



Synthesis and Analysis of Performance-Advantaged Bioproducts
Technology Session Review Area: Performance-Advantaged Bioproducts, Bioprocessing
Separations, and Plastics
PI: Gregg T. Beckham, National Renewable Energy Laboratory

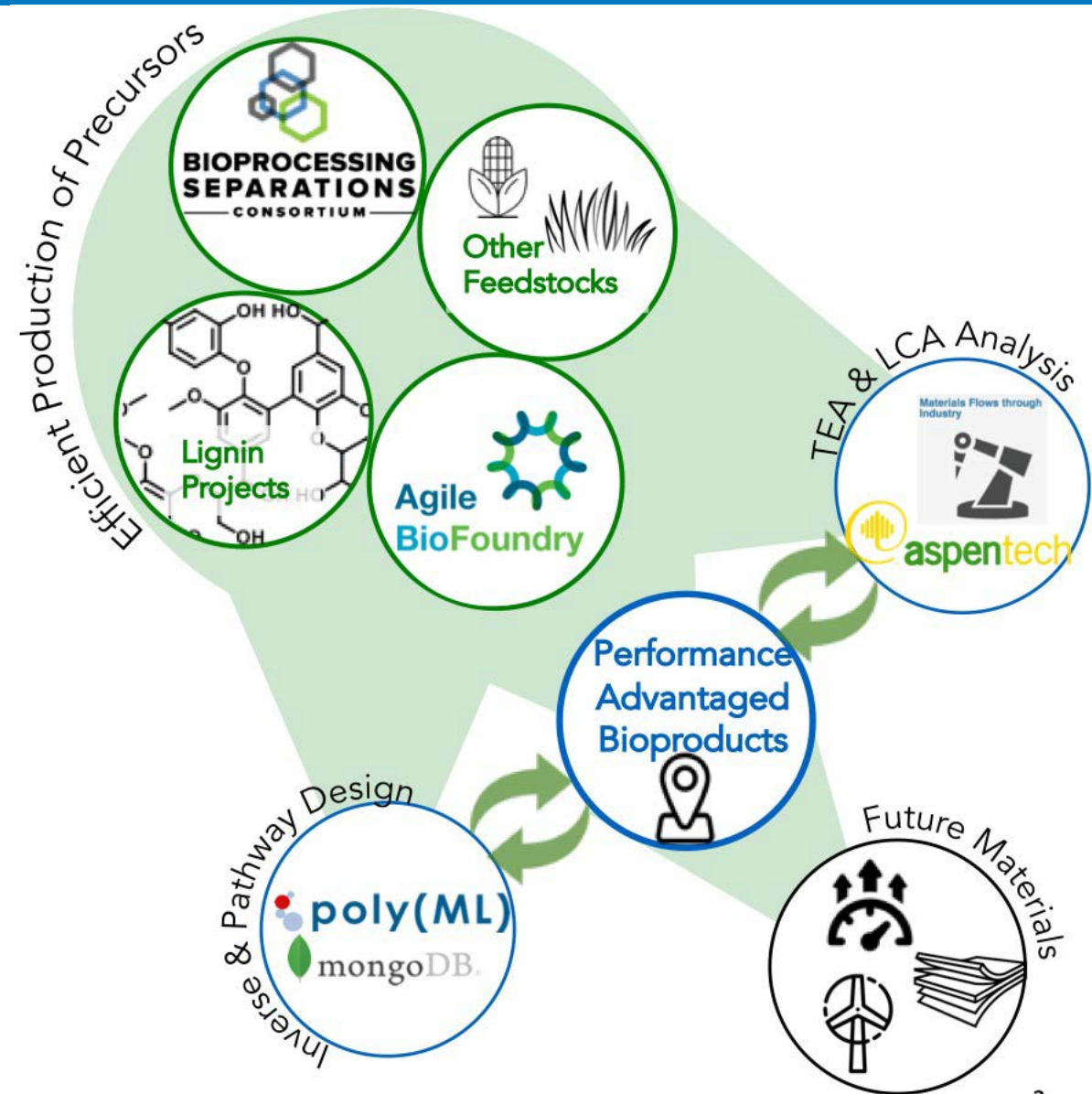
Project overview

Goal: Synthesize, characterize, and conduct analysis for economic, sustainable performance-advantaged bioproducts (PABPs)

- ≥50 candidates in 3-year cycle, ≥10 PABPs
- Work with Inverse Design (ID) *et al.* to develop a computational-experimental framework for PABPs
- Subcontract with Northwestern & Iowa State
- Project started in FY18

Heilmeier Catechism:

- **Aim:** incentivize bioeconomy investments via PABPs
- **Today:** Huge field of biochemicals, Edisonian methods to develop PABPs is resource-intensive
- **Important:** PABPs can accelerate the bioeconomy
- **Risks:** Full PABP characterization not always obvious – requires early collaboration; syntheses often time consuming when building blocks are unavailable



Management

Task 1: PABP Synthesis and Characterization

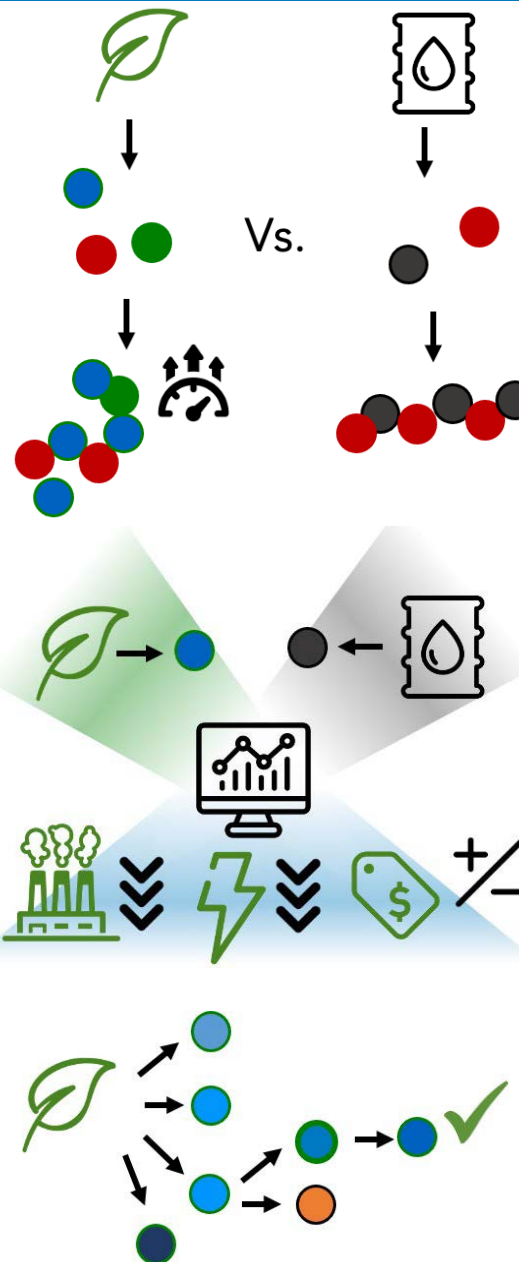
- Experts in synthesis and characterization: R. Cywar, C. Hoyt, N. Rorrer
- Milestones: **PABP synthesis, characterization**
- Collaborate with BETO projects and universities including E. Chen (CSU) Y. Román (MIT), G. Huber and S. Stahl (U Wisconsin)

Task 2: PABP Analysis

- Experts in TEA and LCA: S. Nicholson, A. Singh
- Milestones: **Analysis of PABPs, supply-chain modeling of incumbents and PABPs**

Task 3: PABP Pathway Design

- Led by **Linda Broadbelt** (Northwestern) **Brent Shanks** (Iowa State)
- Milestones: **computational tool development** with Inverse Design and analysis efforts



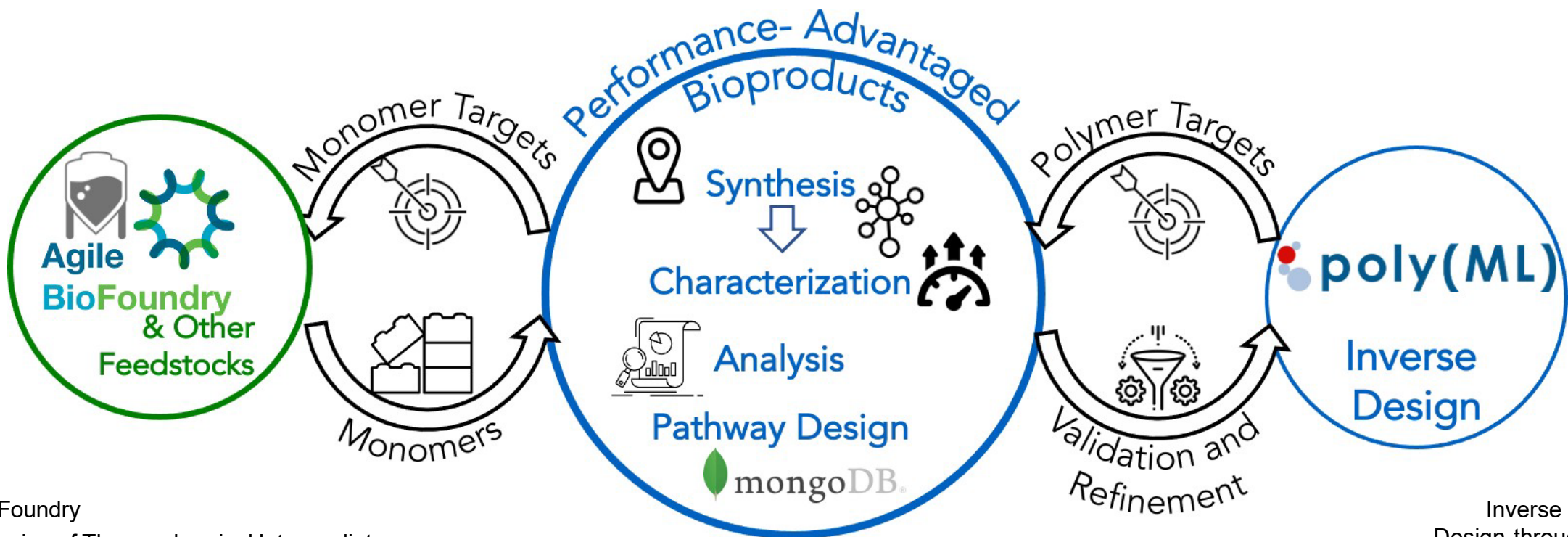
Project organization:

- Fortnightly meeting with ID project
- Monthly mtgs with PI-staff, PI-postdocs
- *Ad hoc* meetings with metabolic engineering, lignin, SepCon projects
- Ops & Project Mgrs – labs, equipment, reporting, finances

Risks:

- Bio-based building blocks for PABPs are often not commercially available
- Potential number of PABPs to synthesize and characterize is vast
- Industrial performance metrics are not fully known
- Current TRL rarely includes prototype production

Management: Project interactions



Projects:

- Agile BioFoundry
- Bioconversion of Thermochemical Intermediates
- Biological Lignin Valorization, Lignin-First Biorefinery Development, Lignin Utilization
- Separations Consortium
- Multiple academic collaborators

Projects:

- Inverse Biopolymer Design through Machine Learning and Molecular Simulation

This project resides at the nexus of multiple projects

- Projects in BETO portfolio and external collaborators provide building blocks for PA chemicals and polymers
- This project receives predictions for target polymers from ID and provides feed back to enhance datasets

Approach

Technical approach:

- Work with ID project to narrow design space and explain experimental observations
- Experiments focus on PABP syntheses & characterizations
- AspenPlus and Materials Flows through Industry (MFI) for analysis
- Report new PABPs via integrated publications and patents



Challenges:

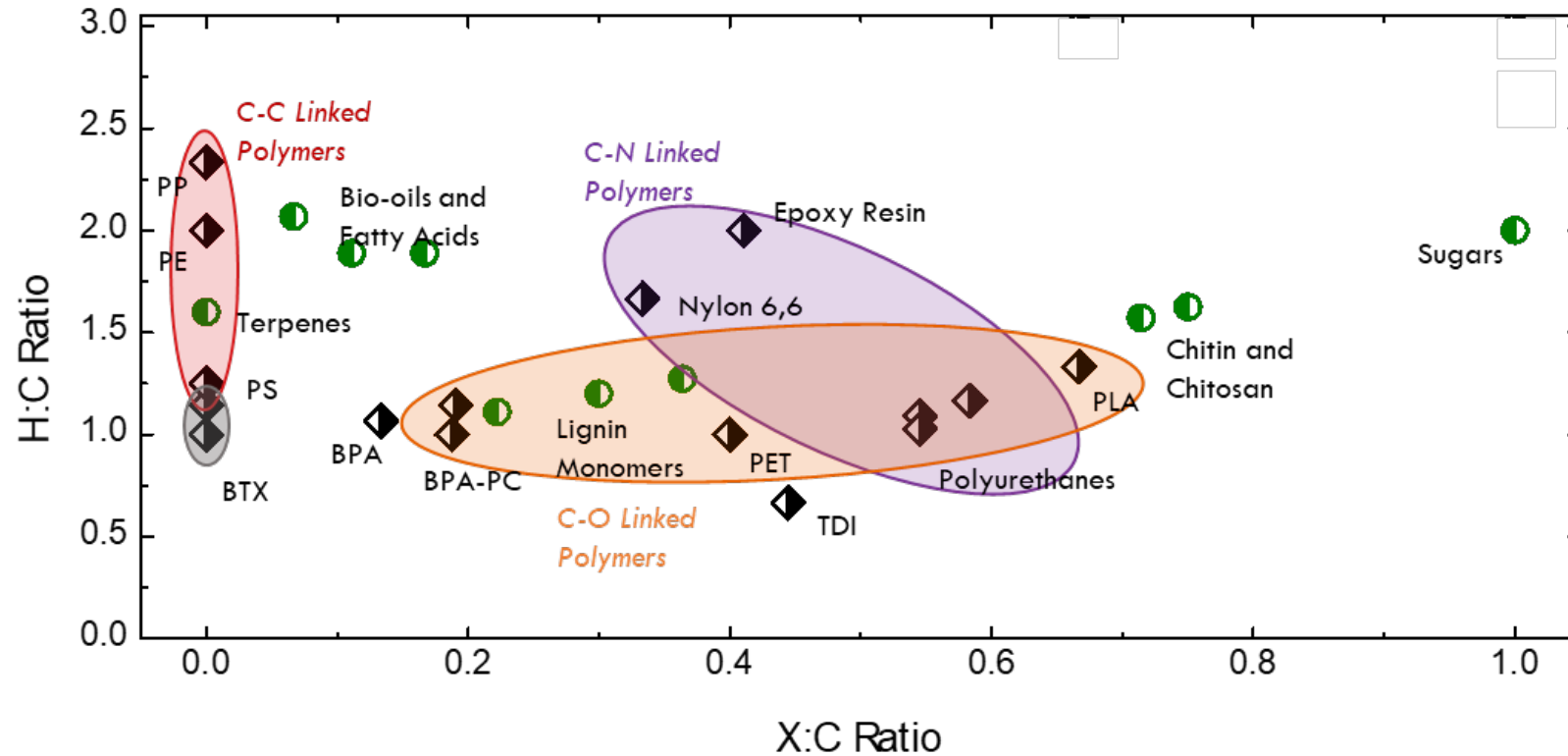


- Comprehensive characterizations not always obvious – requires collaborations with end-users
- Syntheses for new molecules or polymers are often time-consuming
- Tech. transfer often requires kg quantities of PABPs

Major milestones, Go/No-Go Decisions:

- FY21: Produce ≥ 5 polymers from PolyML predicted to be PABPs
- FY21: Quantify the energy and GHG emissions of commodity chemical consumption in the US
- FY22: Conduct TEA and MFI for ≥ 2 non-polymer PABPs
- FY23: Produce ≥ 50 PABPs, demonstrate ≥ 10 as PABPs w/in 25% cost of incumbent

Impact



Van Krevelen diagram showing chemical distances of feedstocks to polymers (X is a heteroatom, typically oxygen or nitrogen)

Scientific:

- The heteroatom functionality of biomass makes it ideal for PABPs, including polymers
- Combine computation (ID) & experiment to narrow design space to target PABPs we *should* produce
- TEA and MFI (LCA) to compare cost and sustainability of PABPs to their fossil counterparts
- Field-leading publications in PABPs (e.g. Johnson *et al. Joule* 2019; Cywar *et al. Nature Reviews Materials*, 2021)
- Ultimate goal – set of analysis, computation, and experimental tools to narrow PABP design space

Industrial:

- Actively pursuing proposals via Technology Commercialization Funds for tech. transfer
- Tech. transfer and industry engagement ongoing via Energy I-Corps
- Experimental R&D coupled with analysis can de-risk technology prior to industry collaboration
- Scaling up polymer production in several cases for industrial partner testing



Overall:

The two PABP projects *together* aim to deliver rigorous tools to **design, produce, and analyze PABPs** in collaboration with BETO projects and with academic and industrial partners

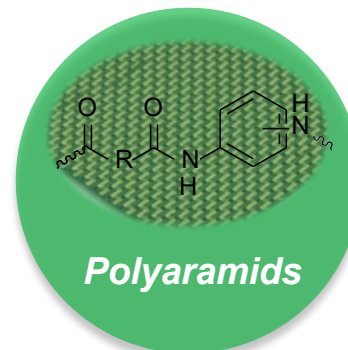
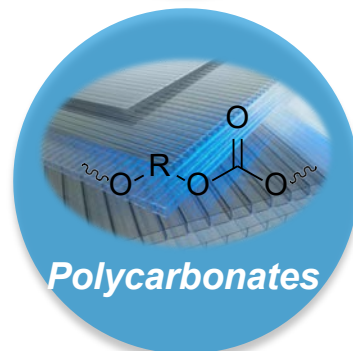
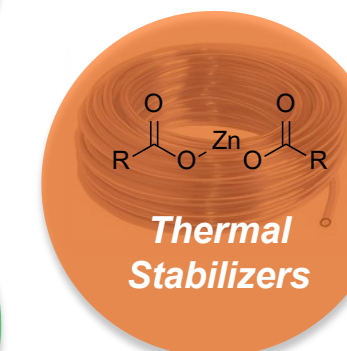
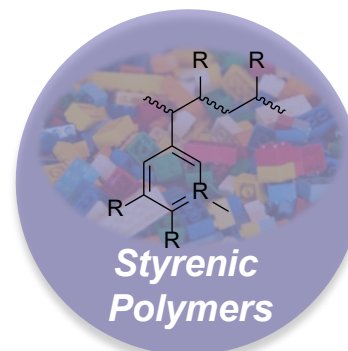
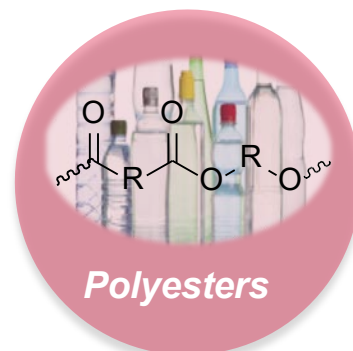
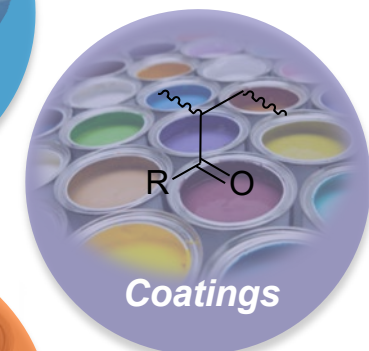
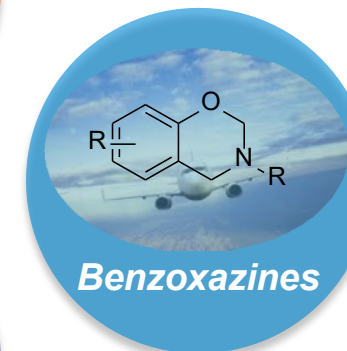
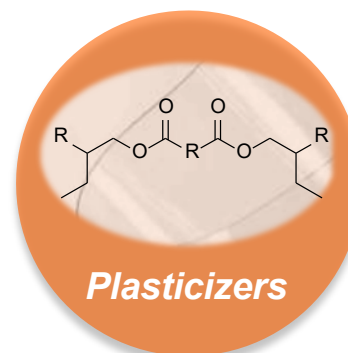
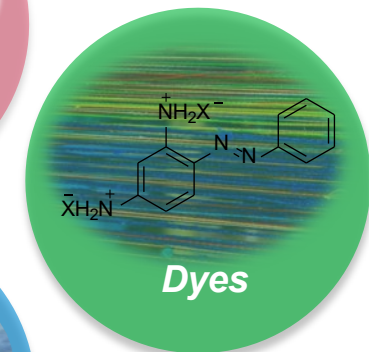
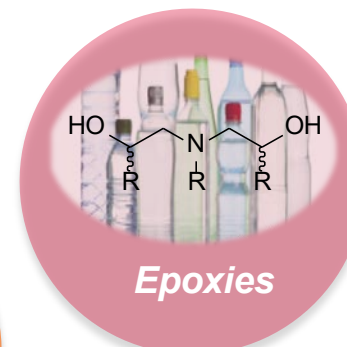
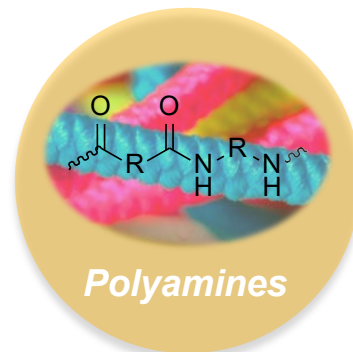
Progress and Outcomes

Synthesis/characterization progress:

- Performance-advantaged nylons enabled by β -keto acids
- New thermosets from aromatic amines and corresponding TEA/LCA
- New directions in plasticizers and stabilizers
- Summary of PABP syntheses
- Synthesis of polymers from ID project

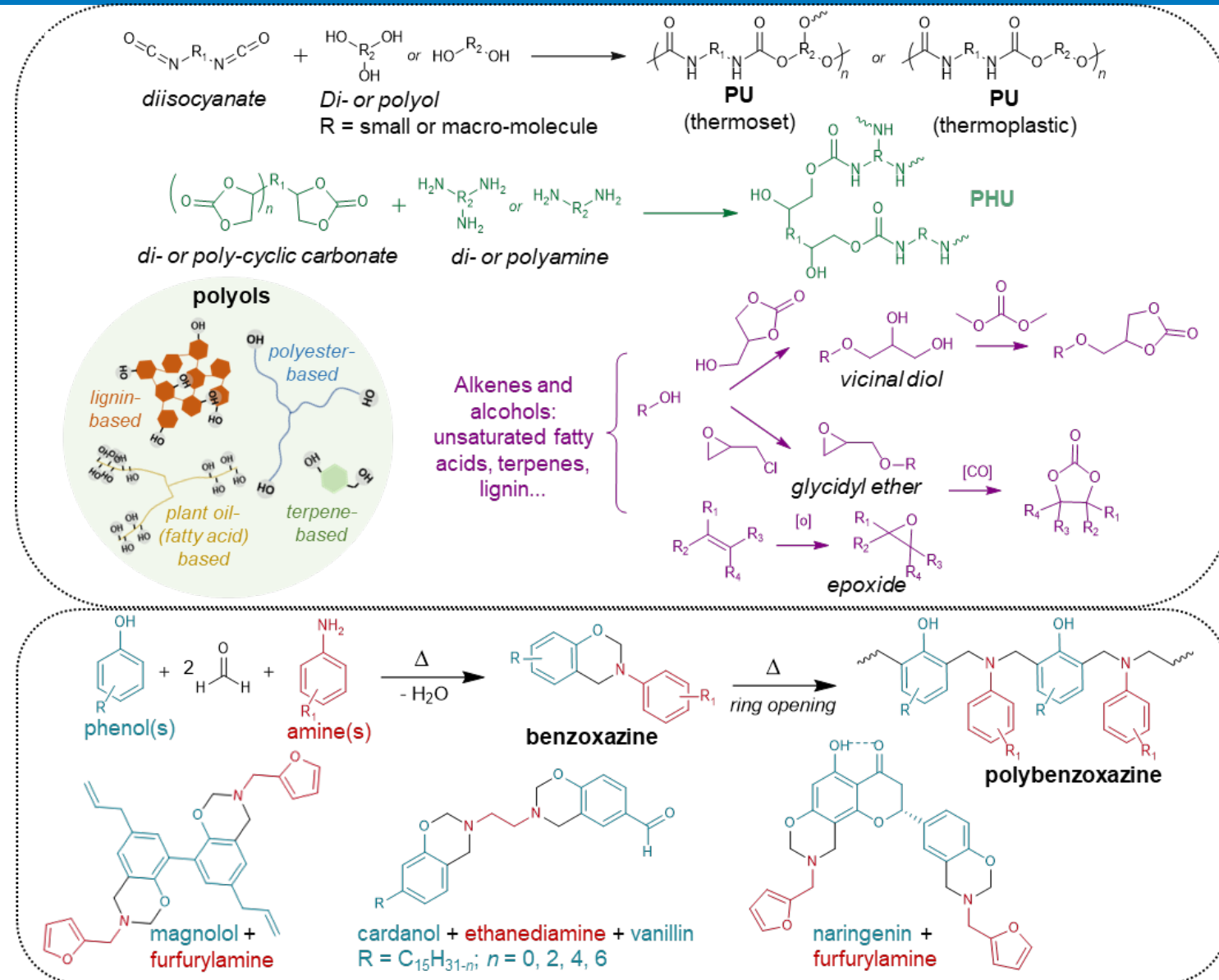
Analysis

- New directions in analysis and computational modeling with ID project



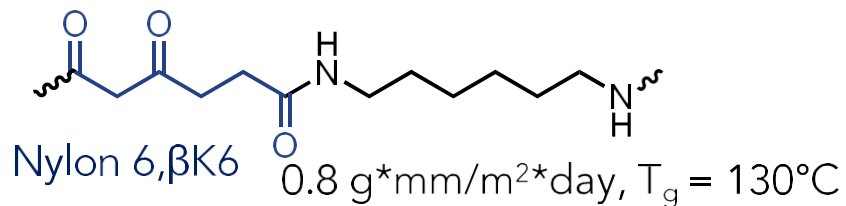
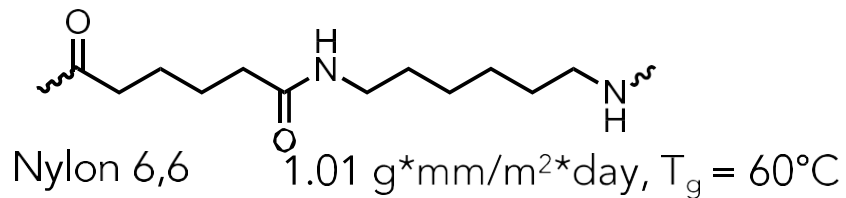
Forthcoming review on performance-advantaged bio-based polymers

- PA properties, derived from bio-based functionality, are critical to commercial success (vs. direct replacements)
- Scope: C-O and C-N linked backbone polymers with demonstrated performance advantages in **Manufacturing, In-Use, End-of-life**



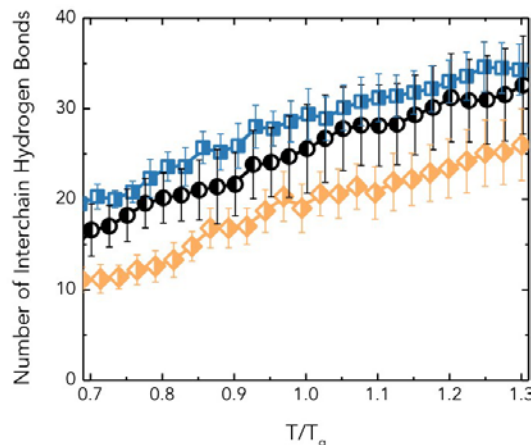
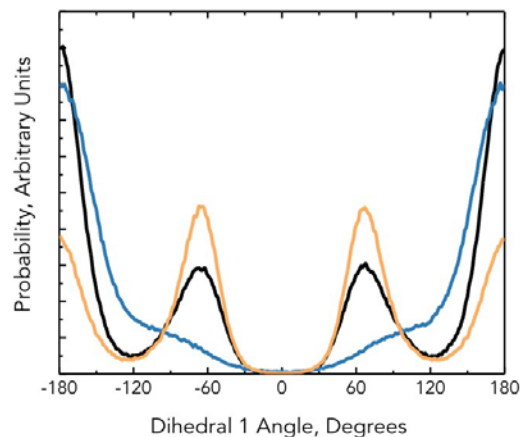
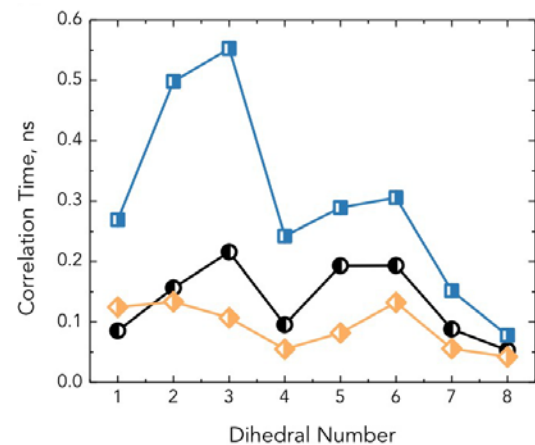
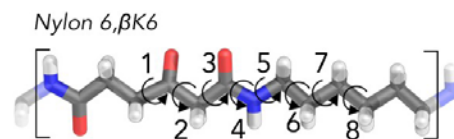
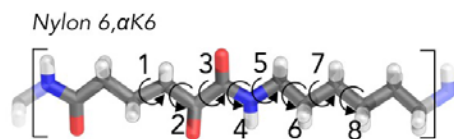
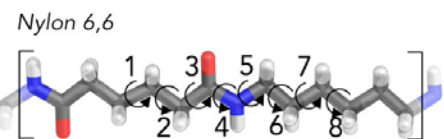
Example figure panels showing how bio-derived functionality (polyols, alkenes, phenols, amine) results C-N polymers (performance-advantages described in-text)

Performance-advantaged nylons enabled by β -keto diacids



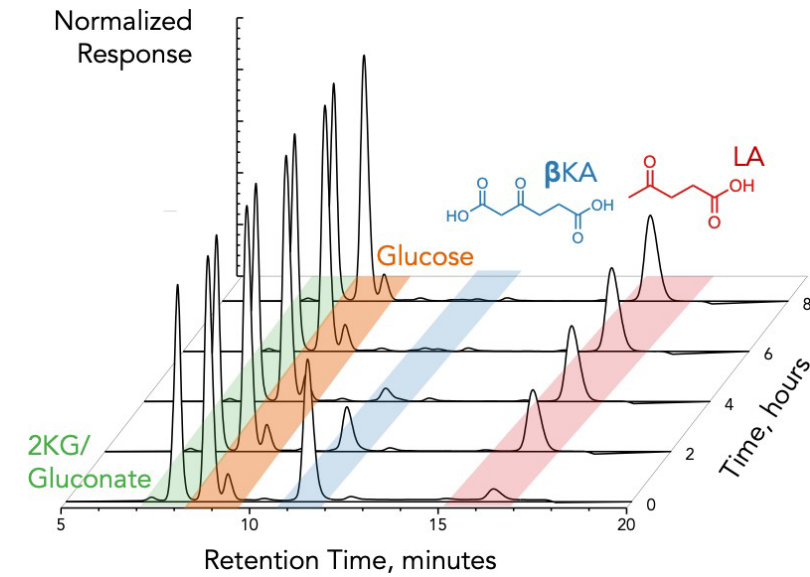
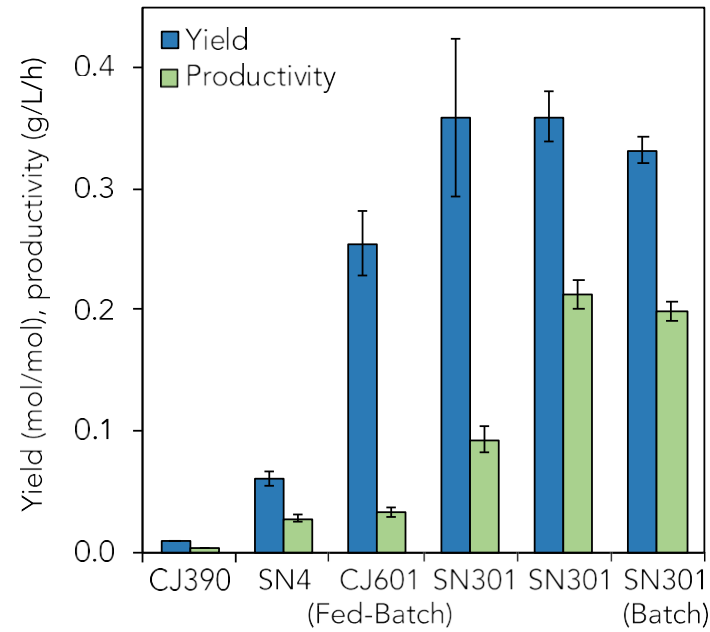
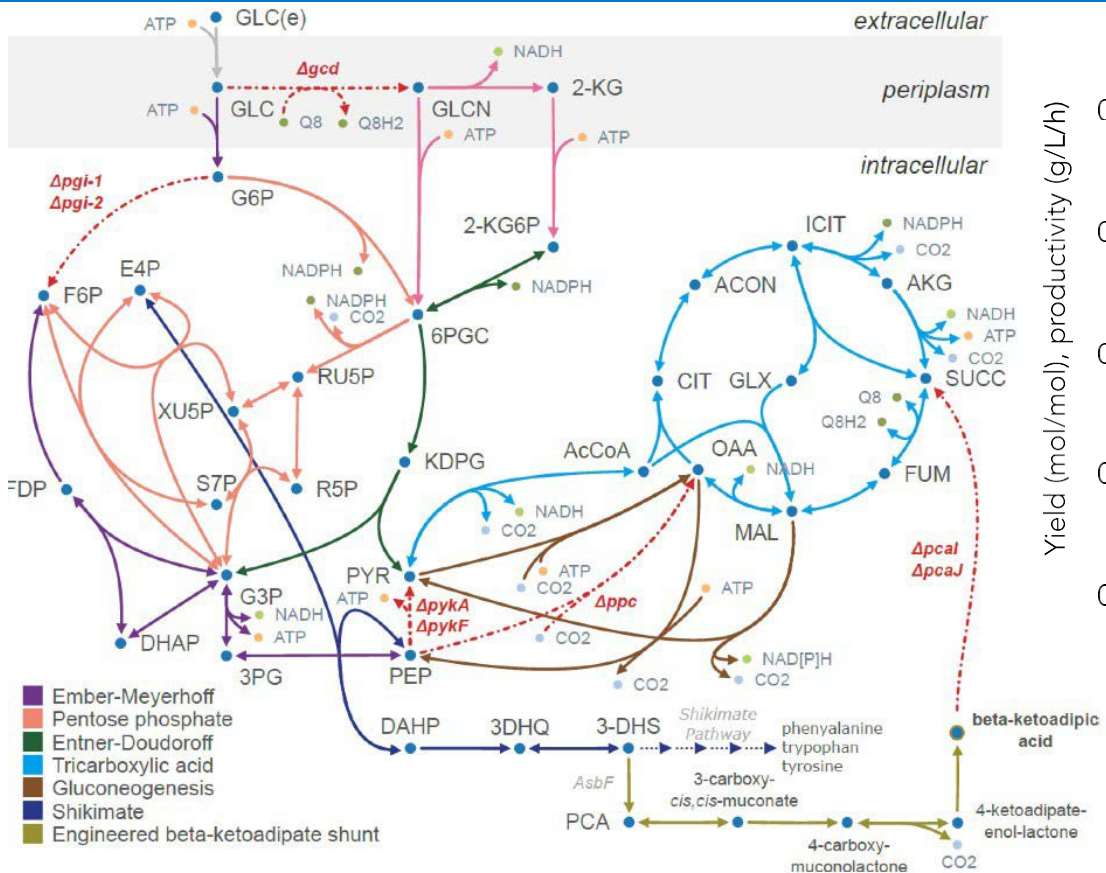
C6 dicarboxylic acids with β -ketone enable enhanced nylon performance

- Nylon 6,6, absorbs water, providing a target for improvement
 - Improved thermal properties can provide robust material performance for automotive and textile applications
- The β -ketone reduced water permeability by 20% while simultaneously increasing the T_g by 216%
- Molecular simulations (ID) used to understand β -ketone properties



● Nylon 6,6
 ◆ Nylon 6, α K6
 ■ Nylon 6, β K6

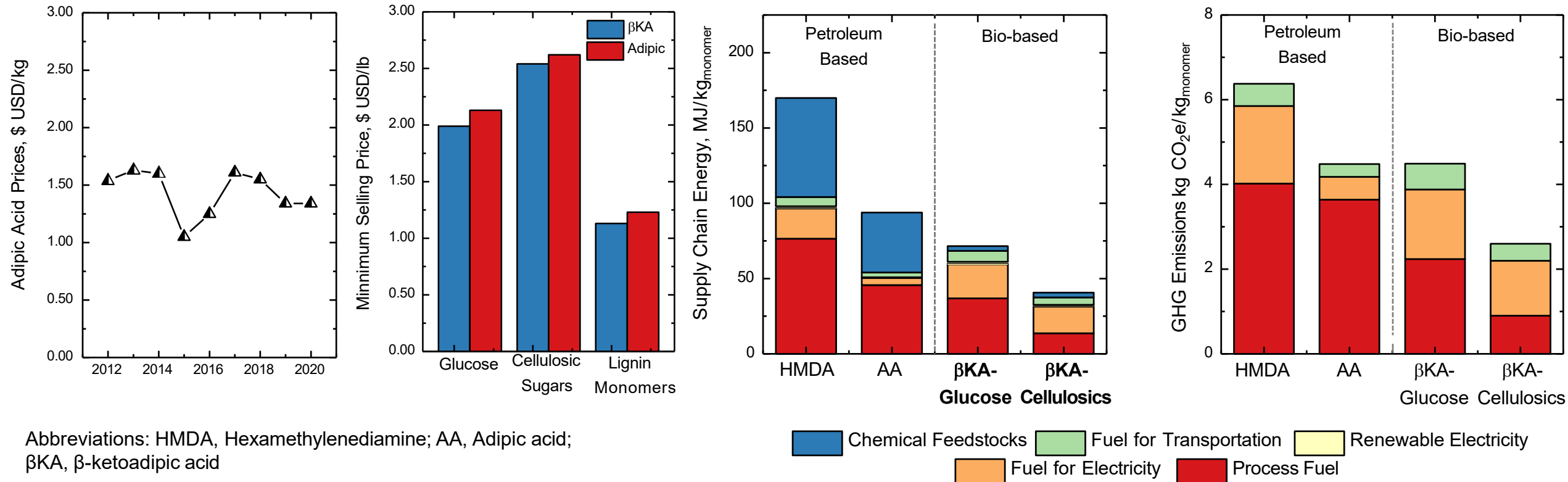
Performance-advantaged nylons: an interdisciplinary approach



β KA investigation spans disciplines

- Strains engineered to produce β KA from sugars (Agile BioFoundry and Biological Lignin Valorization projects)
- Standardized analysis procedures developed for β KA (Lignin Utilization)
- Collaboration with other projects enables de-risking of technology along the entire manufacturing process

Performance-advantaged nylons – advantages in manufacturing



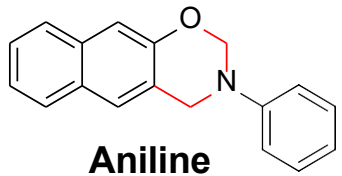
β KA can cost as low as \$1.13/kg with a 22% reduction in GHG emissions

- Lowest cost achieved from lignin feedstock
- Supply chain energies and GHG emissions depend on feedstock: **in all cases**, they are lower for bio-based monomers
- Significant potential to target N-containing monomers in future work (HMDA)

Thermosets from bioderived amines enable multiple performance options

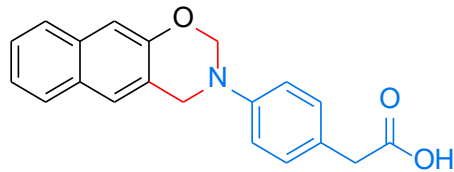
Biologically produced 4APAA bifunctionality ideal for catalytic benzoxazine thermosets

- **4APAA** reduces the processing temperature for polybenzoxazines by $>100^{\circ}\text{C}$



249 °C

Bio-based amine **4APAA** provides built-in catalytic functionality

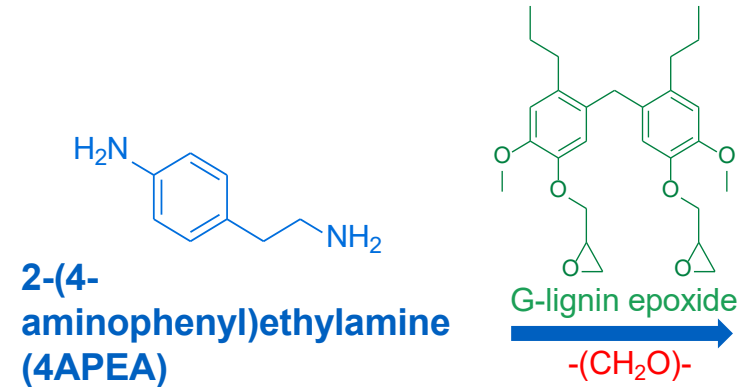


135 °C

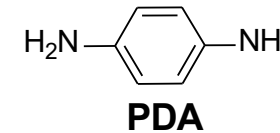
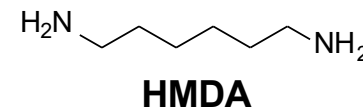
Curing Temperature

Benzoxazine

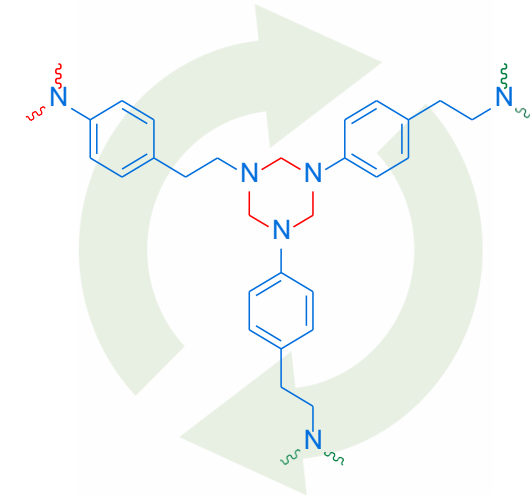
Functionalized Benzoxazine



vs.



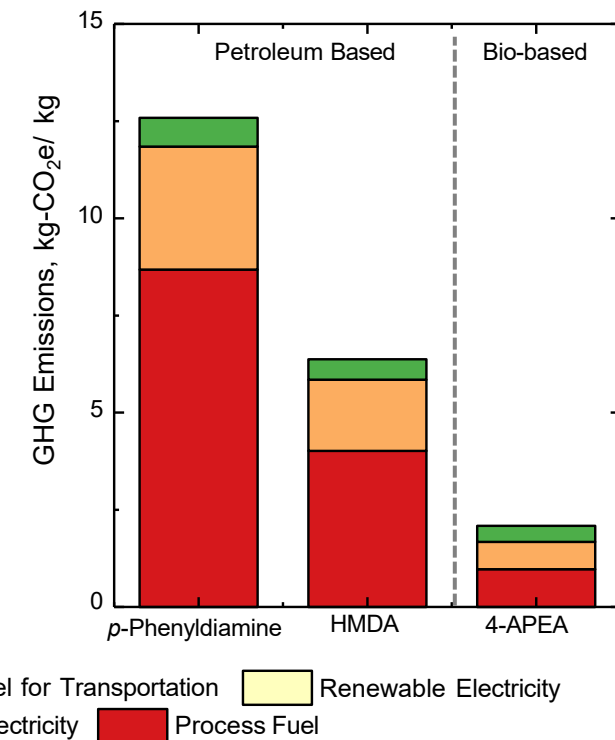
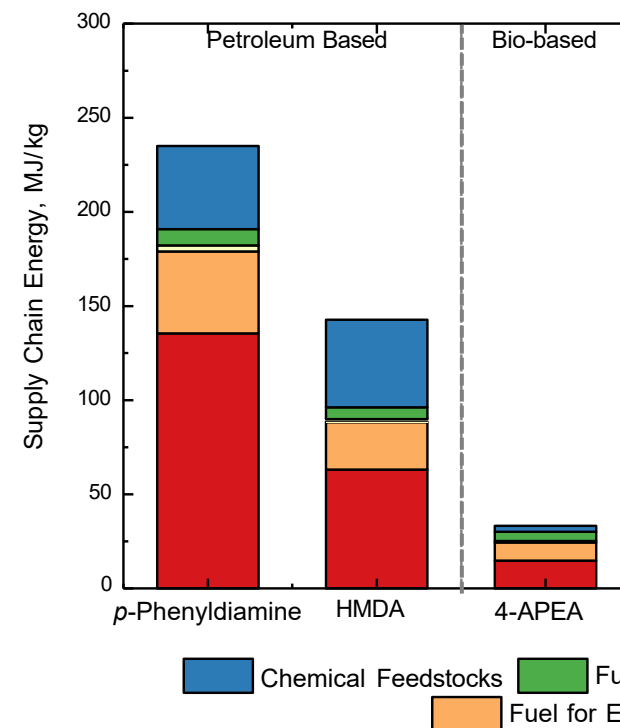
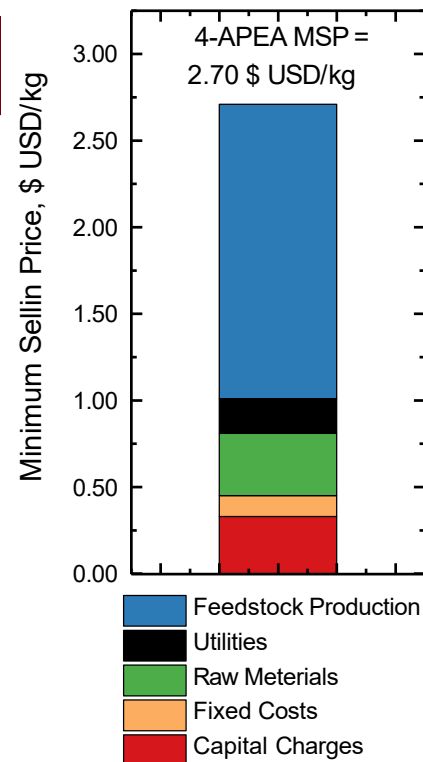
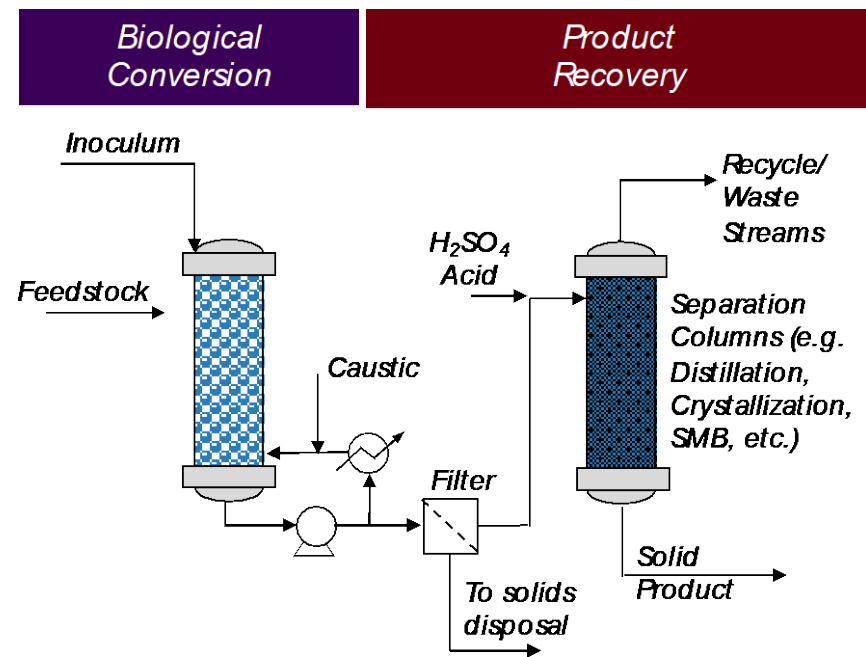
Petroleum Standards



Bio-based 4APEA introduces end-of-life recycling for epoxy thermosets

- Recyclable by acid hydrolysis because of **4APEA triazine** linkages incorporated into epoxy network
 - When lignin monomers are used, health risks are reduced compared to BPA epoxy resins
 - With Lignin-First Biorefinery Development, Agile BioFoundry

Biomass-derived amines exhibit reduced environmental impacts



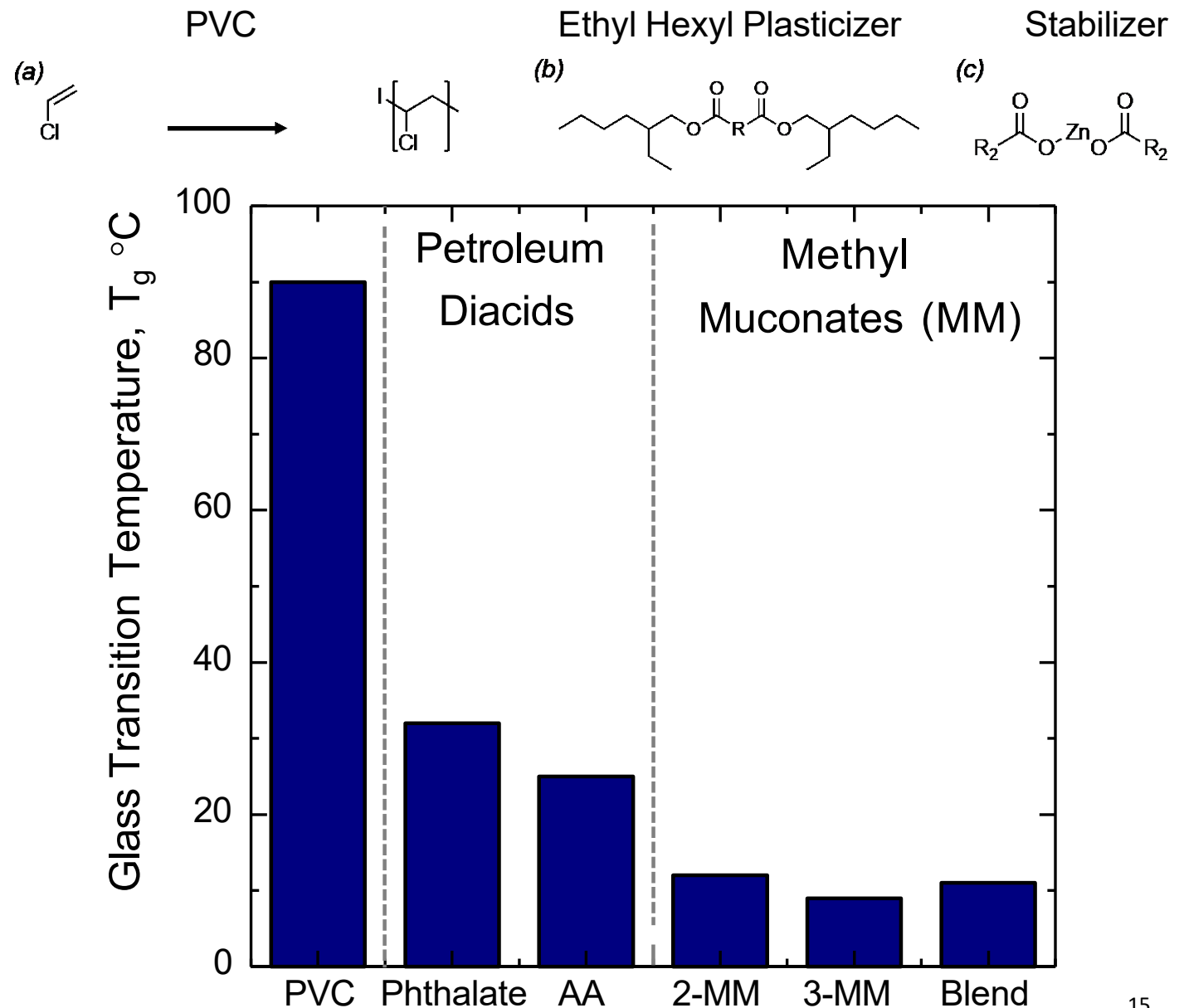
Amines from biomass offer $\geq 85\%$ reduction in supply chain energy and GHG emissions

- Amines can be used in multiple PA applications (e.g. benzoxazines, nylons, etc.)
- Feedstock is a key contributor to cost – analysis is ongoing for reducing feedstock contribution

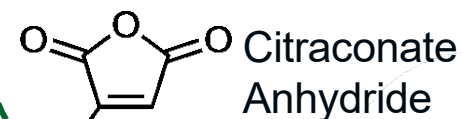
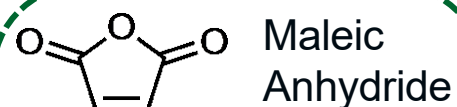
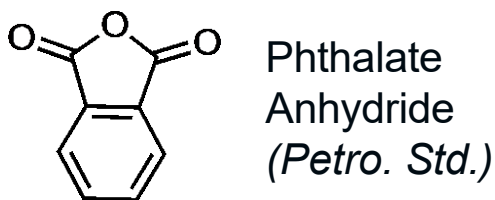
PVC plasticizers

Methyl muconates are highly effective at PVC plasticization

- Methyl muconates (*Bioconversion of Thermochemical Intermediates project*) can be used in plasticizers
- When blended with PVC (10 wt%), bio-plasticizers lead to a 75-83% reduction in T_g , a 12-20% improvement over the petroleum standard
- Methyl muconates are potentially safer – testing and analysis ongoing



PVC thermal stabilizers



Agile
BioFoundry

Sample	TGA, $T_{d, 50}$ °C	% Change to PVC	Other Notes
PVC	300	--	--
Lead- Phthalate	360	20% Improvement	<i>Petroleum Standard</i>
Tin Malate	310		
Tin Citraconate	290		
Zinc-Phthalate	370	23% Improvement	--
Zinc-Malate	390	30% Improvement	Soluble in THF, no thermal mixing needed
Zinc-Citraconate	420	40% Improvement	Soluble in THF, no thermal mixing needed

Stabilizers from anhydrides use safer metals and improve stabilization

- PVC stabilizers often contain metals (lead, tin) to manage HCl emitted in PVC processing
- Additives are an ideal market for PABPs as they can be used in material formulations at low loadings, are coupled with high volume products, and can sell for high prices – analysis ongoing
- **Current efforts:** understanding mechanistic basis for this performance enhancement (ID)

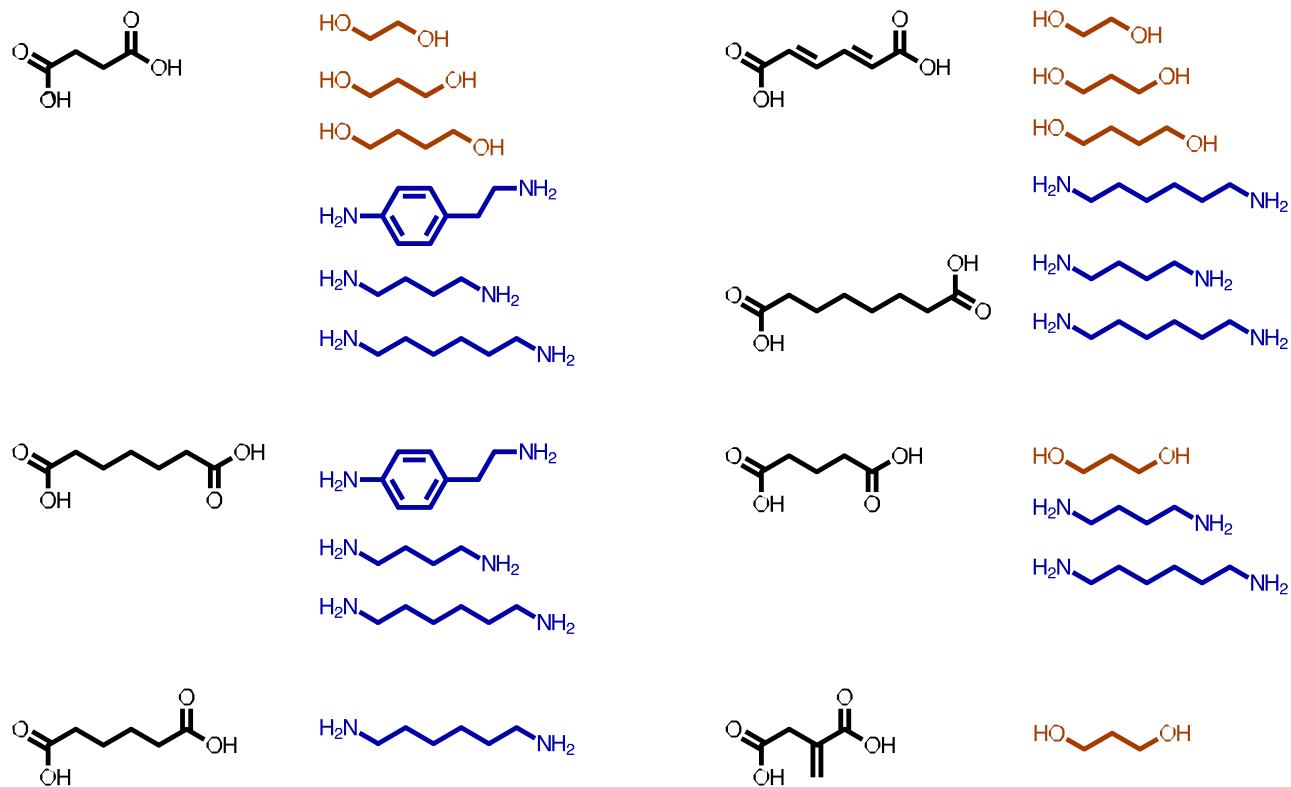
Cumulative PABP syntheses

<i>Petroleum Polymer</i>	<i>Bio-based Monomer</i>	<i>Metric</i>	<i>Property Change</i>	<i>Formulations</i>
Polyamines/Polyaramids				
Nylon 6,6	BKA	Permeability/T_g	20% Reduction/110% Increase	4
	BKG	T_g	105% Increase	4
	Muconic	T_d/Flame Resistance	10% Increase	4
	Methyl-muconates ^a	Permeability	15% Reduction, Large T _g Reduction	9
	ML Monomer Suite ^b	T _g	--	20
Nomex	PDC	Processability	Reduction in T _g	4
Polyesters				
PET (<i>amorphous</i>)	PDC	T_g/Biodegradability	10% Increase/ Acid/Base Reduction Increased	4
Polycarbonates				
BPA-PC	5-5' Linked Dimers	Endocrine Disruption	Reduction	2
	Lactide	Recyclability	Enabled	6
Styrenic Polymers				
ABS	Lignin Monomers	Toxicity/Separation Reduction	80%/60% Reduction	6
Epoxy Resins				
Thermosetting Epoxies	Lignin Monomers/Aromatic Amines	T_g/Recyclability	Maintained/ Acidic Recycling Introduced	11
	Multiple Dimers and Diamines	T _g , Mechanical	Properties Maintained	12
Polymer Additives				
Benzoxazines	Aromatic Amines	T_g, Processibility	Properties Maintained, T _p reduced	10
Phthalate Plasticizers	Methyl Muconates/ Citraconates	Plasticization/ Thermal Stabilization	50% Reduction at same loading	6

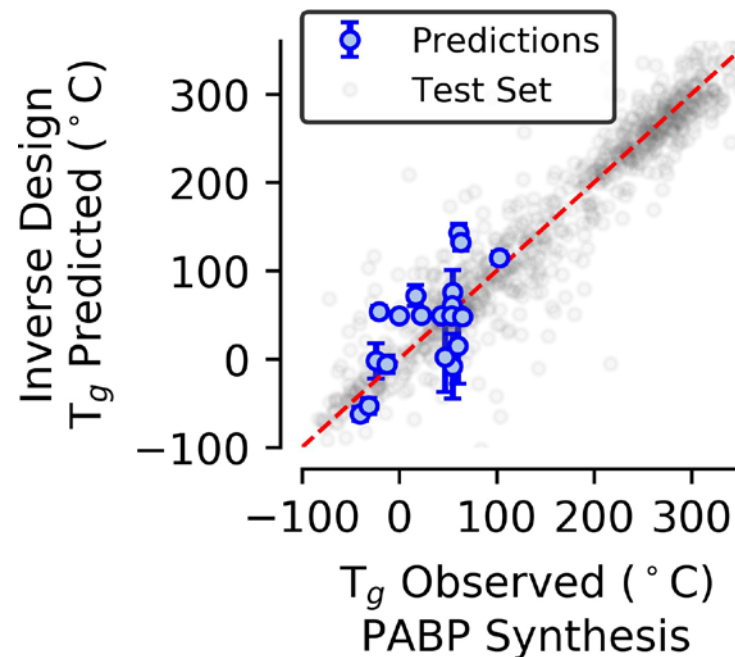
Total: 110 new formulations to date from target 50 (first 3-year cycle), at least 10 are PABPs

- Overall, this project seeks to achieve advantages in manufacturing, performance, and end-of-life
- PA often achieved via elevated T_g, lower permeabilities, higher thermal stabilities, etc.
- Table outlines brief descriptions of PABPs synthesized in the project to date

Synthesis of new polymers predicted from PolyML



poly(ML)

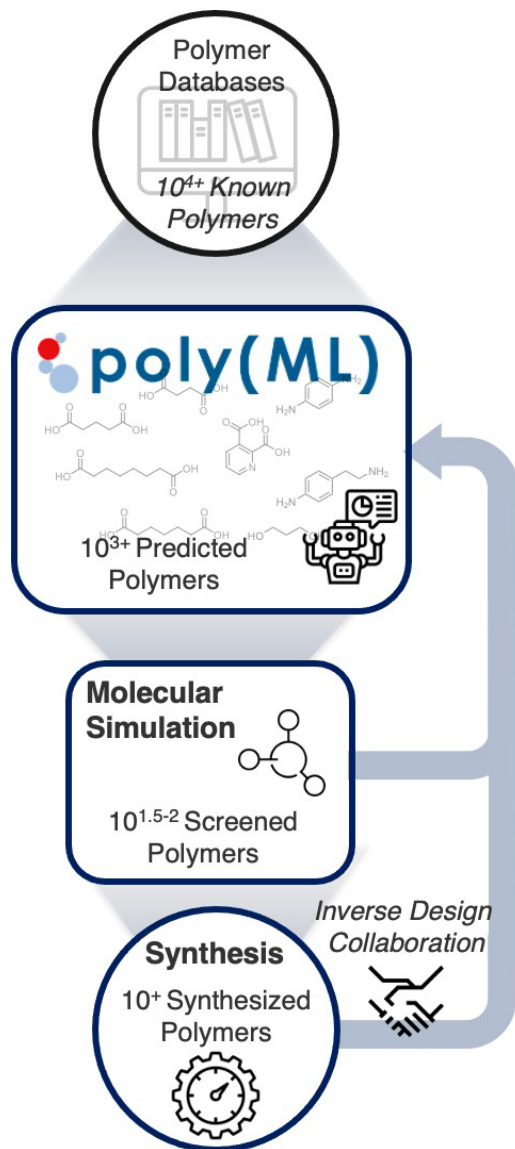


Experimental syntheses corroborate PolyML predictions

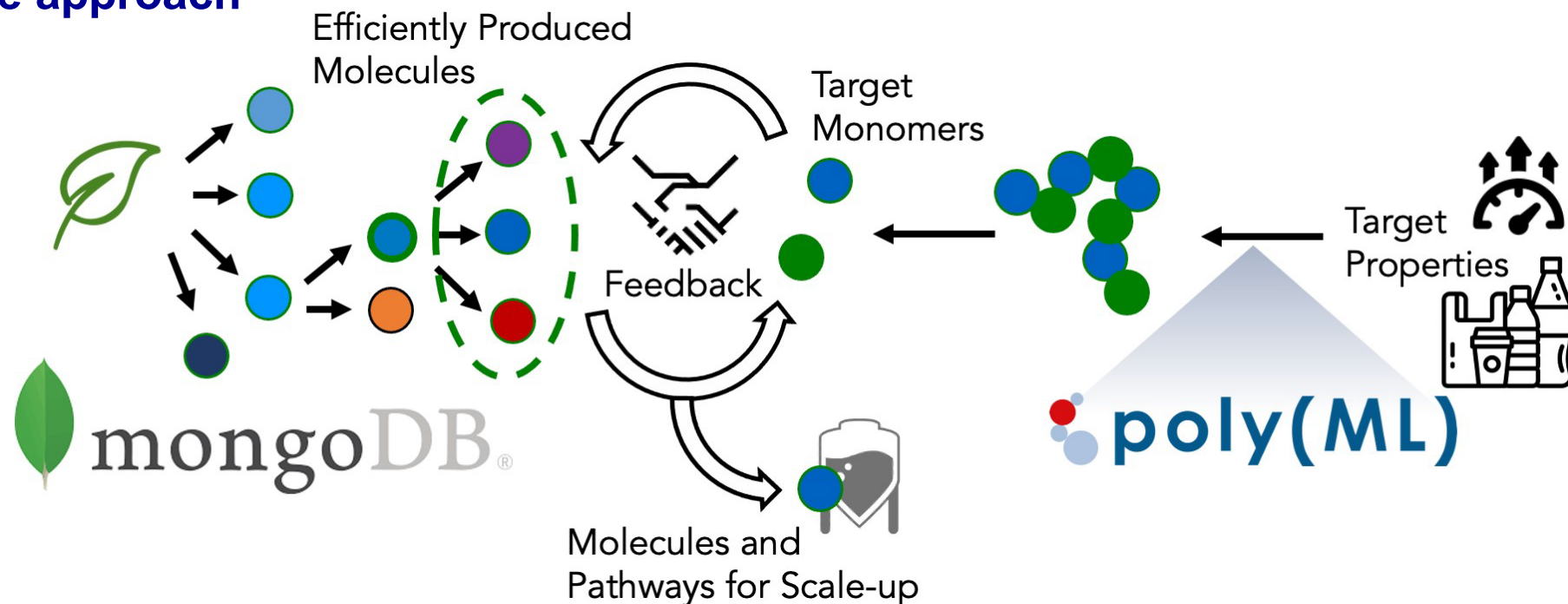
- Synthesized **8 polyesters** and **12 polyamides** to provide validation of PolyML predictions
- The initial syntheses were for heteroatom monomers that can be obtained from biomass
- **Current efforts:** Leveraging new predictions from PolyML to target new high-performance polymers (e.g. high T_g with low permeability)

Identifying pathways to PABPs via PolyML and mongoDB

Current approach



Future approach

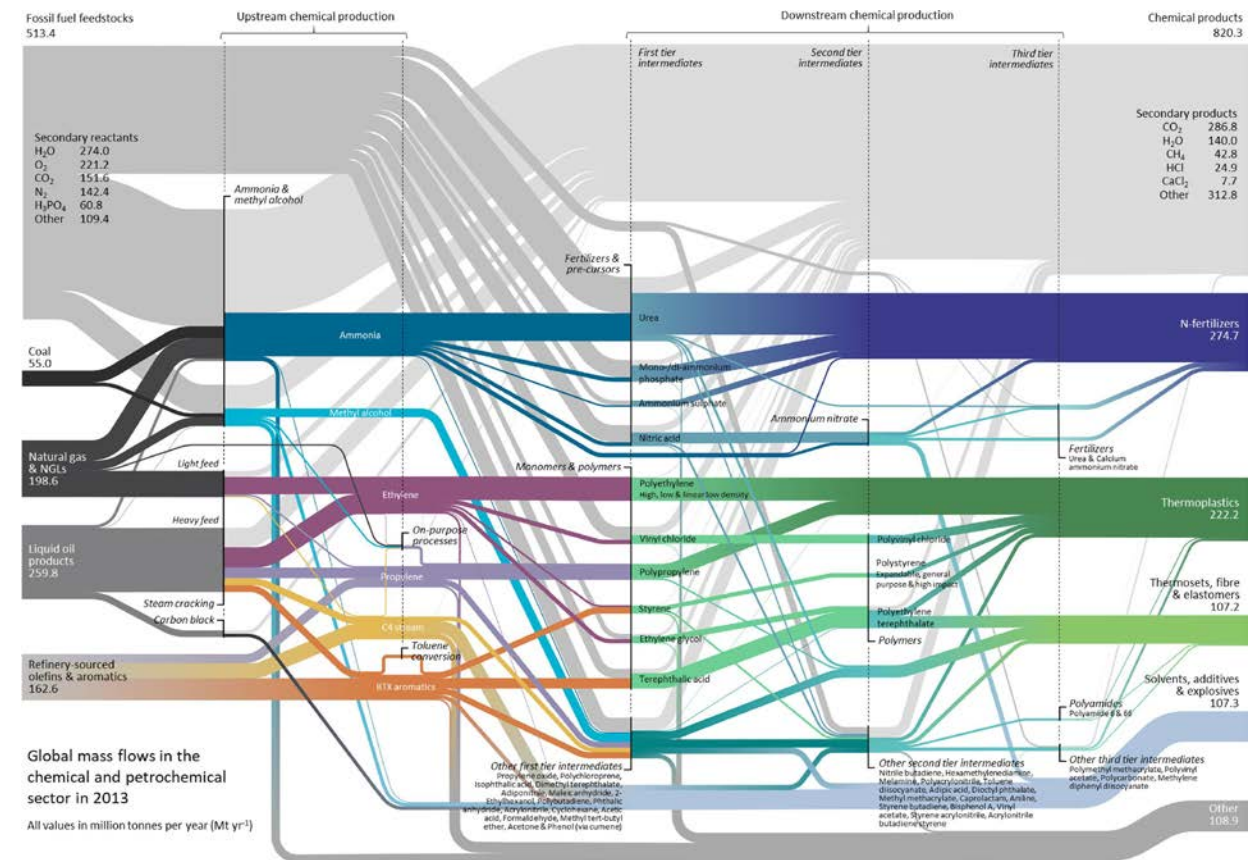
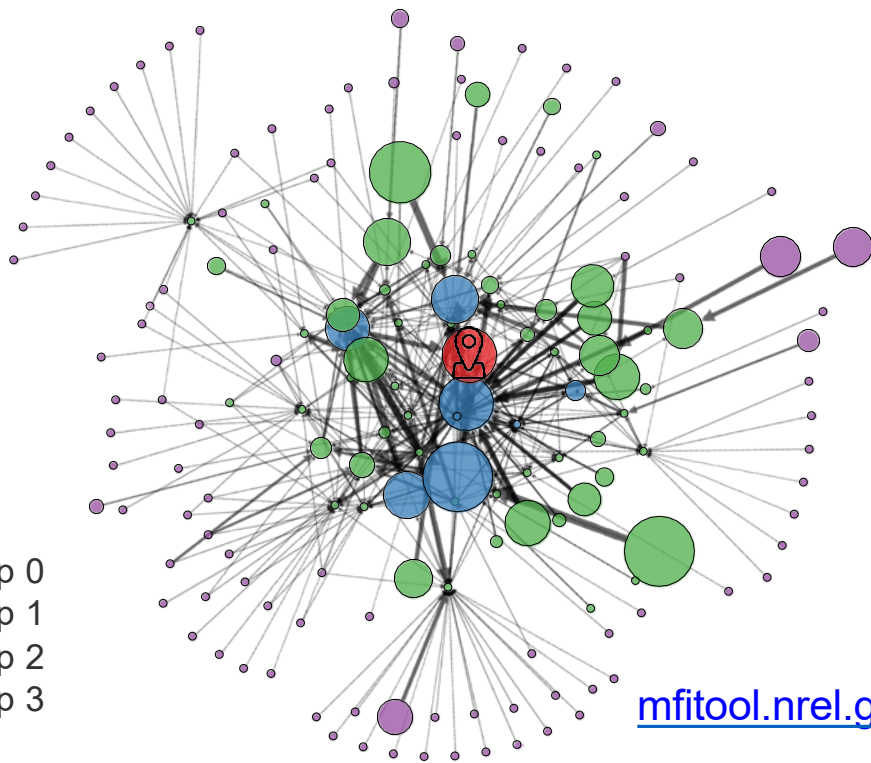


Pathway prediction coupled with polymer prediction aimed at narrowing synthesis and polymer design space

- PolyML identifies target molecules for PA polymers (*what molecule we should make*)
- MongoDB identifies and ranks hybrid chemical and biological pathways to target molecules, including considering rate, selectivity, thermodynamics, & separations (*how to best make the molecule*)

Benchmarking chemicals production to identify PABP targets

MFI models chemicals production as steps of supply chain inputs to the final product



Levi, P. G., & Cullen, J. M. (2018). *Env. Sci. Tech.*, 52(4), 1725-1734

Using MFI to estimate supply chain energy & GHG emissions of today's commodity chemicals

- Analogous to plastics benchmarking analysis in BOTTLE (Nicholson *et al. Joule* 2021)
- Currently identifying case studies based on market size; PABP targets can be benchmarked against these baseline data for supply chain energy and GHG emissions

Summary

Overview

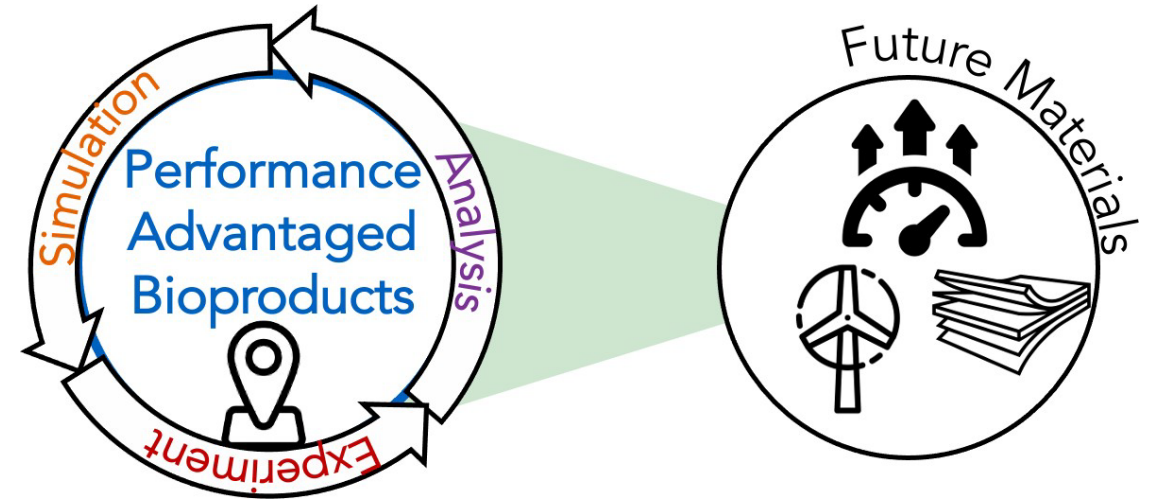
- This project – with Inverse Design – seeks to combine analysis, computation, and experiment to efficiently identify, synthesize, and characterize a suite of cost-effective, sustainable PABPs

Management

- Key collaborations with Agile BioFoundry, BETO lignin projects, SepCon, among others to source monomers and with Inverse Design to narrow design space

Approach

- Experimental efforts focus on PABP syntheses & characterizations
- Employ Aspen Plus and Materials Flows through Industry for analysis
- Disseminate new PABPs via integrated, high-impact publications and patents



Impact and Progress

- Key outputs to date include >100 PABP formulations and multiple bio-based, performance-advantaged polymers

Future Work

- Include additives as a key focus area expand project reach and distinguish work from other BETO projects in polymer design

Quad charts

Timeline

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

	FY20	Active Project (FY21-23)
DOE Funding	PABP - \$450,000 PABP analysis - \$250,000	\$1,560,000

Project Partners

BETO Projects: Biological Lignin Valorization (2.3.2.100), Separations Consortium (2.5.5.502), Biochemical Platform Analysis (2.1.0.100), Inverse Biopolymer Design through Machine Learning and Molecular Simulation (2.5.1.500), Agile BioFoundry (2.5.3.105), Bioconversion of Thermochemical Intermediates (2.3.2.301), Lignin Utilization (2.3.4.100), Lignin-First Biorefinery Development (2.2.3.106)

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

Barriers addressed

Ct-J Identification and Evaluation of Potential Bioproducts
Ct-K Developing Methods for Bioproduct Production
At-D Identifying New Market Opportunities for Bioenergy and Bioproducts

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

Acknowledgements

DOE Technology Managers Andrea Bailey and Nichole Fitzgerald

NREL Contributors:

Jared Anderson, Mary Bidy, Birdie Carpenter, Michael Crowley, Robin Cywar, Rick Elander, Kylee Harris, Caroline Hoyt, Chris Kinchin, Brandon Knott, Megan Krysiak, Daniela Marin, William Michener, Heather Mayes, Joel Miscall, Mark Nimlos, Michelle Reed, Scott Nicholson, Kelsey Ramirez, Nicholas Rorrer, Alison Shapiro, Avantika Singh, Peter St. John, Nolan Wilson

Collaborators:

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



Q&A

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This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.



Additional Slides

Responses to previous reviewer comments

- Excellent work results and progress on polymers. I would have liked to see some end uses that are watersoluble oligomers potentially useful in many consumer goods products and industrial applications; however, I'm glad to see future work on other applications. β -keto adipic acid work is exceptional and I'm glad to see results here as I feel this may be a first work moving forward in industry. Don't rely on weak links and biodegradability of polymers. Better to focus on recyclability because the European Union may in the future ban weak-link polymers and U.S. policy usually takes time to adjust, but often follows stiffer guidelines in the future.
 - We appreciate the positive comments from the reviewers. We agree that it would be ideal to expand beyond the current applications to include others, which additional funding would enable to increase bandwidth. The comment regarding biodegradability is excellent and we fully agree. We are attempting to make polymers that can be more easily chemically recycled.
- It seems like bioproducts do have great potential to deliver better properties. The question becomes how does this reach an innovation level great enough to bring sufficient investment to make a commercialized product.
 - We agree that the bio-based materials need to reach a level of innovation to catalyze industrial investment. To that end, we are in close coordination with industry regarding the innovations coming from this project to offboard them as we reach a sufficient technical readiness level.
- This is an interesting project to build and test new polymers from bio-based monomers and measure their properties. Very good progress on synthesis of new formulations have been reported, some of which exhibit enhanced properties. This program has received extensive input from industry on worthwhile performance characteristics and is nicely synergistic to the inverse learning program, as it will generate novel information to augment databases and improve predictive tools for new polymers.

Responses to previous reviewer comments (Analysis)

- The project must filter down choices quickly to focus on few chemicals to move forward. Two years seems long to filter down. Suggest that they should group materials together in terms of similar functionality to target mixtures that could replace things like chelants, aqueous viscosity modifiers for consumer products, or even lower molecular weight, water-soluble-type oligomers may be easier targets for functional materials in the 20,000 molecular weight average range or lower. This could avoid costly separation of single materials in some cases while providing a bigger cost reduction to fuel cost/GGE and a bigger chance to be successful overall.
- This has potential to be a very valuable publication when completed. Would be good if it could somehow identify pointers to next-generation molecules.
- The project is addressing a core goal in biorefinery development—understanding the properties and performance that are the true products of the chemical industry. Incorporating this understanding with a definition of the technology needs to derive these properties from bio-based building blocks will need to be a key component of any report or white paper resulting from this work.
- The project aims to generate a list of desirable bio-based targets, differing from prior work by including more performance and characteristics criteria to prioritize performance-advantaged bioproducts. With the pressing need to improve biorefinery economics via better valorization of streams, this effort is of strategic importance and, if successful, can be a guiding decision tool to focus valuable R&D time on better target choices.
- Great integrated approach to share information, results, and resources. Very well presented and the explanation of the framework for analysis of evaluating performance-advantaged bioproducts was clear. External advisory panel with eleven advisors provides a wide variety of industry perspectives. This is very thorough research and analysis to outline the value proposition and market pull.
 - We thank the reviewers for their helpful feedback and comments. We will work to incorporate these suggestions in the project going forward.

Publications, patents, presentation, awards, and commercialization

In review or revision:

To be filled in by February 19th, 2021

Robin M. Cywar, Nicholas A. Rorrer, Caroline B. Hoyt, Gregg T. Beckham*, Eugene Y.X. Chen*, Bio-based polymers with performance-advantaged properties, in review at *Nature Rev. Materials*.

In press:

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. Bidy, 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, presentation, awards, and commercialization

Presentations

Performance-advantaged bioproducts from lignin, BioEnergy Society of Singapore (via webinar), December 14th, 2020

Towards sustainable performance-advantaged bioproducts and plastics upcycling, Michigan Technological University (via webinar), November 6th, 2020

Performance-advantaged bioproducts from lignin and carbohydrates, 8th Fuel Science Center International Conference (via webinar), June 24th, 2020

Bacterial aromatic catabolism for lignin and plastics conversion, University of Minnesota BioTechnology Institute, March 5th, 2020

Using selective chemical and biological catalysis to upcycle lignin and plastics, ExxonMobil Research and Engineering, October 25th, 2019

Engineering non-model cell factories to produce novel polymer precursors, Biomass to Biobased Chemicals and Materials, July 17th, 2019

Challenges and opportunities in plastics upcycling, Plenary Invited Lecture, 26th BioEnvironmental Polymers Meeting, June 5th, 2019

Interfacial biocatalysis for breaking down plants and plastics, Boise State University, March 27th, 2019

Interfacial biocatalysis to break down plants and plastics, Colorado State University, February 15th, 2019

Hybrid biological and catalytic processes to manufacture and recycle plastics, USC, January 14th, 2019

Hybrid biological and catalytic processes to manufacture and recycle plastics, Princeton University, November 28th, 2018

Patent applications

Thioester and Thioaldehydes of Lignin Monomers for Reversible Crosslinked Applications: ROI-19-107, pending