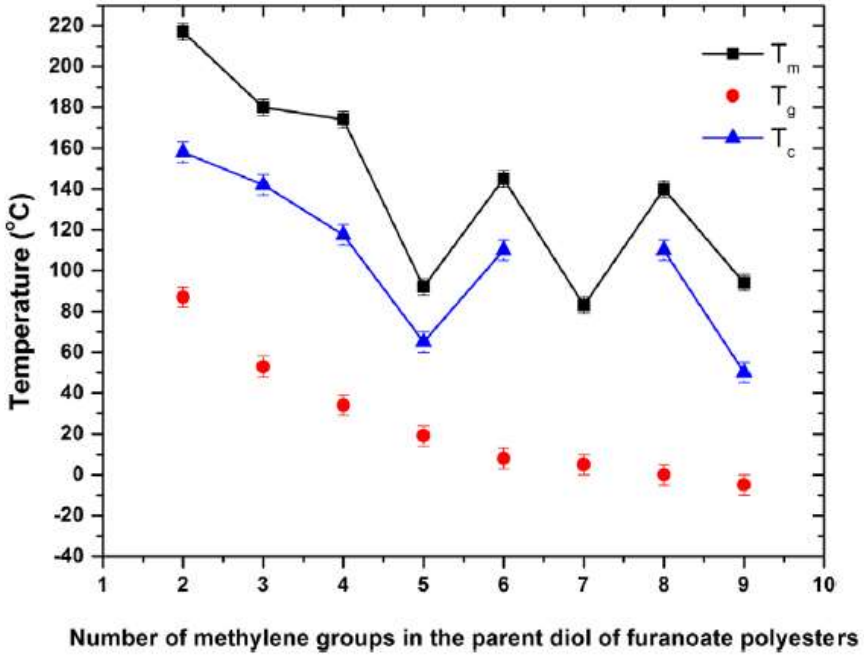
Polyester Polyol =
Linear Diol + Adipic Acid



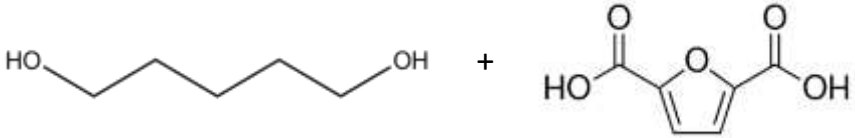
Diol	MW (g/mol)	OH number (mg KOH/g)	Acid number	Viscosity (cP)	Glass transition (°C)	Melting transition (°C)
1,2-ethanediol (EG)	2114	52.8	0.53	1334	-46.9	48.0
1,3-propanediol (1,3-PrDO)	2029	55.3	0.36	1471	-59.7	39.7
1,4-butanediol (1,4-BDO)	2110	53.2	0.61	1482	-53.7	53.3
1,5-pentanediol (1,5-PDO)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

Source: DuPont Tate & Lyle BioProducts

Polyester Polyols:
Diol-furanoates show odd-even effect



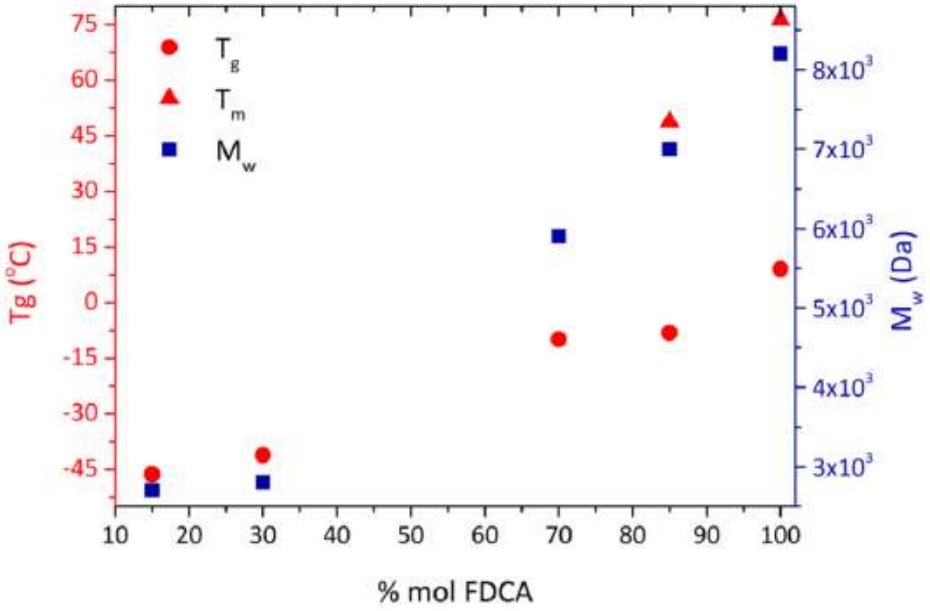
Polyester Polyol =
Linear Diol + Furandicarboxylic acid (FDCA)



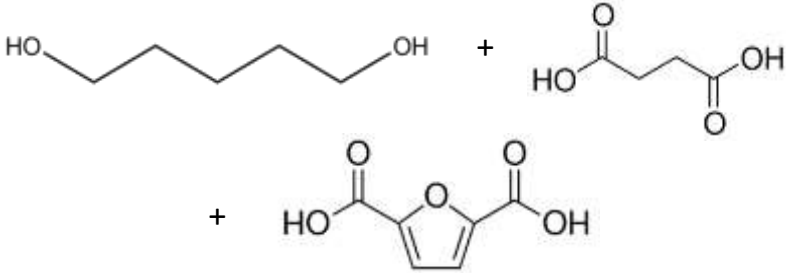
100% renewable resin!!!

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, characterization, process simulation and multiobjective optimization of biomass-derived renewable polyesters: An integrative study toward a sustainable polymer industry." Thesis. August 2017.
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:
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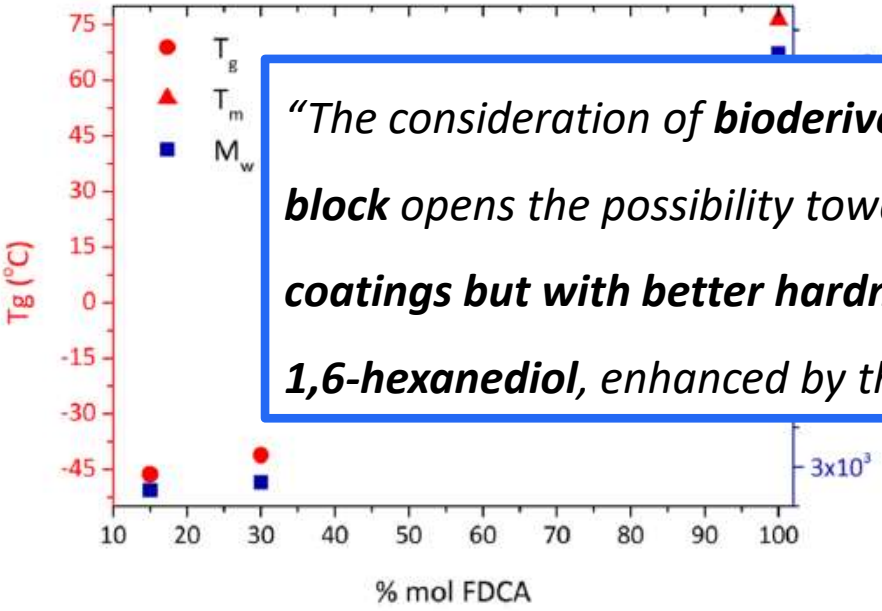
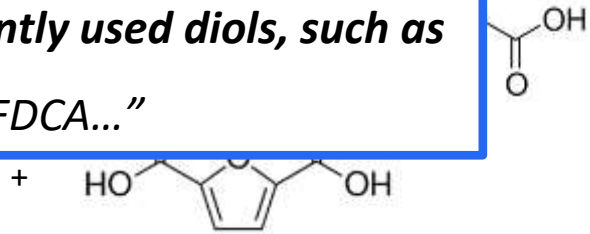


Polyester Polyol =

id +
A)



*"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, characterization, process simulation and multiobjective optimization of biomass-derived renewable polyesters: An integrative study toward a sustainable polymer industry." Thesis. August 2017.
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

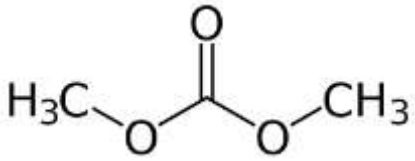
Coatings

Synthetic Leather

Flooring

Renewable polycarbonate diol for enhanced polyurethane applications

- **Monomer #1:** Dimethyl carbonate

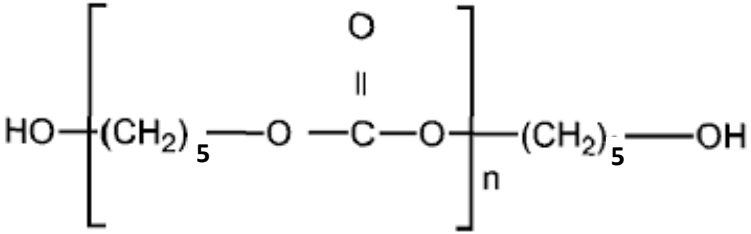


- Produced from methanol and CO via oxycarbonylation

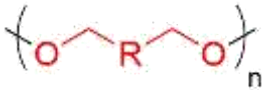
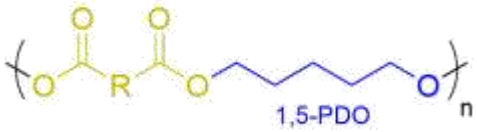
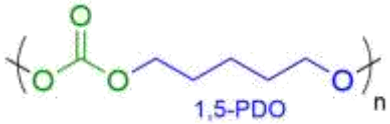
- **Monomer #2:** 1,5-Pentanediol (1,5-PDO)

- Produced from furfural via Pyran's technology

- **Polymer:** Polycarbonate polyol



Polycarbonate Polyols (PCPs) provide value-added properties over Polyesters & Polyethers

	Polyether Polyol	**Polyester Polyol**	**Polycarbonate Polyol**
			
Heat Stability:	Poor	Good	Excellent
Chemical Stability:	Poor	Fair	Good
Hydrolysis Stability:	Good	Poor	Excellent
Cost:	Low	Moderate	High

* 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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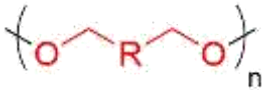
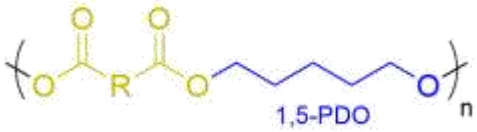
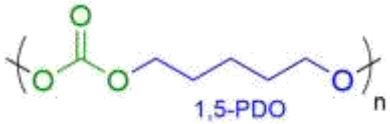
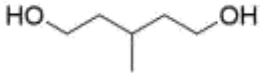
			
Heat Stability:	Poor	Good	Excellent
Chemical Stability:	Poor	Fair	Good
Hydrolysis Stability:	Good	Poor	Excellent
Cost:	Low	Moderate	High

	Oil-based 1,5-PDO	Oil-based 3MPDO	Oil-based 1,6-HDO	Renewable 1,5-PDO
Monomers:				
Price:	**$6000/ton**	**$5000/ton**	**$4500/ton**	**<$3000/ton**

Polycarbonate Polyols made from 1,5-pentanediol are "greener" and more easily processed

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

Polycarbonate Polyol Type	MW (g/mol)	OH Value (mg KOH/g)	Acid Value (mg KOH/g)	Viscosity (cps @ 75 ˚C)	Melting Range (˚C)	Appearance
HDO Homopolymer	2000	51-61	<0.1	1900-2600	**36-50**	**Solid**
PDO:HDO Co-polymer	2000	51-64	<0.1	1600-3400	**N/A**	**Liquid**

- 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

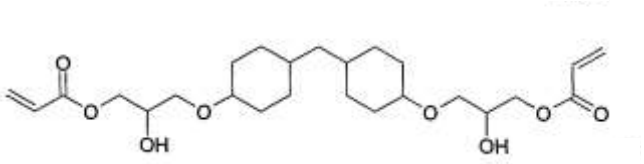
[a] Data summarized from Asahi Kasei (http://www.asahi-kasei.co.jp/pcdlhp/en/product.html), Ube Industries ("Polycarbonates Eternacoll"), Tosoh (https://www.tosoh.com/Image%20Library/Trading%20Companies/Polyurethanes/Polyols/specPolycarbonateDiols.gif) , and Daicel ("Placecel Polyester Polyol") Technical Guides

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

- **Example chemistry:**

Acrylated Oligomer

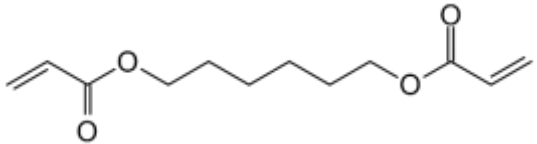
Epoxy acrylate



30-60%

Acrylic monomer

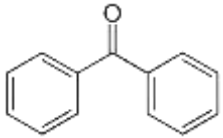
Hexanediol diacrylate (HDODA)



20-60%

Photo-initiator

Benzophenone

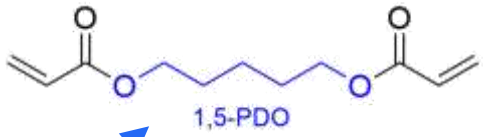


3-5%

…plus flow and other additives: 2-4%

- HDODA a “reactive diluent”: does not contribute much to coating end-properties

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



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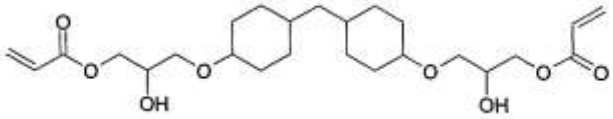

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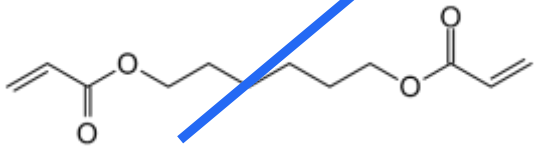

20-60%

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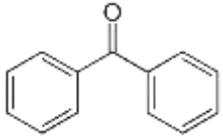

3-5%

…plus flow and other additives: 2-4%

- HDODA a “reactive diluent”: limited contribution to coating end-properties
- **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

Pyran

Renewable chemicals for everyday plastics

Kevin Barnett

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