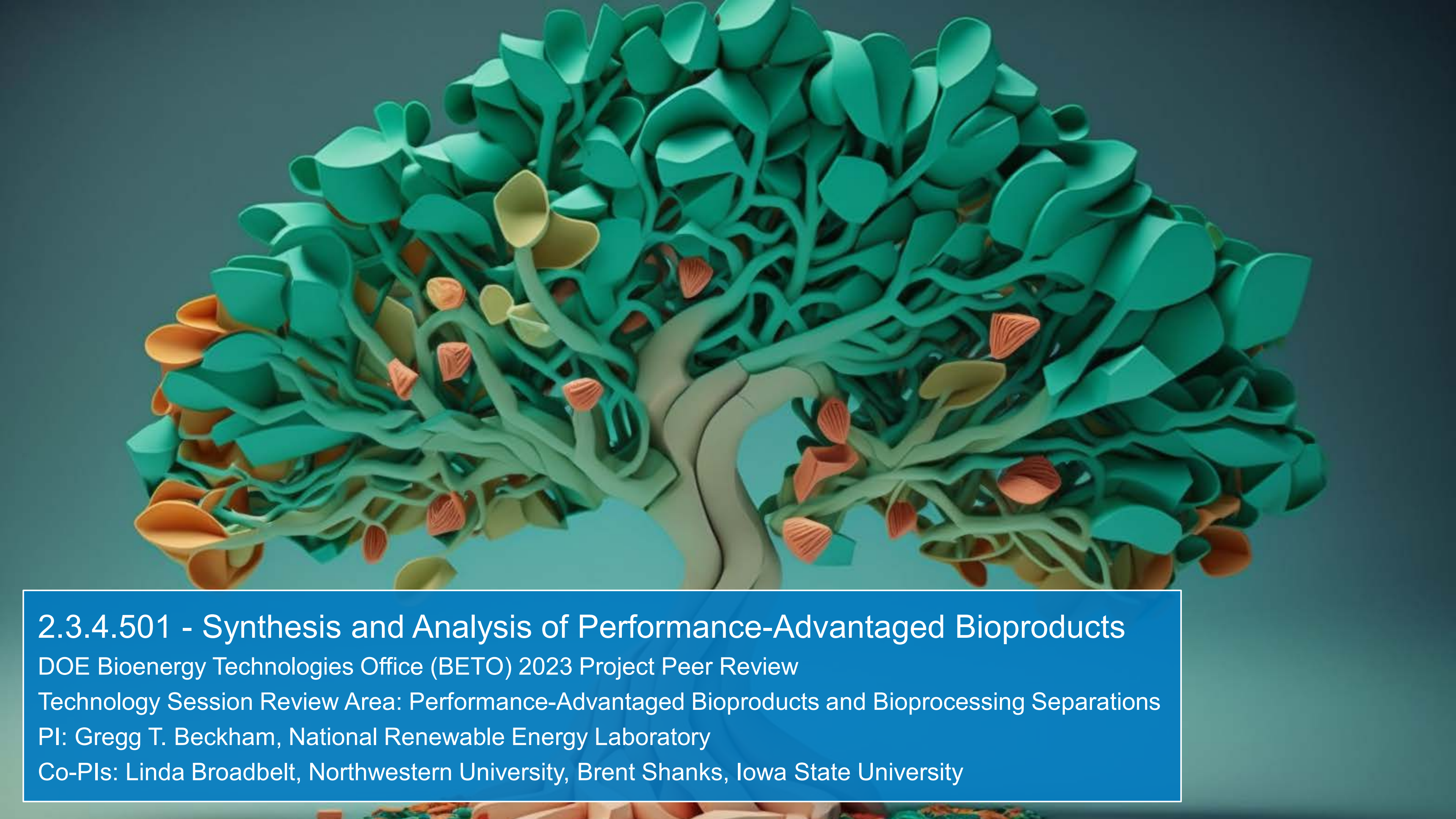


# 2.3.4.501 - Synthesis and Analysis of Performance-Advantaged Bioproducts

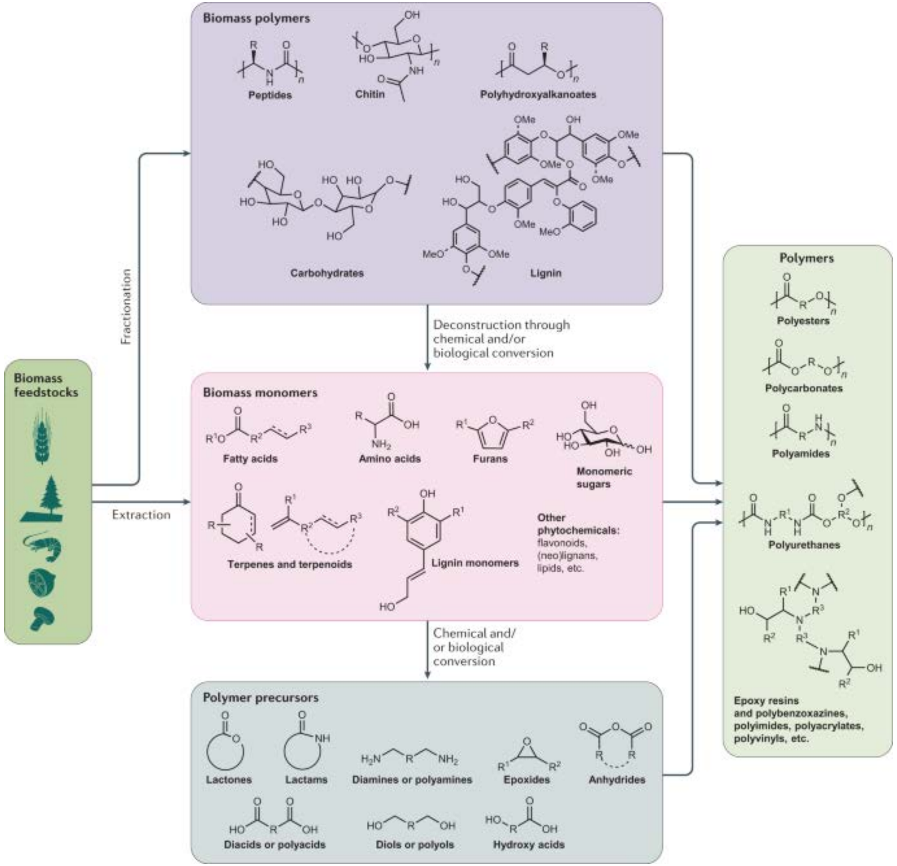
DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Technology Session Review Area: Performance-Advantaged Bioproducts and Bioprocessing Separations

PI: Gregg T. Beckham, National Renewable Energy Laboratory

Co-PIs: Linda Broadbelt, Northwestern University, Brent Shanks, Iowa State University

# Project overview



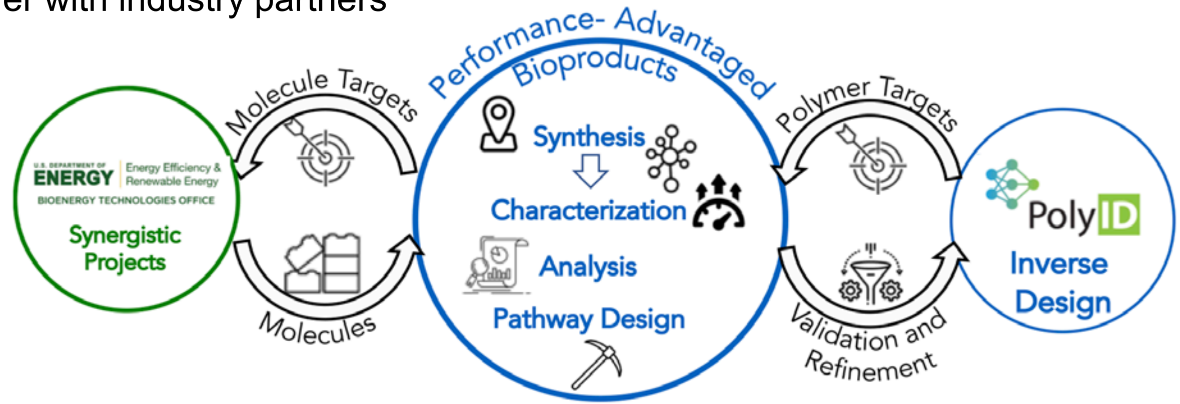
Cywar, Rorrer *et al.* *Nature Reviews Materials* 2022

**Goal:** develop bioproducts that exhibit performance-advantaged properties and conduct corresponding techno-economic analysis, life cycle assessment, and modeling (meets major BETO 2030 goal)

- Bio-based intermediates are functionally-rich building blocks for PABPs
- Collaborate with Inverse Design project
- Source compounds from BETO projects and academic and industrial collaborators
- Focus initially was on bio-based polymers; have transitioned to bio-based polymers and small molecules
- Quantitative metric: screen 50 candidate PABPs in each 3-year AOP cycle, develop ≥10 PABPs
- Engaged in Energy I-Corps to understand market potential for several candidate PABPs
- Project started in FY18

# 1 – Key elements of our technical approach

- Analysis using Aspen for TEA, MFI for supply-chain analysis, and LCA with SimaPro
- Source new building blocks from sugar-derived intermediates, lignin-derived aromatic compounds, lignin-derived intermediates, and more
- Design collaborations with “molecule providers” who have promising technologies
- Focus on both polymers and small molecule PABPs
- Computational method development using PickAxe tool to identify optimal pathways to target molecules (Broadbelt, Shanks)
- Collaborate with Inverse Design to produce and characterize polymers for polyID
- Technology transfer with industry partners



# Milestones and risks in the project

## Risks and mitigation:

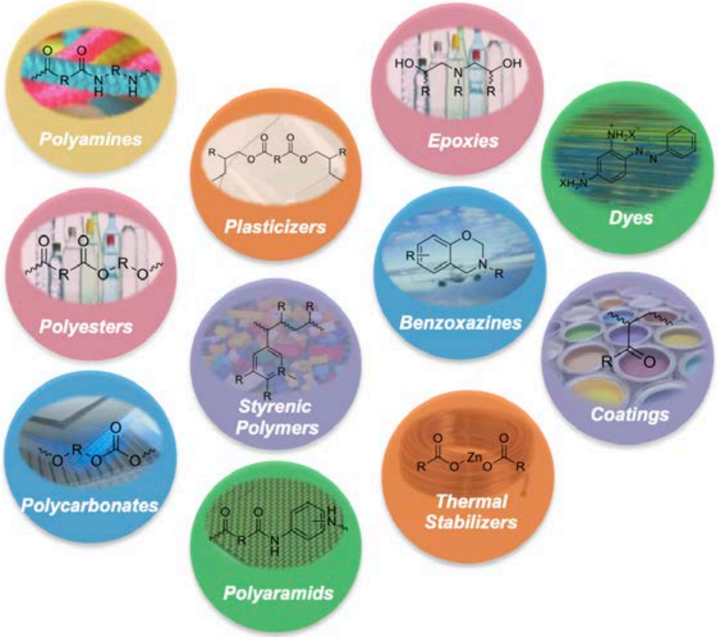
- **Risk**: Properties for some materials are not readily accessible or known
- **Mitigation**: Active tech. transfer, industrial engagement (Energy I-Corps, Tech. Comm. Fund, Directed Funding Opportunities)
- **Risk**: Syntheses for new molecules can be time consuming and expensive
- **Mitigation**: Hired synthetic chemist, work with other BETO projects and partners to source compounds

## Management, communication, & DEI:

- Monthly meetings; *ad hoc* meetings with BETO projects
- Dedicated Project Managers – lab space, equipment, reporting, finances
- Dropbox for data storage/transparency
- Prioritize creating physically and psychologically safe research environments

## Milestones

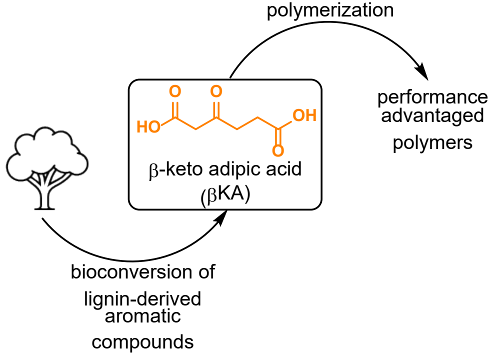
- FY21: ≥ 5 polymers from polyID predicted to be PABPs
- FY22: Energy and GHGs of commodity chemicals
- FY23: ≥50 PABPs, ≥10 as PABPs w/in 25% cost of incumbent



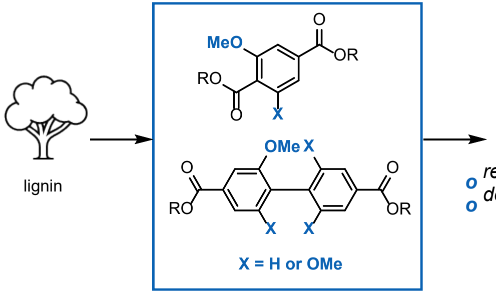
# 2 – Outline of progress and outcomes

## Baselining organic chemical manufacturing energy and GHGs

## β-ketoadipic acid-based polymers



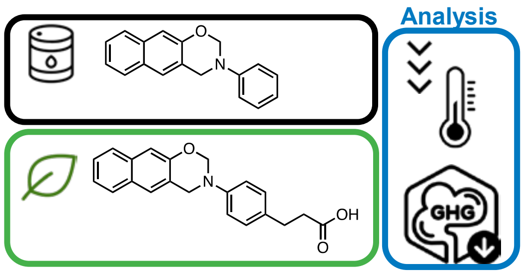
## Lignin-based polymers and plasticizers



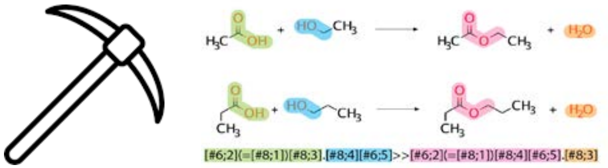
**polyesters and plasticizers**

- *renewable feedstocks*
- *decreased toxicity*

## Organonitrogen compounds for thermosetting materials



## Computational methods to predict optimal synthesis pathways



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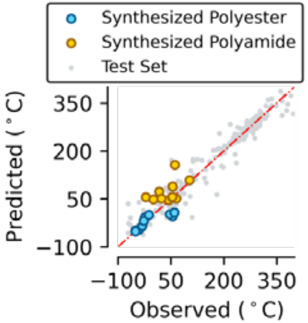
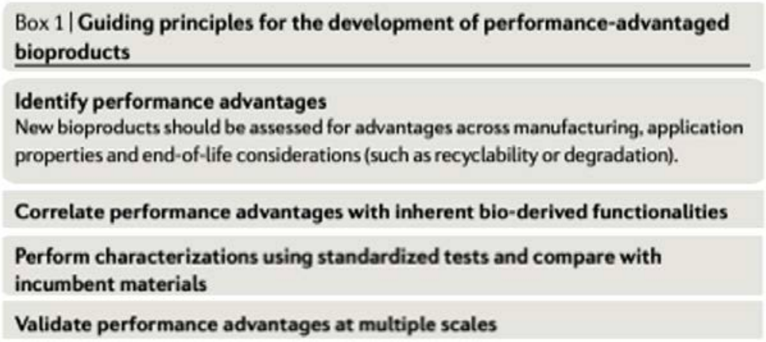
## Synthesis & characterization for polyID



PolyID

# Defining performance advantages and approach to characterize PABPs



Box 1 | **Guiding principles for the development of performance-advantaged bioproducts**

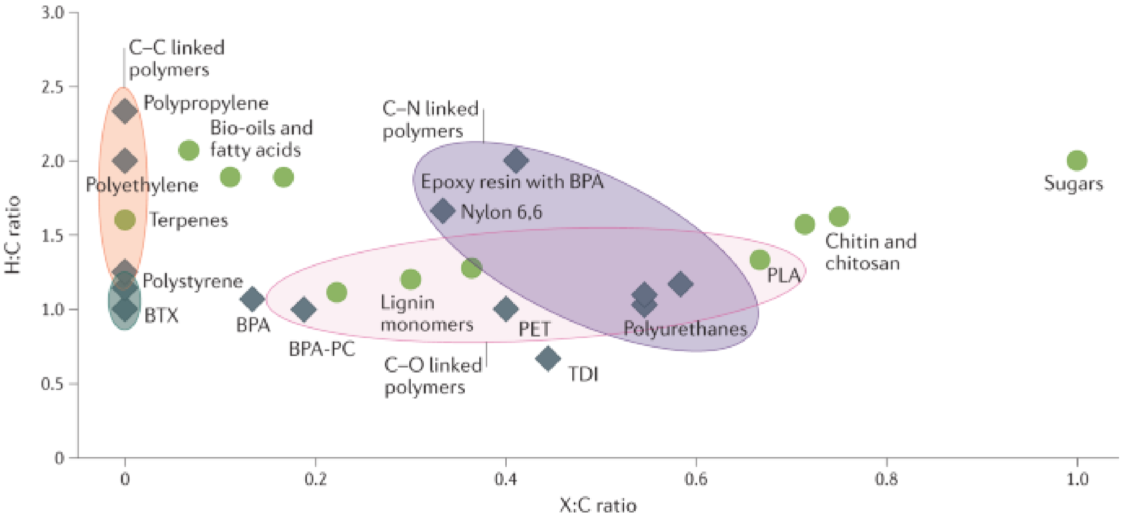
**Identify performance advantages**
New bioproducts should be assessed for advantages across manufacturing, application properties and end-of-life considerations (such as recyclability or degradation).

**Correlate performance advantages with inherent bio-derived functionalities**

**Perform characterizations using standardized tests and compare with incumbent materials**

**Validate performance advantages at multiple scales**

When assessing PABPs, baseline performance against incumbent products

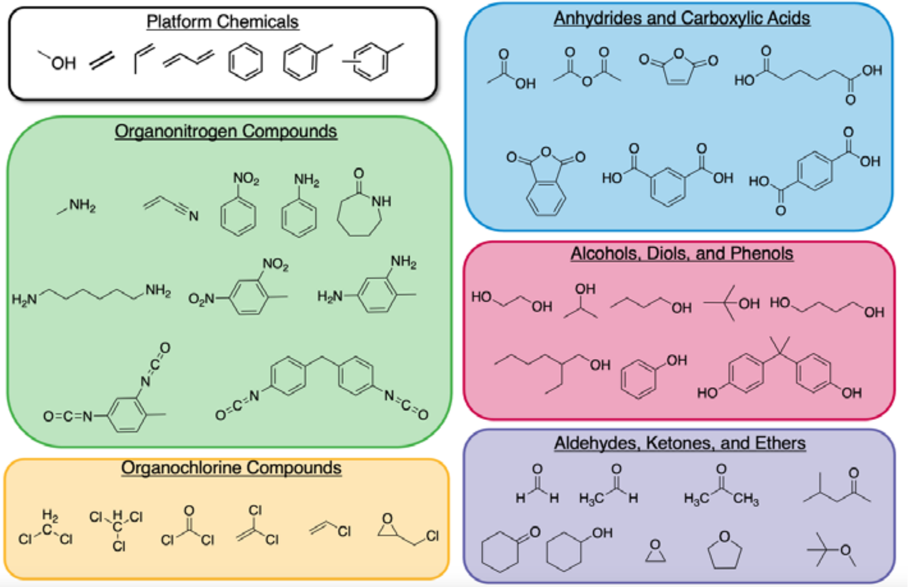


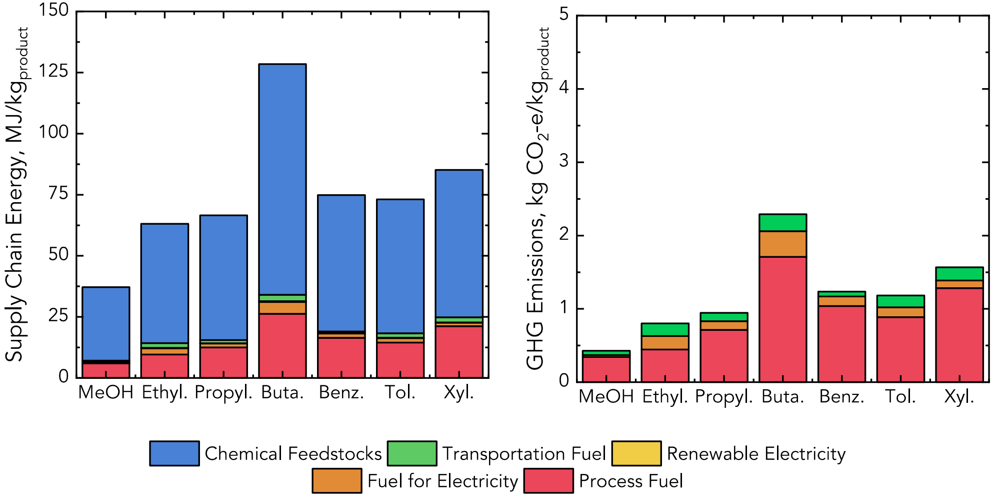
High heteroatom content (i.e. O, N) of bio-derived compounds makes them ideal for PABPs

**Performance advantages possible in 1) manufacturing, 2) performance, and 3) end-of-life**

Cywar, Rorrer *et al. Nature Rev. Mater.* 2022

# Baseline supply-chain analysis for commodity organic petrochemicals





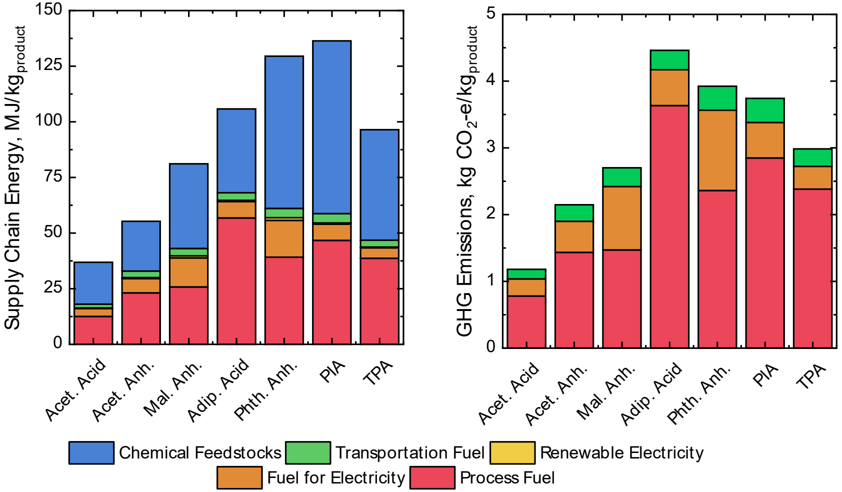
**These data serve as a baseline for energy/GHG emissions in manufacturing**

- Used Materials Flows through Industry tool to quantify energy and GHG emissions for US supply chains
- Examined all organic petrochemicals produced globally over 1 MMT/year

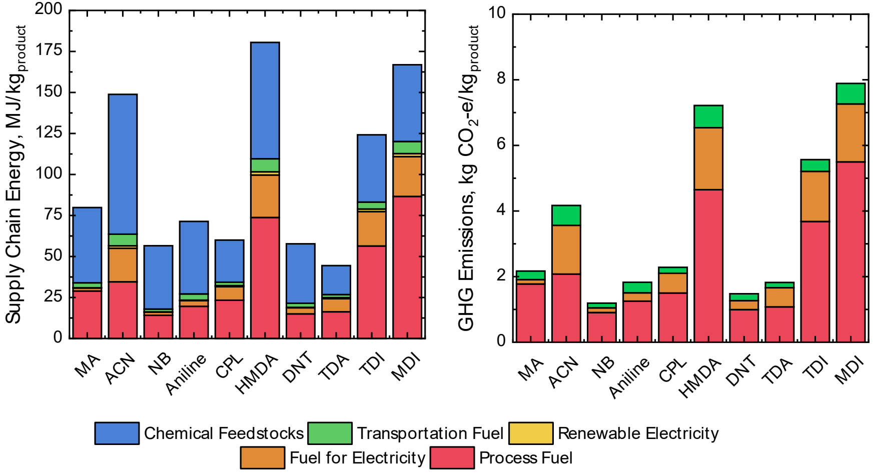
Nicholson, Rorrer *et al. ACS SusChemEng* 2023

# Analysis highlights opportunities in heteroatom-containing chemicals

CHO chemicals



CHN and CHNO chemicals



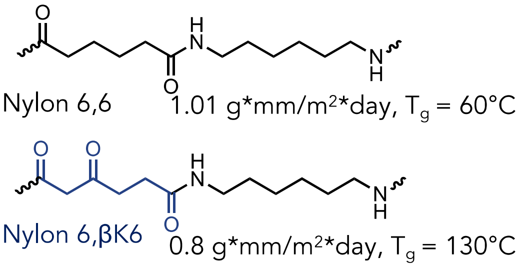
**CHO, CHN(O) chemicals exhibit highest energy/GHG emissions of all chemical classes evaluated**

- For oxygenates, GHG emissions increase typically based on increasing process fuel use
- Organonitrogen compounds exhibit the highest supply chain energies and GHG emissions evaluated

Nicholson, Rorrer *et al. ACS SusChemEng* 2023

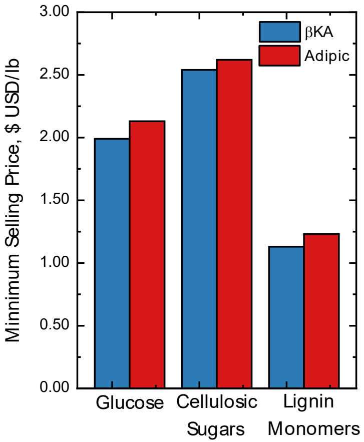
# Performance-advantaged nylons from β-ketoadipic acid

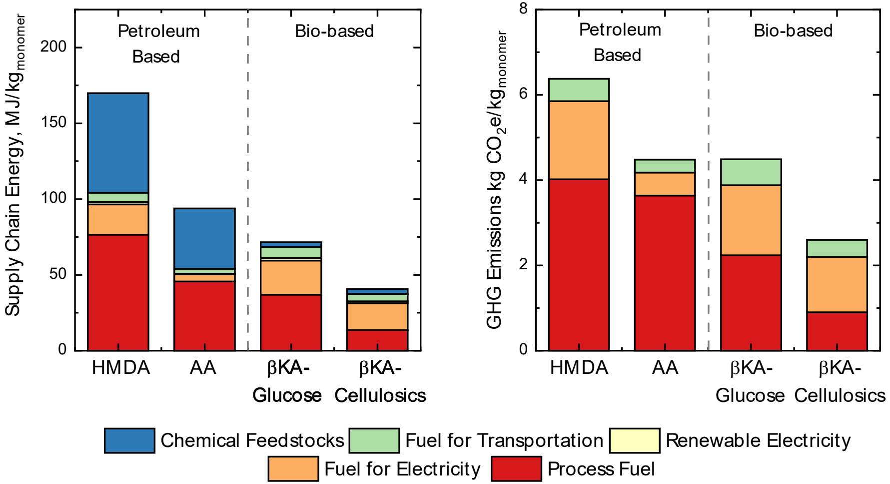
Rorrer *et al. Cell Reports Phys. Sci.*, 2022



Nylon 6,6 1.01 g*mm/m²*day, $T_g$ = 60°C

Nylon 6,βK6 0.8 g*mm/m²*day, $T_g$ = 130°C



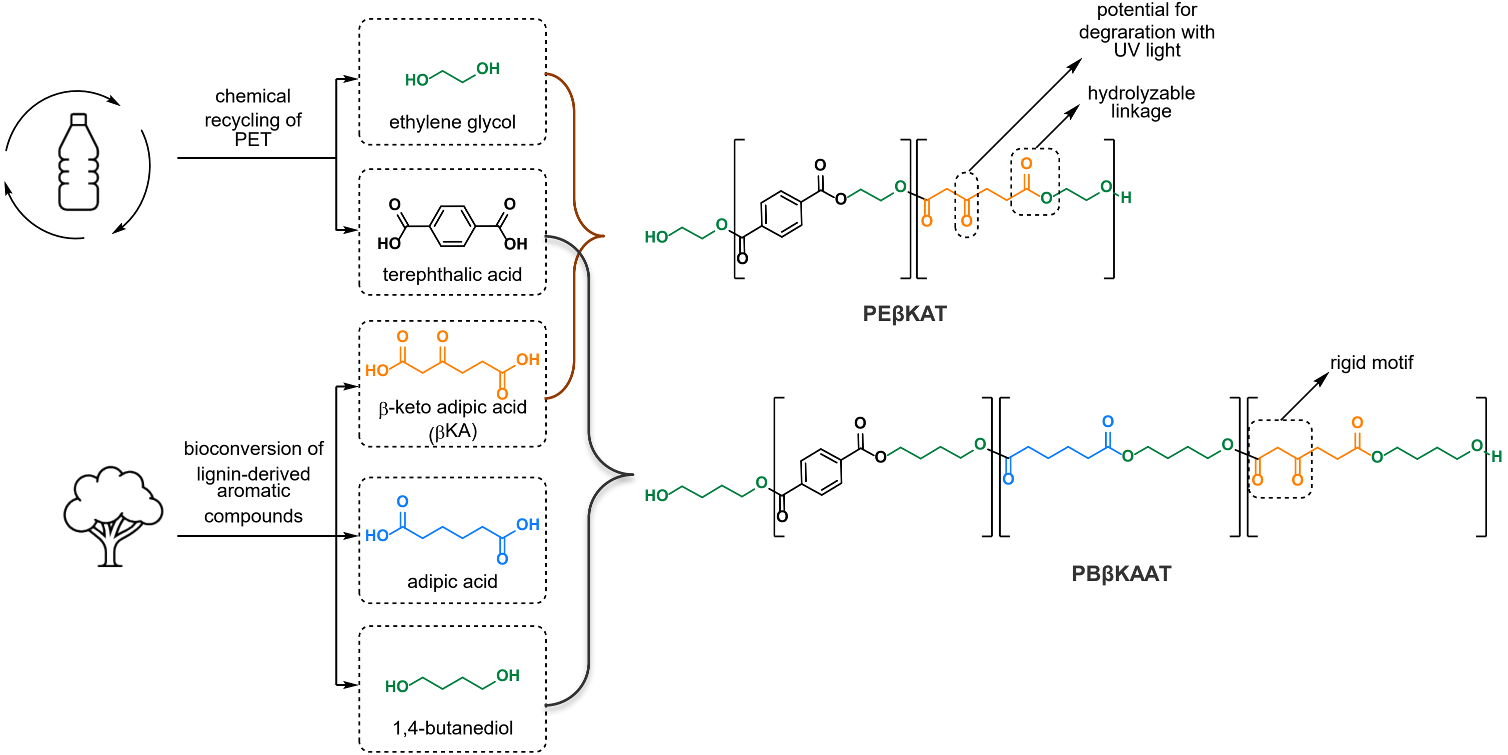


**Incorporation of βKA into nylon-6,6 improves thermal properties and reduces water uptake**

- Collaboration with Agile BioFoundry and Inverse Design
- βKA imparts properties similar to nylon-6,10 (sebacid acid) to make an engineering polymer
- Active technology transfer ongoing now with start-up company and textile major

# Performance-advantaged polyesters from β-ketoadipic acid

Rosetto and Rorrer, ongoing

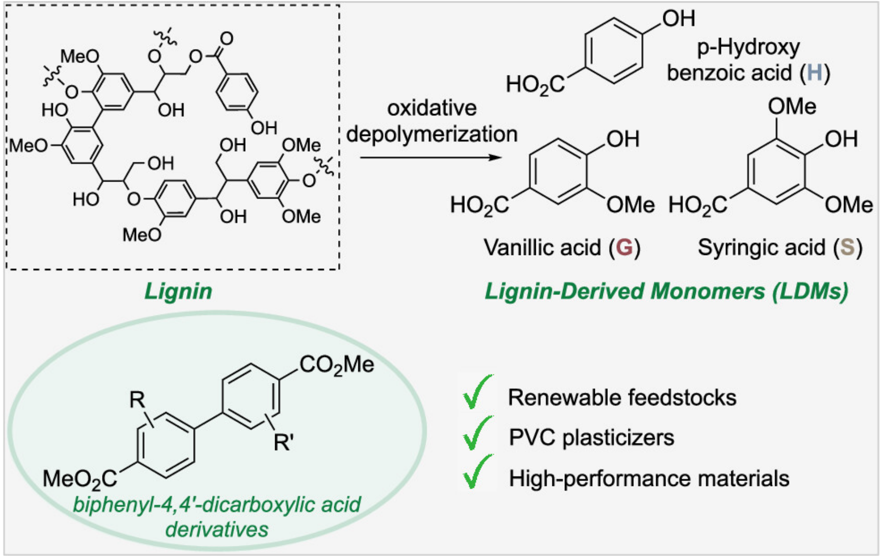


**Incorporation of βKA in PET and PBAT enhances polymer properties, recyclability, and biodegradation**

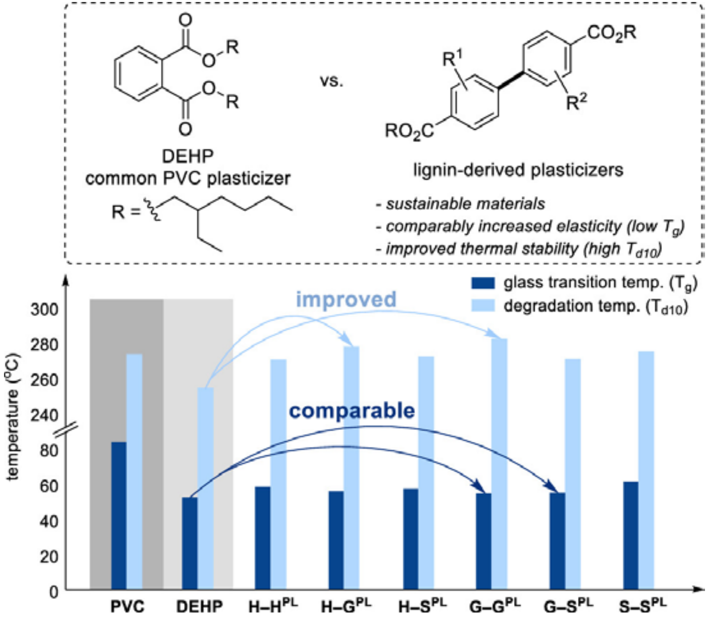
- Results demonstrate polymer degradation is proportional to βKA loading in PEβKAT
- Taking this polyester to kg scale now with a scale-up partner

# Performance-advantaged biphenyl plasticizers from lignin

Su *et al.* *ACS Central Science*, 2023



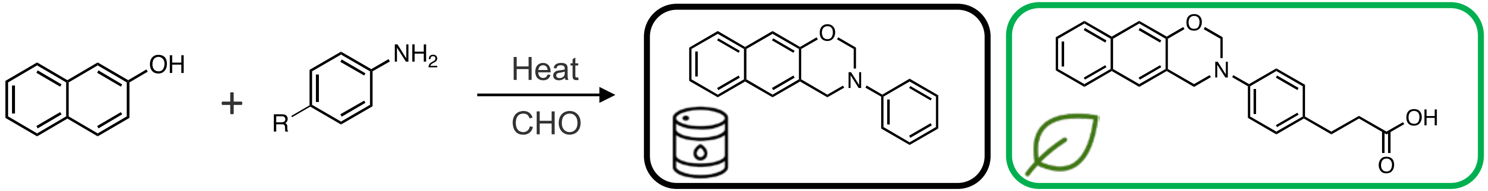
✓ Renewable feedstocks
✓ PVC plasticizers
✓ High-performance materials



## Lignin-derived plasticizers offer performance-advantaged properties vs. phthalate plasticizers

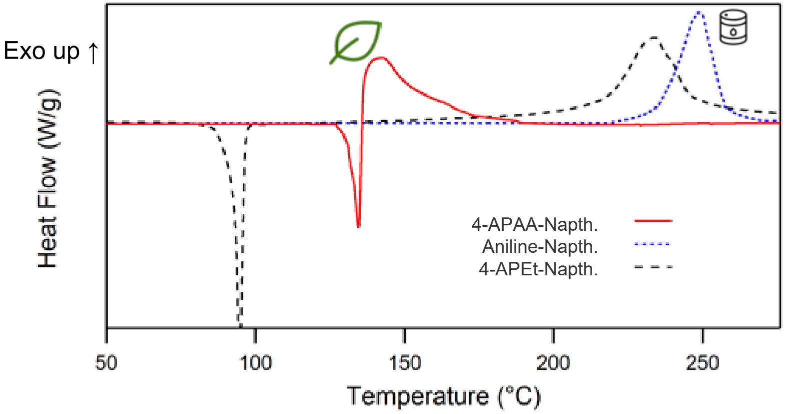
- Collaboration with **Shannon Stahl**, UW Madison, on oxygenated aromatic compounds from lignin
- Pursuing plasticizers based on terephthalate-like monomers as well

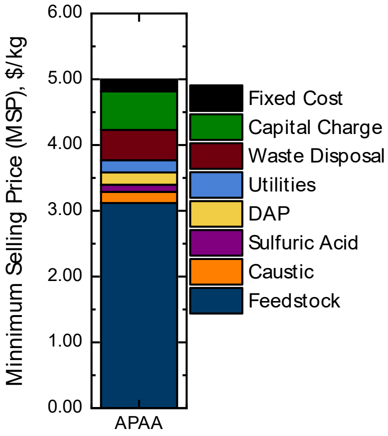
# Performance-advantaged thermosets from organonitrogen compounds

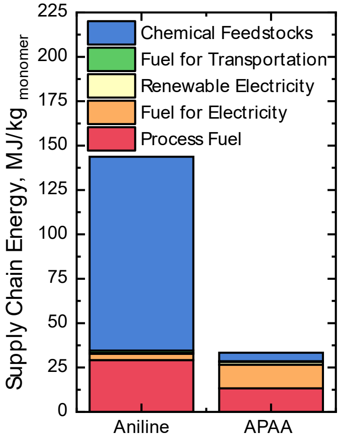


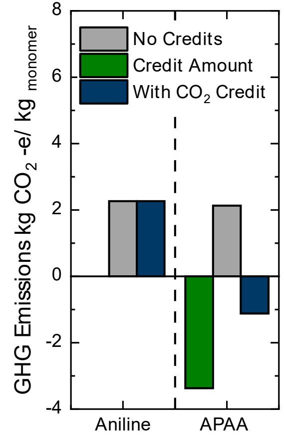
Aniline-Napthoxazine

4-APAA Napthoxazine







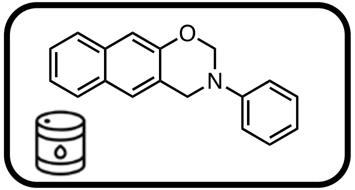


**Organonitrogen monomers enable multiple manufacturing benefits for high-performance thermosets**

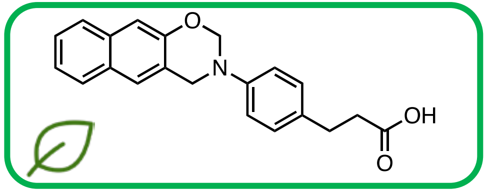
- Napthoxazine & benzoxazines used in high-value thermosets but currently require substantial heat to cure
- APAA manufacture is substantially less energy-intensive relative to aniline

Hoyt and Rorrer, in preparation

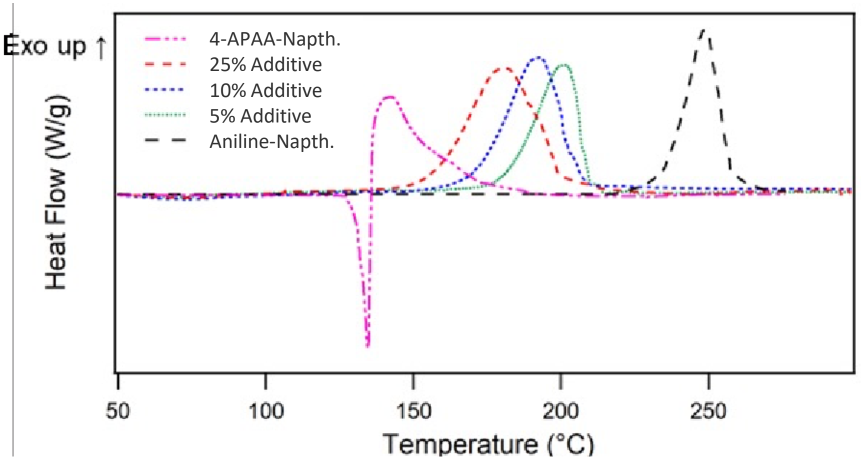
# Performance-advantaged additives in thermosets

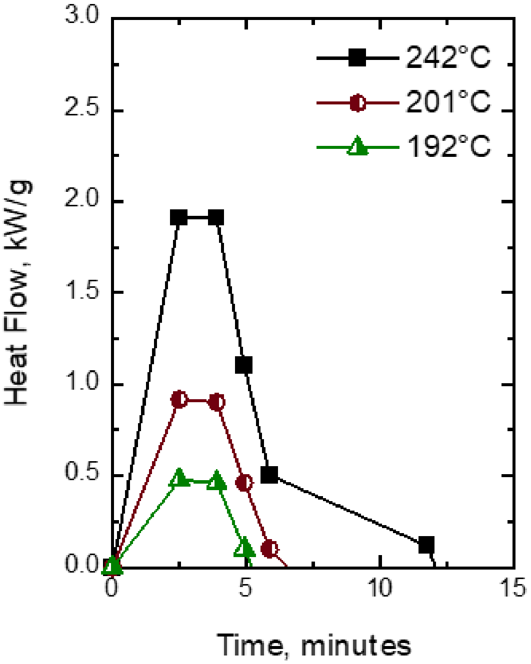


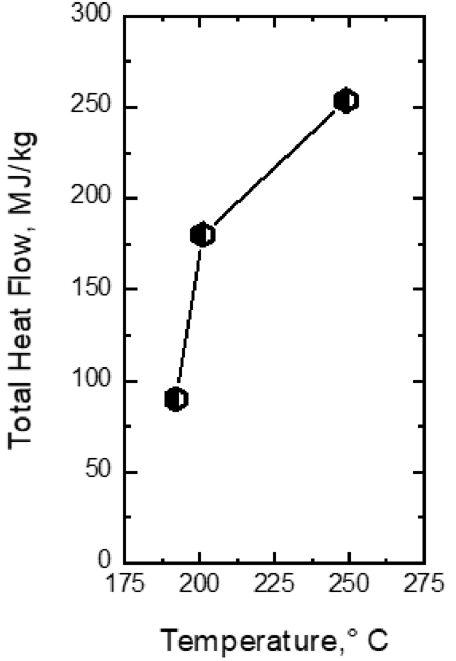
Aniline-Napthoxazine



4-APAA Napthoxazine as an Additive





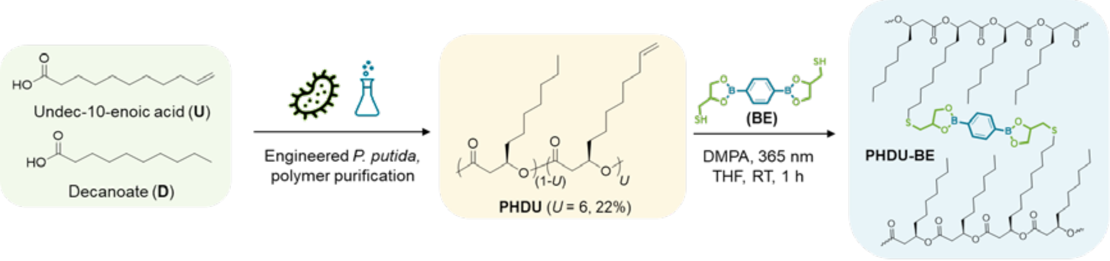


**Utilizing 4-APAA as an additive also yields performance-advantaged benefits in manufacturing**

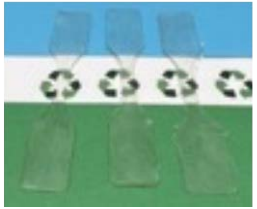
- Reductions in cure T reduce the heating requirement, thus reducing the required process energy by 24%

Hoyt and Rorrer, in preparation

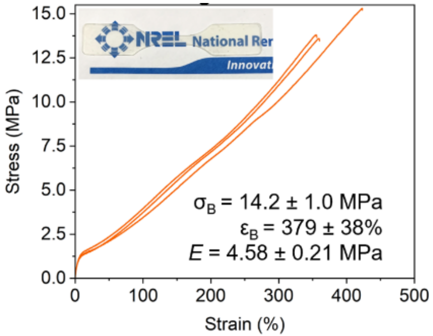
# Performance-advantaged elastomers

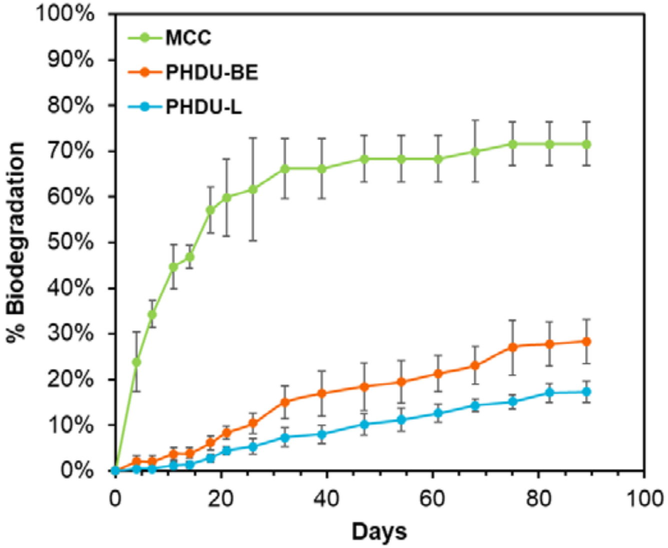


**Virgin:**



**$3^{rd}$ reprocess:**



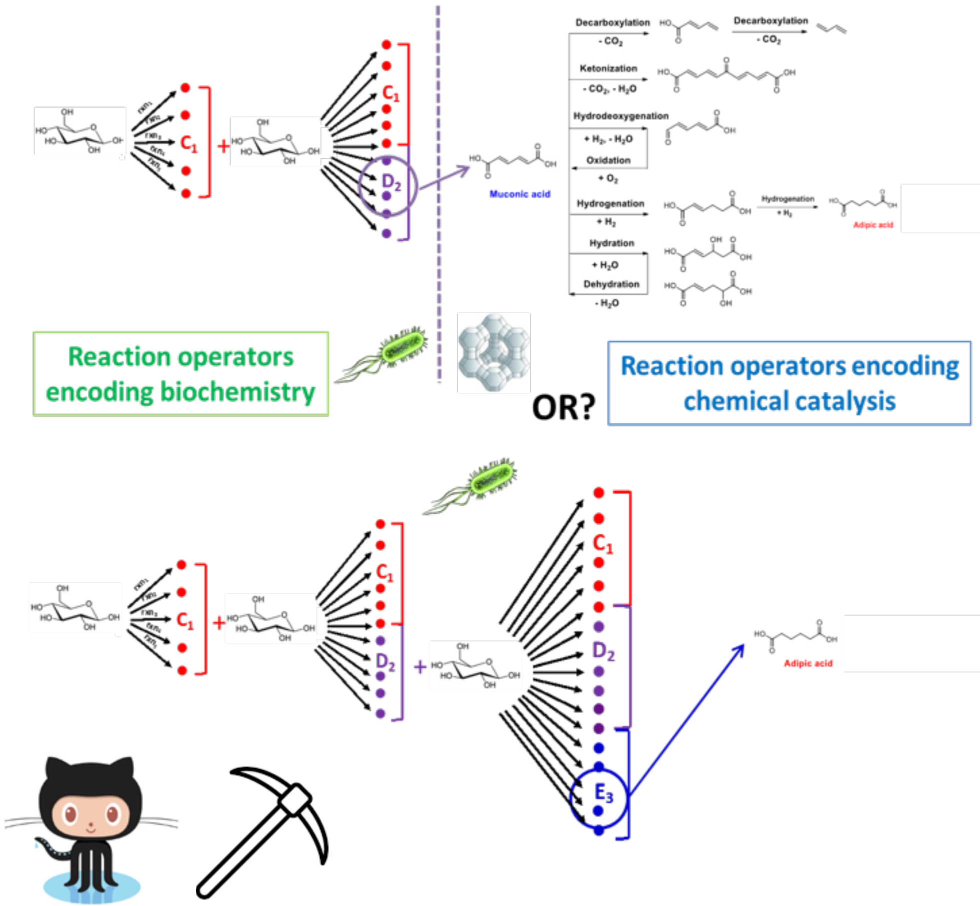


**usPHAs produced biologically are degradable poly(butadiene) replacements**

- Unsaturated group enables installation of additional functionality, e.g. boronic esters as reversible crosslinks
- Material being scaled-up with a large industrial partner for evaluation

Cywar *et al., in review*

# Computational tool development highlights method to produce PA molecules



Reaction operators encoding biochemistry

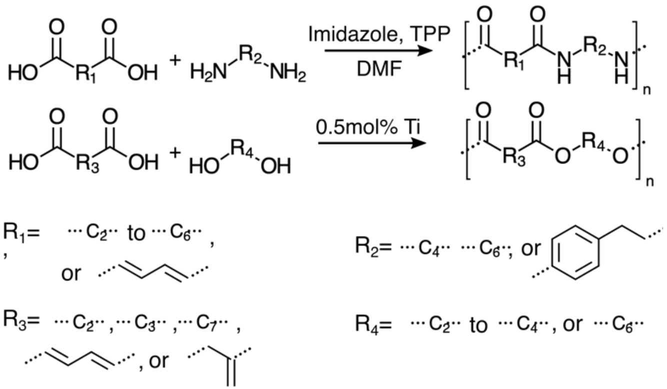
Reaction operators encoding chemical catalysis

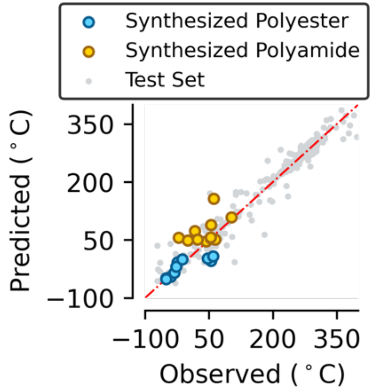
## Goal: Advance molecule and reaction discovery tools to enable hybrid biological/chemocatalytic pathways

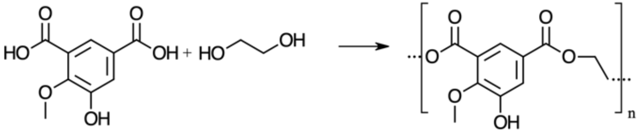
- Chemocatalytic operators need to be developed to cover expanded reaction space
- Software needs to be improved to allow variety of filtering strategies due to combinatorial explosion
- Have added > 120 new chemical operators with new chemical approaches and new heteroatoms (including CHN/CHNO compounds)
- Incorporated separations-relevant variables into predictions
- Developed new pathway ranking procedures

# Polymer synthesis and characterization for polyID

Wilson *et al. in revision*







| Glass Transition Temperature | |
|---|---|
| Predicted (°C) | Observed (°C) |
| 106 ± 9 | 85 - 112 |

**Validating predictions and increasing prediction accuracy through synthesis**

- Validated the prediction set with >25 new formulations and synthesized a novel PABP

# 3 – Impact

**Scientific:**

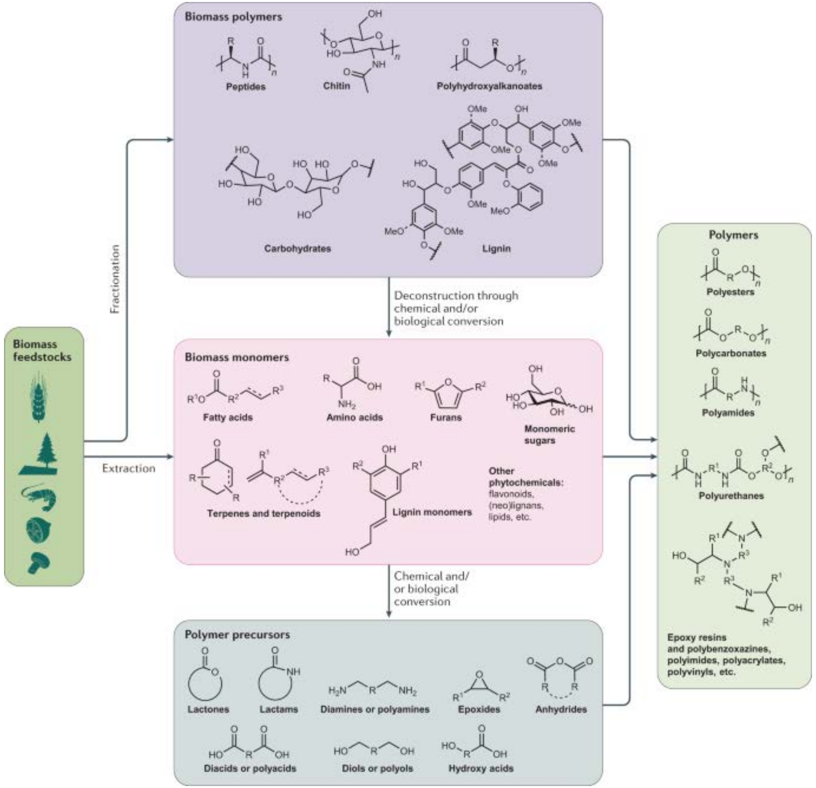
- > 200 formulations to date, > 100 since FY21, > 10 are PABPs since FY21
- *Nature Reviews Materials* paper to describe framework for benchmarking PABPs
- Multiple patent applications and high-impact, interdisciplinary, and analysis-guided studies published
- Benchmarking study published for organic petrochemical benchmarking for energy and GHG emissions
- Data science and pathway synthesis tools together can enable efficiency in materials design
- Tools are open-source for the community to use

PolyID

**Industrial:**

- Industry engagement when PABPs are shown to be promising, including ongoing work with scale-up companies and consumer-facing companies
- Multiple industrial collaborations, including with a textile major, scale-up biomanufacturing company, *et al.*

# Summary



Cywar, Rorrer *et al. Nature Reviews Materials* 2022

## Overview

- Develop new PABPs for polymers and chemicals with viable, economical, and GHG-advantaged manufacturing pathways

## Approach

- Collaborations with promising technologies for new molecules
- Analysis-experimental-data science cycle for new PABPs

## Progress and outcomes

- Multiple new polymers based on C6 diacids accessible from sugars and lignin
- Multiple polymers and additives from lignin-derived aromatics (with UW Madison colleagues)

## Impact

- Work with multiple projects to enable PABPs, including with industry and academic partners

# Quad chart overview

## Timeline

- Active Project Duration: 10/1/2020 – 9/30/2023
- Total Project Duration: 10/1/2017 – 9/30/2023

| | FY22 funding | Total Award |
|---|---|---|
| **DOE Funding** | $520,000 (10/01/2021–9/30/2022) | $520,000 – FY23<br>$1,560,000 – Active Project (FY21-23) |

## Project Partners

**BETO Projects**: Biological Lignin Valorization, Separations Consortium, Biochemical Platform Analysis, Inverse Biopolymer Design through Machine Learning and Molecular Simulation, Agile BioFoundry, Bioconversion of Thermochemical Intermediates, Lignin Utilization, Lignin-First Biorefinery Development

**University Partners:** Iowa State, Northwestern University, University of Wisconsin-Madison, Colorado State University, MIT

## Project Goal

Synthesis, characterization, and analysis of performance-advantaged bioproducts

## End of Project Milestone

Produce ≥50 bioproducts hypothesized to offer a performance advantage. Demonstrate ≥10 bioproducts with a performance advantaged property >10%. Demonstrate that these bioproducts can be produced within 25% of the cost of the petro-derived counterpart

## Funding Mechanism

Bioenergy Technologies Office FY21 AOP Lab Call (DE-LC-000L079) – 2020

TRL at Project Start: 2

TRL at Project End: 4

**Acknowledgements**:
DOE Technology Managers Coralie Backlund and Andrea Bailey

**NREL Contributors**:
Birdie Carpenter, Robin Cywar, Kylee Harris, Chris Hawkins, Caroline Hoyt, Brandon Knott, Megan Krysiak, Clarissa Lincoln, William Michener, Heather Mayes, Joel Miscall, Mark Nimlos, Michelle Reed, Erik Rognerud, Gloria Rosetto, Scott Nicholson, Kelsey Ramirez, Nicholas Rorrer, Avantika Singh, Taylor Uekert, Kevin Wernke, Nolan Wilson

**Collaborators:**

**Linda Broadbelt** (Northwestern), **Eugene Chen** (CSU), **Yuriy Román** (MIT), **Brent Shanks** (Iowa State University), **Shannon Stahl** (University of Wisconsin-Madison)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

# Q&A

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NREL/PR-2A00-85669

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# Additional Slides

# PABPs produced in FY21-FY23

| *Petroleum Polymer* | *Bio-based Monomer* | *Metric* | *Property Change* | *Formulations* |
|---|---|---|---|---|
| **Previous Years Formulations** | | | | |
| Nomex, PET (Amorphous), Polycarbonates, ABS, Epoxies, Plasticizers | BKA, BKG, muconic, methyl muconates, Lignin Monomers, etc. | Various | Multiple. Perf. Adv. Include: **Reduce Toxicities, Recyclability, Lower Permeabilities, Increased Additive Efficacy** | 67 |
| **PolyID Collaborations** | | | | |
| Nylon 6,6 | PolyID Monomer Suite | -- | -- | 20 |
| PET | 5CVA, etc. | $T_g$, permeability | $T_g$ aligned with predictions. **20+% increase** | 10 |
| ***Polyesters*** | | | | |
| PET | Oxidative Ligning Monomers, Biphenyl Monomers | $T_g$ | -- | 8+ |
| Aliphatic Polyesters | Various - Butanediol, Citraconate, etc. **(Poly(β-hydroxy esters)** | $T_{g,,}$ permeability | Increased inter-polymer interactions. **10+% $T_g$ increase** | 31 |
| **Thermosets** | | | | |
| Epoxy Amines | Biobased Diamines | $T_g$, Mechanical | Properties Maintained, **Reduced GHG** | 32 |
| Elastomers | usPHAs | Recyclability | **Degradation and Recyclability Enabled** | 10+ |
| **Polymer Additives** | | | | |
| Benzoxazines | Aromatic Amines | $T_g$, Processibility | **20% + Cure temp reduction. Decarbonized Monomers** | 10 |
| Plasticizers | Oxidative Lignin Monomers, Biphenyl Monomers | $T_g$, Additive Efficacy, Toxicity | **Toxicity reduced** | 15+ |

+ indicates planned or on-going reactions

# Responses to previous reviewers’ comments

- Excellent team composition for defining potential pathways to PABP’s from inherent bio-based sources. Developing performance targets would benefit from additional participation of materials companies early in the design process. Additional access to prototyping candidates will accelerate go/no go decisions. Focusing on molecular structure/property relationships is paying big dividends by helping screen thousands of candidates to a promising few. TEA and routes to market analysis needed to further refine selection of candidates for scale up.
  - We fully agree that performance targets for new PABPs cannot be fully defined by our project’s efforts alone, and that industry collaboration to that end will be critical. Our focus is thus on synthesizing new PABPs, determining their baseline properties, reporting them in the patent and peer-reviewed literature, and then working with industrial partners who can help us define additional performance criteria that must be met. As described in the presentation, this project has spawned multiple Energy I-Corps teams, active technology transfer, and active partnering efforts with the industrial community – all towards exactly what the reviewer suggests – namely that we need industry collaboration and input to make any of these PABPs ultimately successful in the marketplace.
  - In terms of the need for TEA, we have this effort embedded in this project, as described during the presentation, and we are using TEA and MFI as key tools to identify opportunities for scale-up activities.

# Responses to previous reviewers' comments

- Would like to see replacements for currently expensive HMDA for polyamide monomers, potentially over adipic acid replacements. This approach, when fully developed, will open up many renewable and sustainable replacements for polymers, plasticizers and additives. Potentially exciting game-changers. Despite limitations on prototyping, the candidates identified so far have great potential. Low productivity of beta-ketoadipate production is a concern. The polyamide polymer has promising properties, but cost may be a potential show-stopper.

  - In terms of HMDA, this is an excellent suggestion, and as discussed during the Q&A session, we have several strategies to make this molecule (and related molecules) now, which we will test when bandwidth allows. For the concern regarding the low productivity of beta-ketoadipate, we note that from lignin-derived aromatics in the Biological Lignin Valorization project, we are currently able to achieve 0.9 g/L/hr, and we are actively working to improve the productivity from sugars in the Agile BioFoundry project beyond the current level of ~0.2 g/L/hr.

# Responses to previous reviewers' comments

- This project utilizes the expertise that resides in the national labs, extending from bioproduct acquisition to formulation, characterization, and TEA/GHG analysis, to identify performance advantaged biomaterials. An impressive array of targets and formulations have been examined and multiple PABP's identified and communicated in publications. Several polymers are being scaled up for testing by industrial partners. I'm left with the following questions: When is the right time to shift focus away from identifying additional PABP's to pushing several PABP's to the point necessary to garner significant industrial investment? Alternatively, would it make sense to spin a small number of PABP's off into separate projects for more focused efforts on pathway engineering, materials validation and applications?

  - The reviewer brings up an excellent point related to spin-off into separate projects for individual PABPs. Our current mechanisms to are to leverage other projects (e.g., the Agile BioFoundry, Biological Lignin Valorization, Lignin Utilization, et al.) for the pathway engineering and catalysis development (to make the necessary molecules in a cost-effective manner) and to collaborate with industry via Technology Commercialization Fund projects, SBIRs, FOAs, and other mechanisms that DOE has established to aid in viable technology transfer. Certainly, we fully realize, as the reviewer does, that this project alone will not be able to wholly develop the full potential of some of the promising PABPs developed herein, but there are mechanisms in place that DOE has enabled to aid in this transition. In addition to leveraging DOE mechanisms, we are continuously investigating methods to enable a single molecule to be used in multiple applications which can further de-risk technology development and enable a more facile pathway to market.

# Publications, patents, and presentations

**Publications**

**In preparation**

Robin M. Cywar, Chen Ling, Ryan W. Clarke, Donghyun Kim, Colin M. Kneucker, Davinia Salvachúa, Bennett Addison, Sarah A. Hesse, Christopher J. Takacs, Shu Xu, Meltem Urgun Demirtas, Sean P. Woodworth, Nicholas A. Rorrer, Christopher W. Johnson, Christopher J. Tassone, Robert D. Allen, Eugene Y.-X. Chen, Gregg T. Beckham, Elastomeric vitrimers from designer polyhydroxyalkanoates with recyclability and biodegradability, Pending Submission to *Nature Communications.*

Caroline B. Hoyt, Chen Wang, Nicholas A. Rorrer, Renee Happs, Bennett Addison, Gregg T. Beckham, High performance renewable epoxide resins reinforced with a biobased triazine network, in preparation, (Target Journal: *Green Chemistry*).

Caroline B. Hoyt, Nicholas A. Rorrer, A. Nolan Wilson, Avantika Singh, Scott Nicholson, Robert A. Allen, Gregg T. Beckham, Bio-based aromatic amines for catalytic naphthoxazine synthesis and effects on ring opening, in preparation (Target Journal: *Green Chemistry*).

Alex W. Meyers, Nicholas Rorrer, William R. Henson, Caroline B. Hoyt, Todd Vander Wall, Rui Katahira, Lahiru Jayakody, William E. Michener, Davinia Salvachúa, Christopher W. Johnson, Gregg T. Beckham, "Biological upgrading of cresols to alkylated muconates for polymer production," publication in preparation (Target Journal*: Green Chemistry*).

# Publications, patents, and presentations

**Accepted**

Scott R. Nicholson, Nicholas A. Rorrer, Alberta C. Carpenter, Gregg T. Beckham, "Manufacturing energy and greenhouse gas emissions associated with the production of organic petrochemicals," Provisionally Accepted at ACS Sustainable Chemistry & Engineering.

Nicholas A. Rorrer, Sandra F. Notonier, Brandon C. Knott, Brenna A. Black, Avantika Singh, Scott R. Nicholson, Christopher P. Kinchin, Graham P. Schmidt, Alberta C. Carpenter, Kelsey J. Ramirez, Christopher W. Johnson, Davinia Salvachúa, Michael F. Crowley, Gregg T. Beckham, "Production of β-ketoadipic acid from glucose in Pseudomonas putida KT2440 for use in performance-advantaged nylons," Accepted at Cell Reports Physical Science.

William R. Henson, Nicholas A. Rorrer, Alex W. Meyers, Caroline B. Hoyt, Heather B. Mayes, Todd Vander Wall, Rui Katahira, Jared J. Anderson, Brenna A. Black, William E. Michener, Lahiru Jayakody, Davinia Salvachúa, Christopher W. Johnson, Gregg T. Beckham, "Bioconversion of wastewater-derived methyl phenols to methyl muconic acids for use in performance-advantaged polymers and plasticizers," Accepted at Green Chemistry.

**2022**

Robin M. Cywar, Nicholas A. Rorrer, Caroline B. Hoyt, Gregg T. Beckham*, Eugene Y.X. Chen*, Bio-based polymers with performance-advantaged properties, *Nature Rev. Materials.* (2022) 7, 73-103.

# Publications, patents, and presentations

**2019**

Christopher W. Johnson, Davinia Salvachúa, Nicholas A. Rorrer, Brenna A. Black, Derek R. Vardon, Peter C. St. John, Nicholas S. Cleveland, Graham Dominick, Joshua R. Elmore, Nicholas Grundl, Payal Khanna, Chelsea R. Martinez, William E. Michener, Darren J. Peterson, Kelsey J. Ramirez, Priyanka Singh, Todd A. Vander Wall, A. Nolan Wilson, Xiunan Yi, Mary J. Biddy, Yannick J. Bomble, Adam M. Guss, Gregg T. Beckham, Innovative chemicals and materials from bacterial aromatic catabolic pathways, *Joule*. (2019) 3, 1523-1537.

# Publications, patents, and presentations

**Presentations**

“Towards a Better Steel Replacement: Performance Advantaged Thermosets from Bioderived Resources.” Invited talk, Virginia Tech, Rowan University, and Stanford University, October 2022

“Performance Advantaged Thermosets from Bioderived Amines: Benefits in Manufacturing, Performance, and End-of-Life” Invited Talk – ACS Fall Meeting, August 2022

Bio-based, recyclable-by-design polymers, ACS Fall Meeting, August 2022

“β-ketoadipic acid for performance advantaged nylons” Invited Talk – Society for Industrial Microbiology and Biotechnology (SIMB), May 2022

Donald L. Katz Lectureship in Chemical Engineering, The University of Michigan, April 2022

“New building blocks for performance-advantaged renewable and recyclable polymers,” Pacifichem (via webinar), December 2021

# Publications, patents, and presentations

| ROI Number | Title |
|---|---|
| ROI-18-81 | Bioderived biphenyl-containing compounds and their conversion to polymers and macromonomers |
| ROI-19-107 | Thioester and thioaldehydes of lignin monomers for reversible crosslinked applications |
| ROI-20-130 | Bioderived benzoxazines |
| ROI-21-137 | Alternative amines for epoxy thermosets |
| ROI-22-57 | Electrochemical Ni/Pd-catalyzed reductive coupling of lignin derived aromatics |