Kevin Barnett
CEO, Pyran
kjbarnett@pyranco.com

Bio-based Pentanediol Diacrylate (PDDA): A New Renewable Monomer for the UV and EB Curable Industry

Daniel McClelland, PhD
Kevin Barnett, PhD

Abstract

Pyran has developed a novel process to manufacture renewable 1,5-pentanediol (1,5-PDO) - a building block chemical used to produce coatings, adhesives, and plastics – at <25% of the cost of similar oil-based chemicals. Pyran's 1,5-PDO is made from furfural, a chemical derived from renewable hemicellulose (biomass) sources such as wood and crop wastes. 1,5-PDO can be used to synthesize 1,5-pentanediol diacrylate (PDDA), a multifunctional acrylic monomer for use in UV and EB cure formulations. Acrylic monomers are currently used in energy cure formulations to reduce viscosity and increase crosslink density.[1] Currently, hexanediol diacrylate (HDDA) produced from oil-based 1,6-hexanediol (1,6-HDO) is a widely used acrylic monomer in UV and EB cure formulations. Pyran tested our hypothesis that PDDA produced from 1,5-PDO could replace HDDA in most applications with little effect on properties or need for intensive reformulation. A baseline comparison of PDDA and HDDA in formulations for 4 key UV/EB cure applications found that PDDA produces nearly identical properties compared to HDDA in most formulations, with opportunities for improved performance in ink jet and adhesives formulations. **Incorporating Pyran's 1,5-PDO into UV/EB cure formulations presents an opportunity for significant cost savings while improving the sustainability of UV/EB curable products.**

Current Diols Market

Diols are a class of chemicals used by the chemical industry to produce pre-polymers for the manufacturing of paints, coatings, plastics, and adhesives (**Figure 1**). These pre-polymers are made by reacting a functional co-monomer (such as acrylate, adipic acid, etc.) with 4- to 6-carbon (C4-C6) α,ω-diols. Currently these C4-C6 diols are manufactured from oil (petroleum), using complex, expensive, and hazardous processes. Pyran's renewable 1,5-PDO is expected to be able to quickly replace two oil-based diols – 1,5-PDO and 1,6-hexanediol (1,6-HDO) – across a wide variety of applications and market segments. A rigorous technoeconomic analysis validated by the U.S. Department of Energy (DOE) and a large chemical company indicates that Pyran's 1,5-PDO can be produced at 50% lower costs versus oil-based 1,5-PDO and 25% lower costs versus oil-based 1,6-hexanediol (1,6-HDO),[2] and can therefore immediately deliver a strong value proposition for these markets.

Figure 1. Major market uses for 1,5-PDO and 1,6-HDO.

Production of 1,5-Pentanediol

1,5-PDO is currently manufactured in small volumes as a byproduct in the production of Caprolactam and 1,6-HDO from benzene (**Figure 2).** This route involves numerous reaction steps with low conversions, high separation and recycle costs, and flammability hazards, leading to higher production costs and poor economics.[5,6]

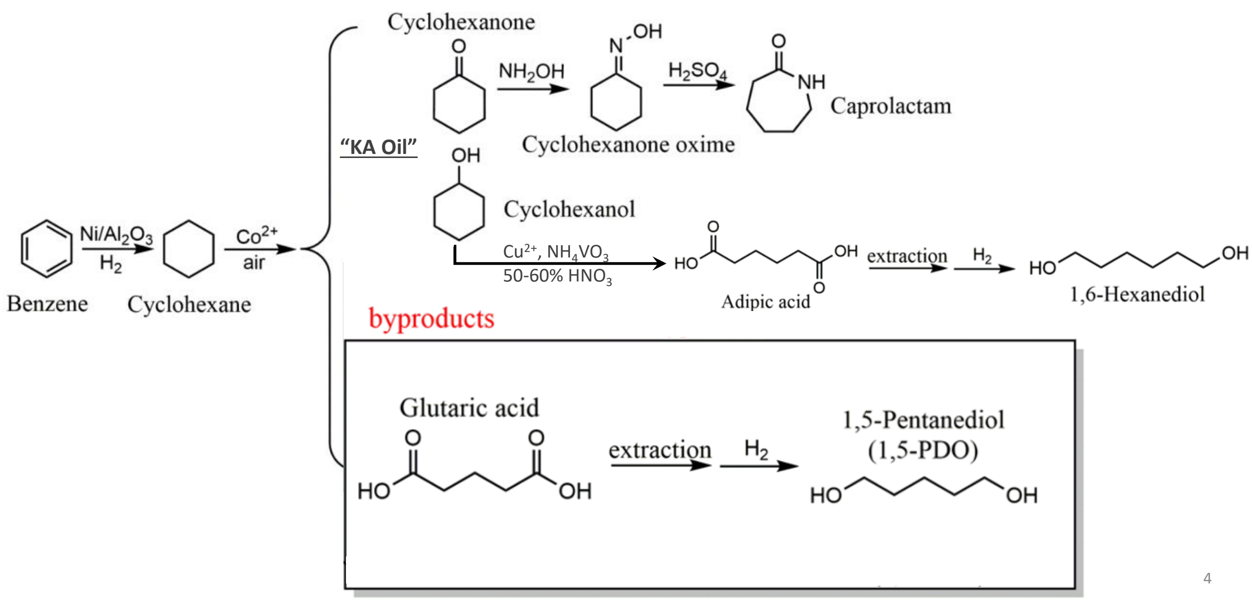

Figure 2. Production of Caprolactam, 1,6-Hexanediol, and 1,5-Pentanediol from oil-derived benzene.

Pyran's Innovation

Pyran uncovered and improved upon a novel 4-step chemical pathway to produce 1,5-PDO from biomass-derived furfural with high economic potential (**Figure 3**). Pyran's process to produce 1,5-PDO starts from the renewable 5-carbon platform chemical, furfural. Furfural is produced primarily from corn cobs but can also be produced from wood wastes and other agricultural residues. Globally, over 600,000 MT of furfural capacity was available as of 2015.[6] No commercial process currently exists that converts furfural into 1,5-PDO. Pyran's approach is lower-cost and contributes less to climate change than current approaches because it uses carbon from biomass resources instead of petroleum. Pyran's rigorous economic and life cycle models have shown that it can have over three times cost reduction and >60% lower carbon footprint than petroleum-derived diols.[2]

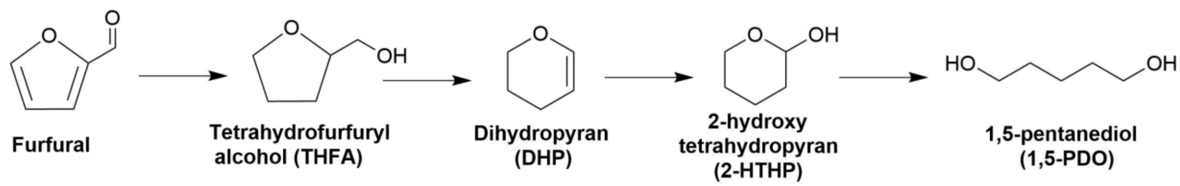

Figure 3. Pyran's novel route to produce 1,5-pentanediol from biomass-derived furfural.

Pyran's process comes with significant advantages that correspond to our high yields and low selling price:

1. Stable and inexpensive catalysts
2. Clean process – no solvent or water solvent
3. No byproducts (only wastewater)
4. No liquid recycle streams
5. Thermochemical conversion (vs. biological)

1,5-PDO in UV and EB Cure Coatings

UV and EB cure coatings are produced by polymerizing a mixture of chemicals that include an epoxy acrylate oligomer, a multifunctional acrylic monomer, and a photo-initiator (**Figure 4**). Hexanediol diacrylate (HDDA) produced from oil-based 1,6-hexanediol (1,6-HDO) is a widely used multifunctional acrylic monomer for these formulations. Pyran's 1,5-PDO can produce an acrylic monomer called pentanediol diacrylate (PDDA) which could be used to replace HDDA in these formulations.

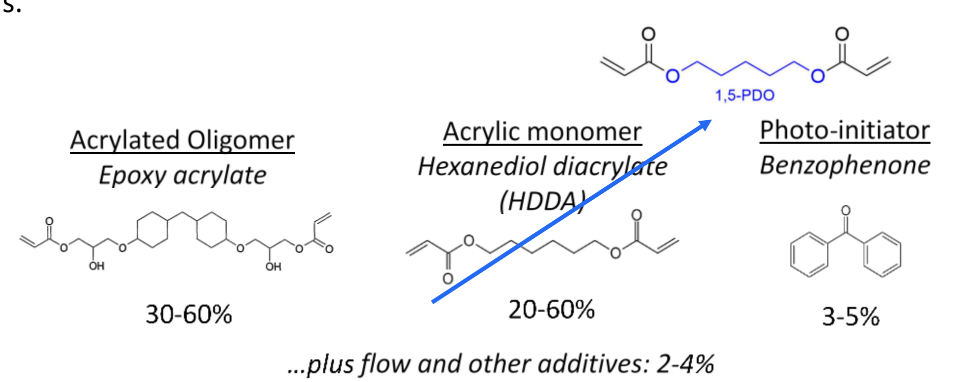

Figure 4. A typical UV/EB cure formulation. 1,6-hexanediol-based HDDA can be replace with 1,5-pentanediol-based PDDA as the acrylic monomer.

HDDA is used in UV/EB cure formulations as "reactive diluent" mostly to lower overall viscosity and has limited contribution to end-properties.[1] **Pyran hypothesized that PDDA could replace HDDA in most applications with little effect on properties or need for intensive reformulation.**

UV/EB Cure Markets- Basis for comparison of PDDA and HDDA

The UV/EB cure market encompasses a large variety of applications as displayed in **Figure 5.** Graphic arts-OPV, graphic arts-inks, and wood coating are the majority by volume at 26%, 22%, and 18% respectively and as such, our testing has focused on formulations for these applications. Additionally, we have tested a formulation for adhesives which requires properties dissimilar to the other applications.

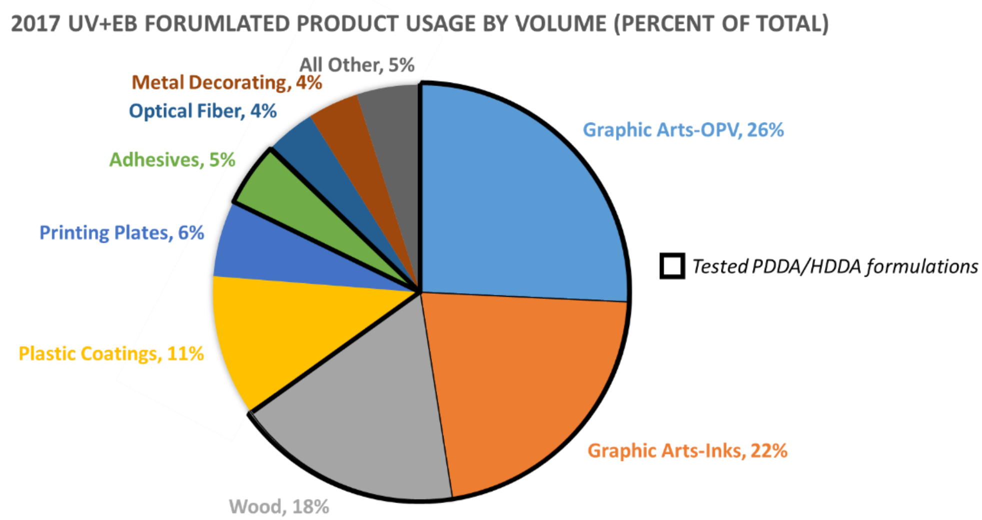

Figure 5. North American UV Cure Market by volume percent. Modified from Cohen, G. In North American Market Overview, RadTech 2018, Chicago, IL, 2018.[8]

PDDA versus HDDA – Baseline Comparison

Generic formulations with PDDA and HDDA were made for four applications, overprint varnishes (OPV), ink jet, wood coatings, and adhesives. These formulations were compared by their tensile, flexural, and other physical properties to understand the difference induced by using PDDA instead of HDDA. The generic formulations for each application are displayed in **Table 1** where higher monomer contents of PDDA and HDDA were utilized to observe the outsized effects on the coating properties. True formulations will vary greatly but these generic formulations provide a baseline comparison for utilizing PDDA in a formulation over HDDA.

Table 1. UV cure formulations tested with HDDA and PDDA

Formulation	Components	Ratio
OPV	**HDDA or PDDA**/PE2120/CPK	**50** / 50 / 3
Ink jet	**HDDA or PDDA**/PEA/CPK	**50** / 50 / 3
Wood	**HDDA or PDDA**/CN992/CN374/CPK	**47.5** / 47.5 / 5 / 3
Adhesive	**HDDA or PDDA**/CN975/IBOA/SB405/CPK	**40** / 30 / 20 / 10 / 3

Tensile Properties

A cured type IV bar (35 x 6 x 0.5 mm gauge, width, thickness) was prepared for each formula and pulled at 10 mm/min with the results displayed in **Figure 6**. The PDDA OPV and wood coating formulations had minimal variations in the tensile modulus, strength, and elongation. The PDDA ink jet formulation had increased tensile modulus and strength over the HDDA formulation with minimal differences in tensile elongation. Additionally, the PDDA adhesive formulation had increased tensile strength and elongation with similar tensile modulus. Overall the PDDA formulations performed similarly with increased performance in select areas.

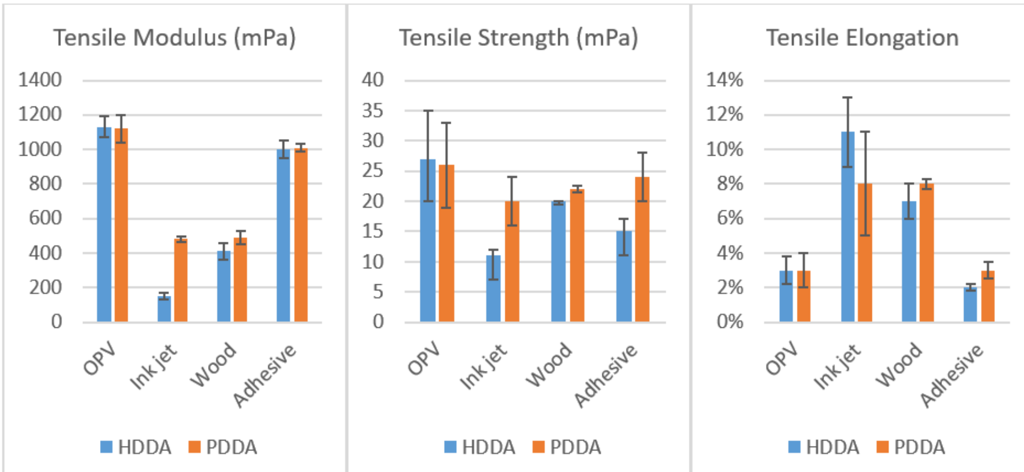

Figure 6. Comparison of tensile properties between HDDA and PDDA formulations for OPV, ink jet, wood coatings, and adhesives.

Flexural Properties

The flexural properties were tested using a 20 x 2 x 2 mm bar with a 1 mm/min test and the results are displayed in **Figure 7**. The HDDA and PDDA formulations had minimal differences for the OPV, wood coating, and adhesives in flexural modulus, strength, and deflection. The PDDA formulation provided improved flexural modulus and strength and decreased deflection for the ink jet formulation. The PDDA formulations as a whole performed very similarly to the HDDA formulations with improved properties for the ink jet formulation.

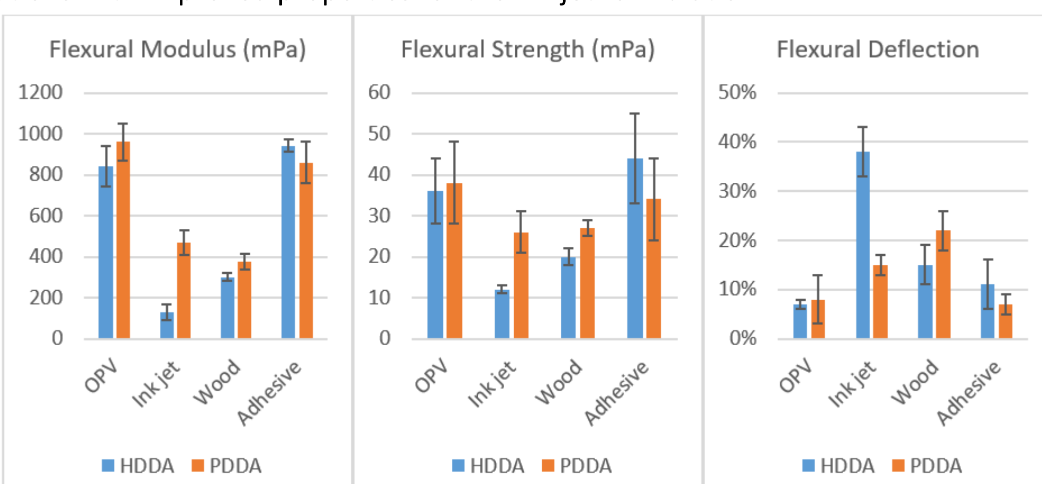

Figure 7. Comparison of flexural properties between HDDA and PDDA formulations for OPV, ink jet, wood coatings, and adhesives.

Other Physical Properties – Viscosity, Shore Hardness, Tack-free belt speed

The HDDA and PDDA formulations were also tested for viscosity, shore hardness, and tack-free belt speed which are displayed in **Figure 8** along with the final acrylate conversion. The viscosities were tested with Brookfield Viscometer and HDDA and PDDA formulas were found to be similar. The shore hardness was determined with a Shore D durometer on disks approximately 1 mm thick while the tack-free belt speed was determined by drawing down a coating using a #100 bar (250 mil) and running the material under a conveyer system at various speeds. Both the shore hardness and tack-free belt speeds were found to be similar for HDDA and PDDA formulations. Acrylate conversion was determined with a Nicolet 6700 FTIR and was monitored in real time. The final acrylate conversions were found to be lower in the PDDA formulations though this was not considered detrimental since the other properties for PDDA formulations were found to be similar or improved over the PDD formulations.

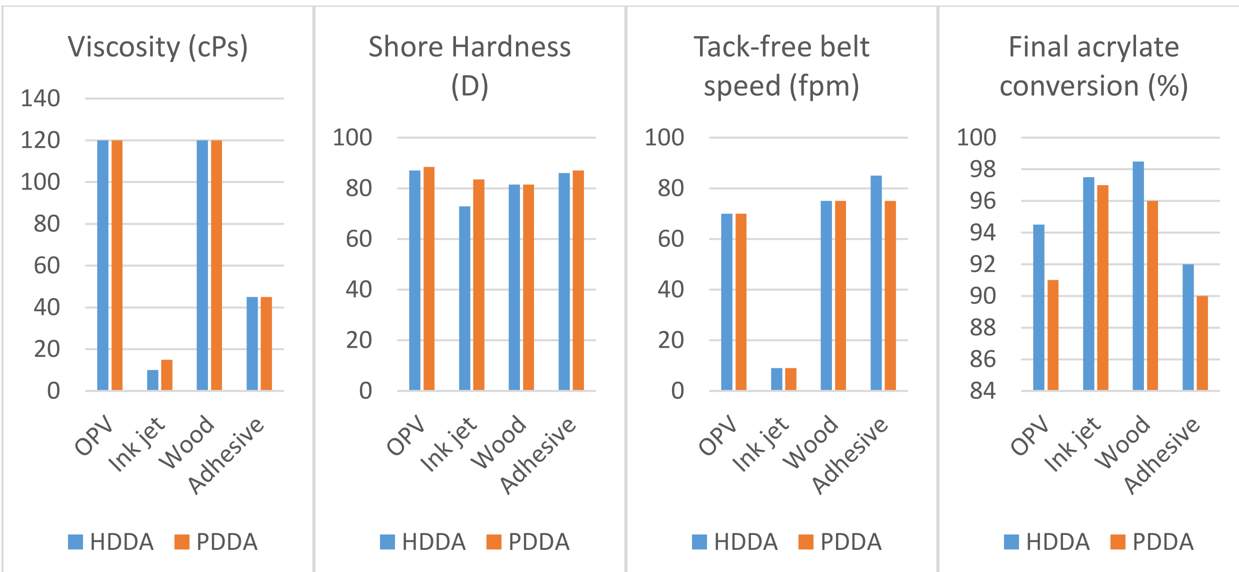

Figure 8. Comparison of other physical properties between HDDA and PDDA formulations for OPV, ink jet, wood coatings, and adhesives.

Lastly, the adhesive properties were tested with ASTM 3359-09 on glass, PC, ABS, and Delrin with the results displayed in **Table 2**. The adhesive properties were found to be the same for HDDA and PDDA formulations on all surfaces. Overall, the properties of the PDDA formulations were similar to the HDDA formulations aside from the final acrylate conversion which although lower for PDDA formulations did not appear to have an effect on the physical properties cured formulations.

Table 2. Comparison of HDDA and PDDA formulations for adhesive properties on various substrates.

	Glass	PC	ABS	Delrin
Adhesive-HDDA	0/25- 0B	25/25- 5B	25/25- 5B	0/25- 0B
Adhesive-PDDA	0/25- 0B	25/25- 5B	25/25- 5B	0/25- 0B

PDDA Synthesis

Pyran is currently performing testing the production and applications of PDDA from Pyran 1,5-PDO. On the lab scale we are testing the production of PDDA and HDDA through the transesterification of commercial 1,6-HDO and 1,5-PDO with methyl acrylate and methyl methacrylate. This process will later be tested with Pyran produced PDO to identify and eliminate differences incurred from the production of Pyran 1,5-PDO. After the initial lab scale testing, the process is being scaled up to produce liter quantities of PDDA from Pyran PDO for further application testing. With this, we plan to confirm that PDDA from Pyran 1,5-PDO is able to replace currently used petroleum based HDDA in various UV and EB cure applications.

Conclusion

Pyran's low-cost renewable 1,5-pentanediol (1,5-PDO) presents a promising new molecule for the UV and EB cure industry. 1,5-PDO can be used to synthesize 1,5-pentanediol diacrylate (PDDA) as a potential replacement for hexanediol diacrylate (HDDA), a widely used acrylic monomer in UV/EB cure formulations. PDDA produced from our 1,5-PDO could potentially replace HDDA in many formulations without need for intensive reformulation. A baseline comparison of PDDA and HDDA in formulations for 4 key UV/EB cure applications found that PDDA produces nearly identical properties compared to HDDA, with potential properties improvements in ink jet and adhesive formulations. Pyran's 1,5-PDO presents an opportunity for the UV/EB cure industry to lower costs while supporting a sustainable product.

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