NREL
Transforming ENERGY

Performance-Advantaged Bioproducts via Selective Biological and Catalytic Conversion

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Technology Session Review Area: Performance-Advantaged Bioproducts

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Goal statement

Goal: Develop performance-advantaged bioproducts that take advantage of efficient biological and/or catalytic conversions of biomass

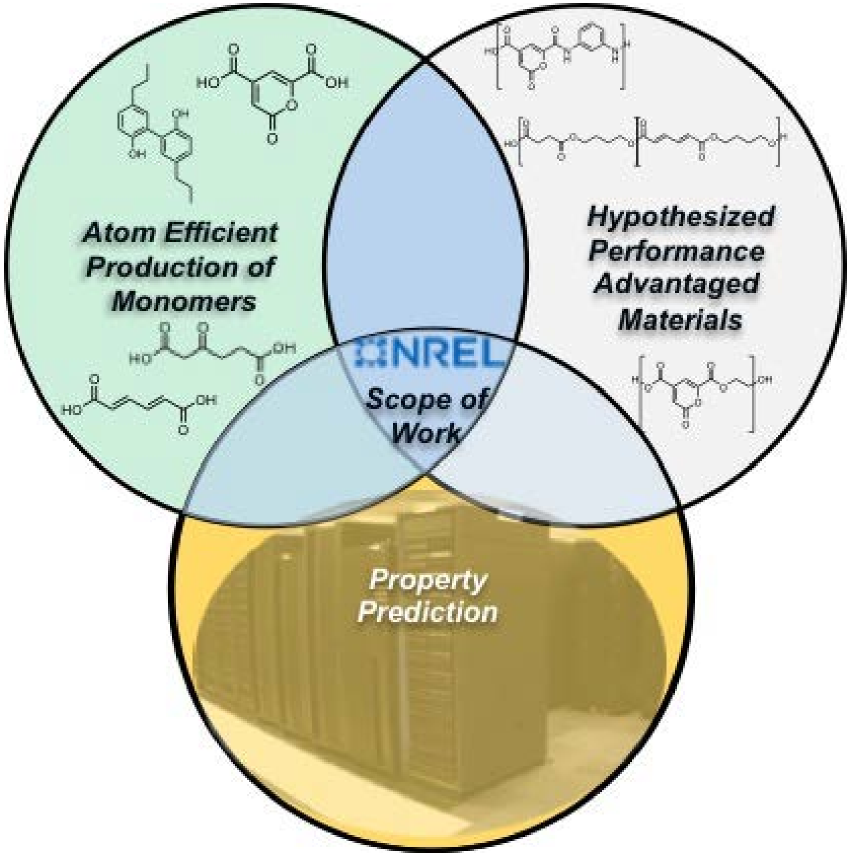
- Performance advantages include function, composition, manufacturing, and recyclability
- Harness oxygen/chemical handles in sugars, lignin, bio/catalytic intermediates

Outcome: ≥ 50 new bio-derived polymers for multiple applications at gram scale

- Demonstrate improvements in ≥ 10 new materials that are "performance-advantaged" over petro-derived materials

Relevance: Contribute to bioenergy industry by identifying and testing products not readily accessible from petroleum

- Contribute to methods for target identification
- Work with industry to ultimately enable new bio-based materials



Quad chart overview

Timeline

- Start date: October 2017
- End date: September 2020
- Percent complete: 50%

	Total Costs Pre FY17	FY17 Costs	FY18 Costs	Total Planned Funding (FY19-Project End Date)
DOE funded	--	--	$307k	$900k

Partners:

BETO Projects: Inverse Biopolymer Design through Machine Learning and Molecular Simulation, Performance Advantaged Bioproducts from Catalytic Fast Pyrolysis, Tailored Polymers Through Rational Monomer Development (LANL), Analysis in support of novel bio-based products and functional replacements, Lignin-First Biorefinery Development, Biological Conversion of Thermochemical Aqueous Streams, Biological Lignin Valorization, Agile BioFoundry, Separations Consortium

Nat'l labs, universities, companies,: Los Alamos National Laboratory, MIT, University of Minnesota, USDA-ARS, Colorado School of Mines, Denmark Technical University, Endolytics

Barriers addressed

- **Ct-J Identification and Evaluation of Potential Co-products**
  - Evaluating materials that can be produced from atom-efficient oxygenates
- **Ct-K Developing methods for co-product production**
  - Working with many BETO projects for product identification

Objective

Produce and characterize PABPs including thermoplastics and thermosets from monomers derived from selective biological and catalytic transformations of bio-derived substrates

End of Project Goal

Synthesize, characterize, and test 50 new bio-derived materials and demonstrate improvements in 10 materials that exceed petroleum-derived material properties by sufficient thresholds to consider the materials "performance advantaged"

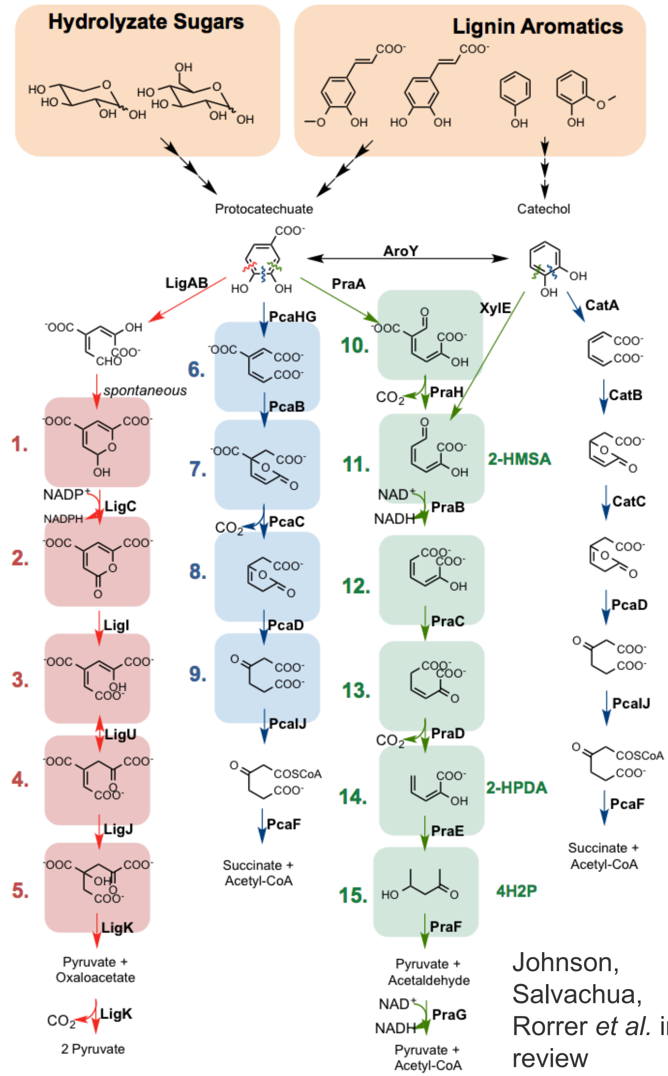
Project overview

History: Availability of novel monomers inspired new materials

- Focus: compounds from biology/catalysis that are difficult to make from petroleum
- Biology/catalysis from across BETO portfolio, *et al*.
- Early work on muconic acid for composites[1,2]

Context: Harness functionality inherent to biomass

- Drop-ins must compete against amortized industry
- Biomass and other renewable oxygenates offer potential for performance-advantaged materials



Johnson, Salvachua, Rorrer *et al.* in review

Project Goals:

- Produce multiple PABPs from sugar and lignin-derived intermediates
- Design and test for properties that are considered performance-advantaged
- Collaborate with computational inverse design project in PABP mini-consortium
- Creative advantage: new bio-based intermediates from a broad portfolio, expertise in thermoplastics and thermosets, computational design

1. Rorrer *et al. ACS SusChemEng* 2016
2. Rorrer *et al. Green Chem.* 2017

Management approach

Team composition and structure:

- Materials engineer (Nicholas Rorrer), polymer chemist (Caroline Hoyt), and synthesis interns
- Experts in chemical and materials synthesis, polymer property testing

Project Interfacing:

- Meet with other PABP BETO projects biweekly
- Meet with BETO Tech. Manager once a month
- Interface with other projects where interesting molecules are being made

Milestones:

- Mostly "**new molecule to new material**"
- Equipment installation, industry engagement
- Joint milestones with PABP, BETO projects

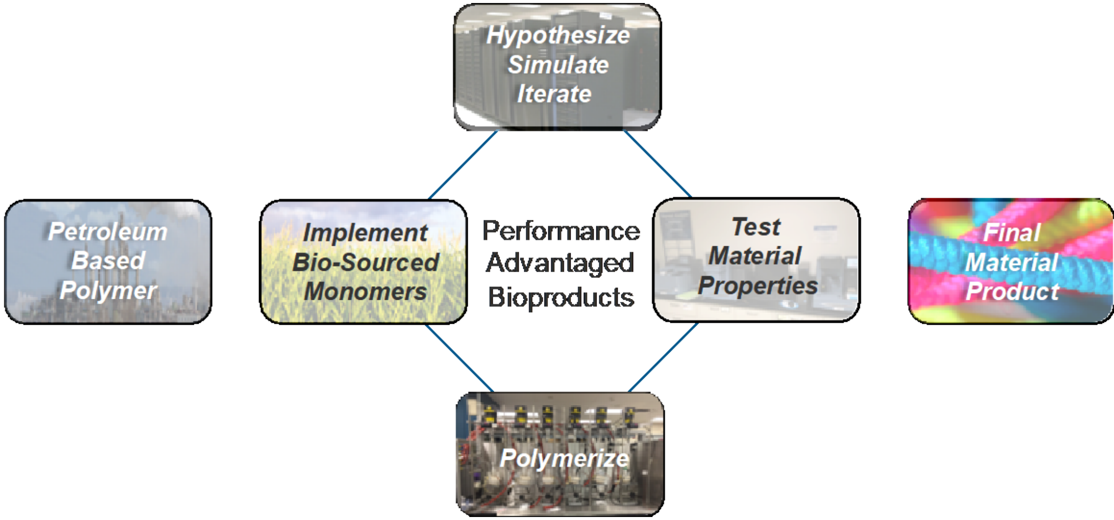
Industry engagement:

- Conduct customer discovery interviews
- Review what industry considers "performance advantaged"; feedback informs R&D directions

Technical approach

Workflow for producing new performance-advantaged materials:

- Identify new molecules we can readily access from bio-based sources
- Employ monomers or convert to expanded slate through chemical transformations
- Produce sufficient quantities (via collaborations) for materials testing
- Synthesize and test new materials that harness unique functionality of monomers; provide feedback to the monomer production teams
- Include “traditional” bio-based co-monomers where possible (e.g., succinic acid)
- Focus on commodity/specialty materials like thermoplastics and thermosets
- Protect composition of matter IP via patent applications, publish findings



Challenges

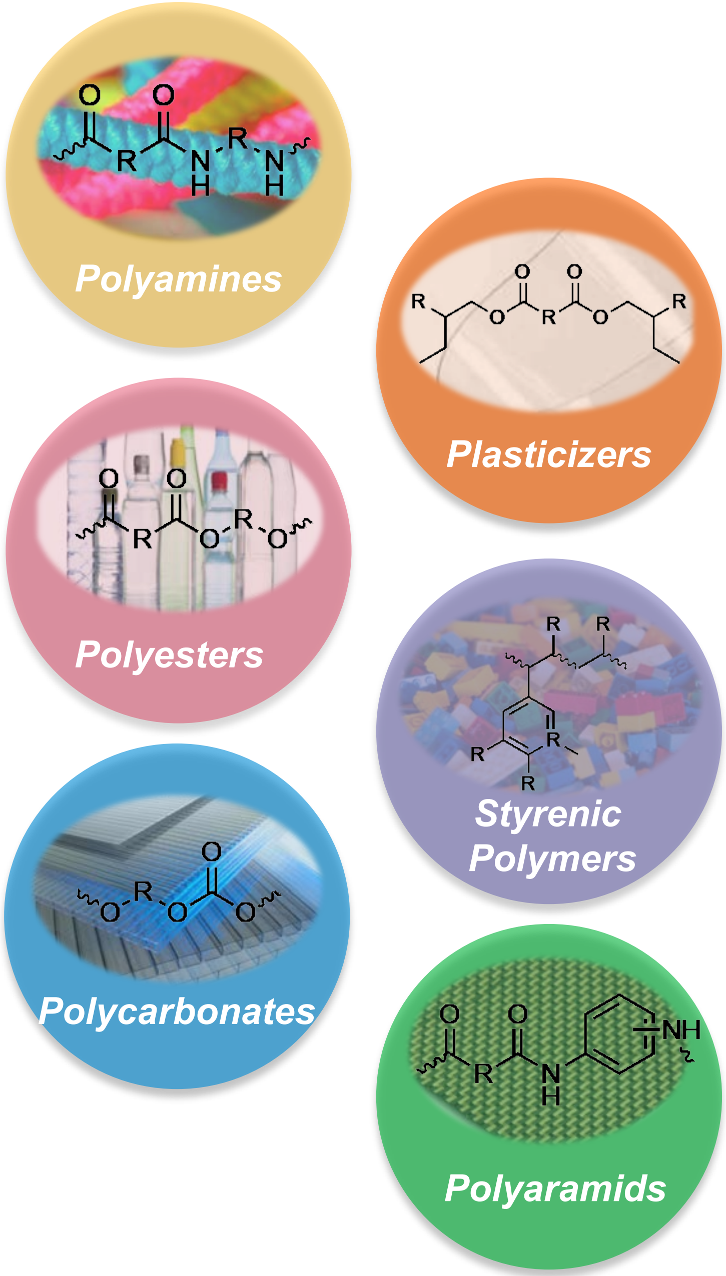
- Monomer availability
- Facile syntheses of monomers/polymers
- Appropriate tests/equipment for application

Critical Success Factors:

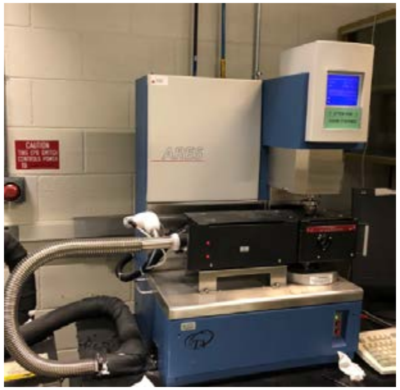
- Identification of targets and markets for performance advantaged materials
- Collaboration with downstream material users to understand applications space
- Note: cost of production not modeled in this project

Outline of technical accomplishments

- **Equipment:** Laboratory commissioning for small-scale polymer synthesis and characterization
- **Industry Engagement:** Customer discovery interviews with industry
- **New Materials:**
    - New monomers from aromatic catabolism
    - PA nylons from ß–keto diacids
    - Plasticizers from wastewater bioconversion
    - Replacing isophthalate in PET and Nomex
    - Replacing styrene via lignin-first technology
    - Replacing bisphenol A replacements from lignin
- Target identification going forward



Laboratory for small-scale polymer synthesis and characterization



- Established laboratory for small-scale polymer synthesis and characterization
- Up to 30 polymerization reactions in parallel
- Thermal properties via DSC, TGA, mat'l properties via permeability measurements, water uptake, DMA, Instron, biodegradability via acid/base chemistry and soil trials
- **Outcome:** Capabilities to rapidly produce and test polymers with ~1 gram of starting material

Customer discovery interviews with industry

- Goal: determine what industrial representatives consider "performance advantaged"
- Contacted over 50 companies and conducted >15 in-depth interviews
- Will be updated each year to identify industrial collaborations and new directions

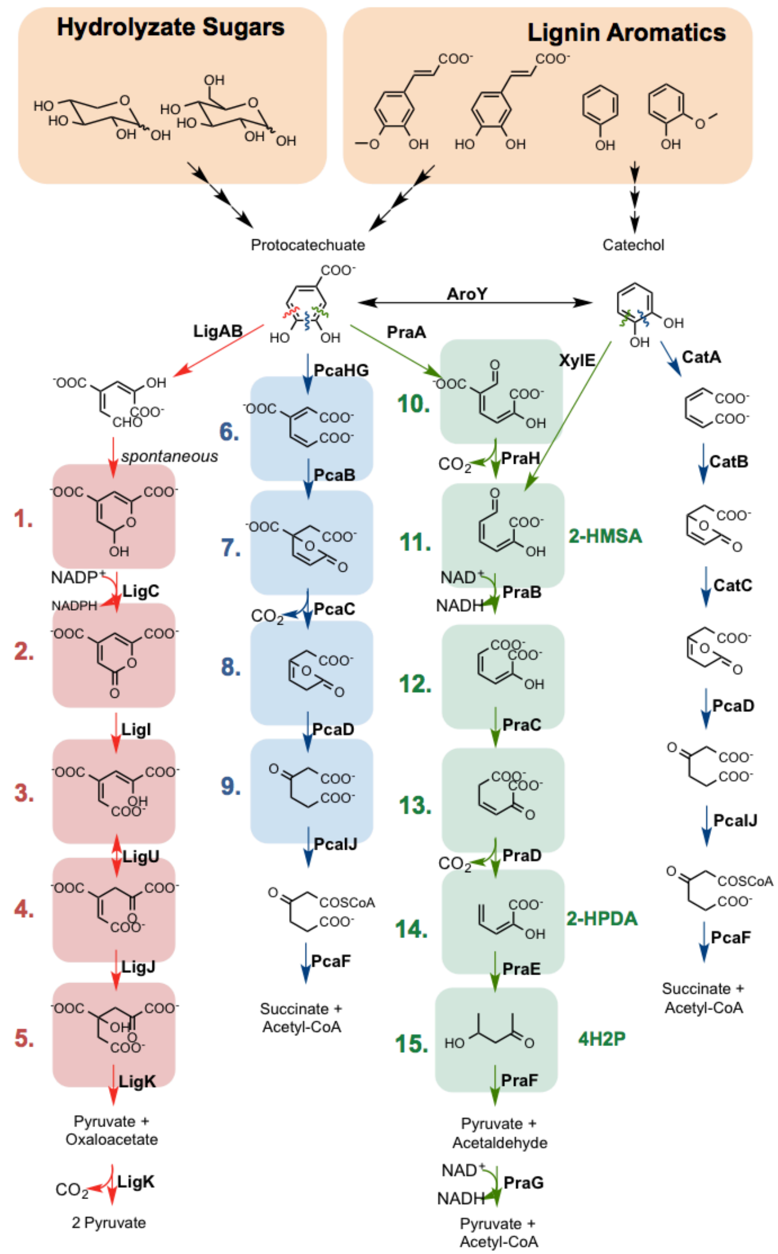
Lessons Learned :

- Direct replacements are of little interest
- Cost is the main driver
- Recyclability ***not*** biodegradability
- More bench-scale characterization leads to easier implementation

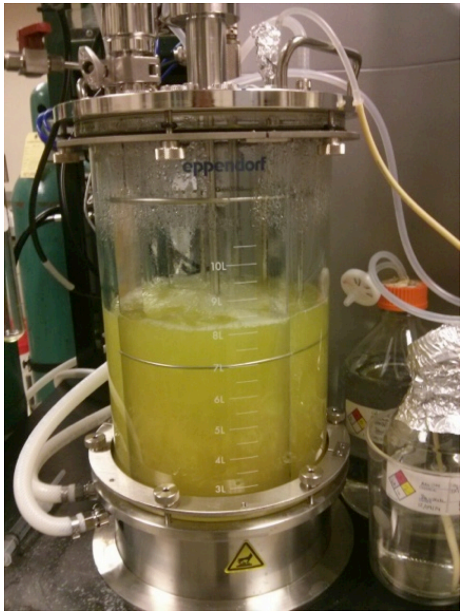
Desired PA properties:

- Improved mechanical properties (stiffness, toughness)
- Improved thermal properties (T_g for application or synthesis)
- Higher flame resistance
- Lower additive loadings
- Easier dyeing

Source of novel monomers from aromatic catabolism



- Aromatic catabolism enables 16 monomers including muconic acid, ß-ketoadipic acid, and pyrone-4,6-dicarboxylic acid (PDC)
  - Produced in 10-L bioreactors
- Can be produced from aromatic monomers (Biological Lignin Valorization project)
- Muconic acid from sugars in Agile BioFoundry

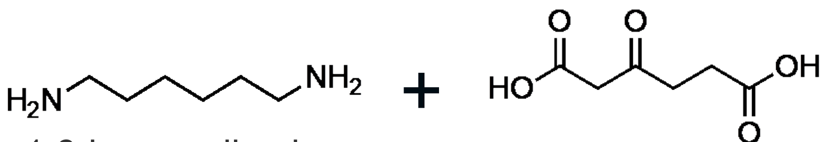


Outcome: starting portfolio of new biomolecules for production of novel PA materials

Johnson, Salvachua, Rorrer, Black, Vardon, St. John *et al.* in review

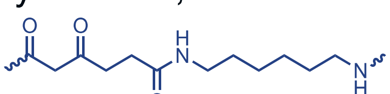
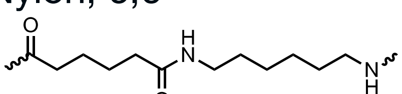
Performance-advantaged nylon from ß-ketoadipic acid

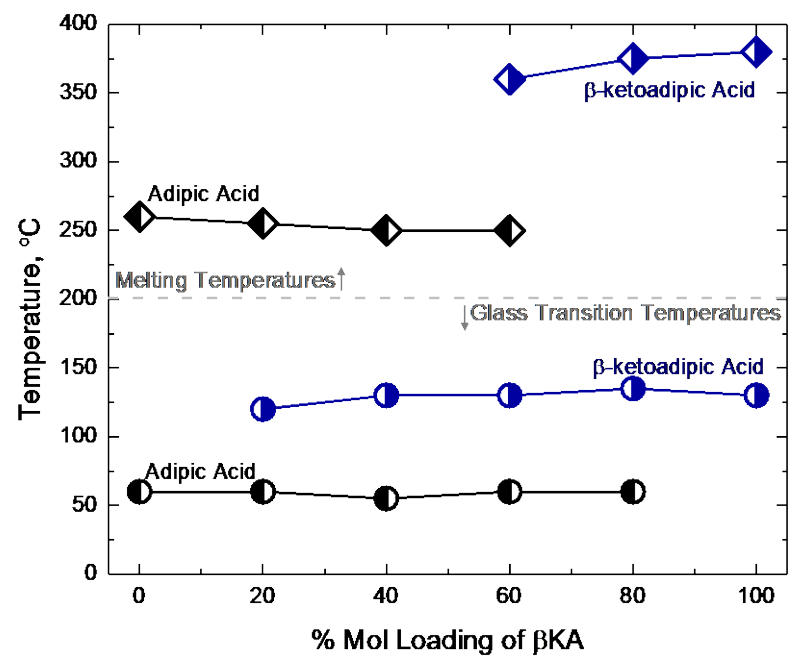
- Nylons are used in automotive parts, molding, packaging, coatings, fabrics, etc.
- **PABP need**: improved thermal properties and flame resistance, lower water permeability
- **Hypothesis**: ß-keto diacids can improve thermal/barrier properties due to increased rigidity
- **Bio-based monomer**: ß-ketoadipic acid (in place of adipic acid)



1,6-hexanediamine

ß-ketoadipic acid

Polymer	T_g (°C)	T_m (°C)	Permeability (g*mm/m^2*day)
Nylon BKA,6 	130	380*	0.80
Nylon, 6,6 	60	260	1.01



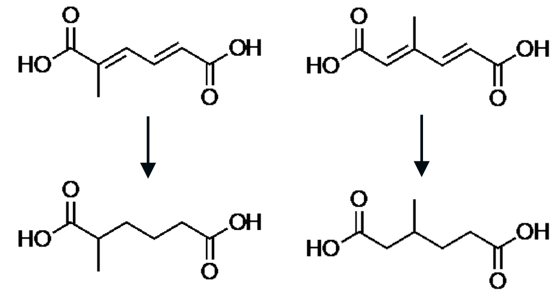
Outcome: β-ketoadipic acid imparts enhanced thermal properties and lower water permeability

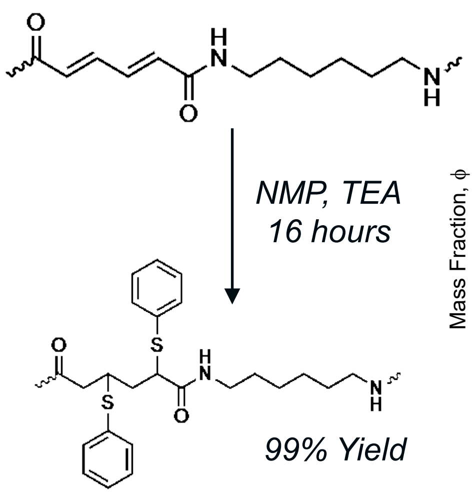
Collaborating with Inverse Design project to understand molecular basis for differences

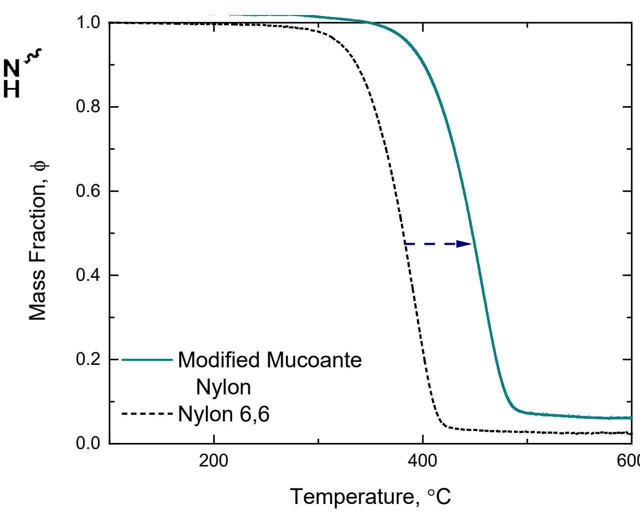
Rorrer, Notonier, Knott *et al.* in preparation

Multiple applications for methyl muconates

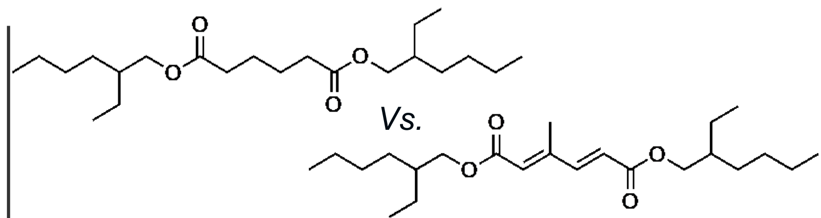
- **PABP needs**: Flame resistance in nylons, plasticizer reductions
- **Hypotheses**: Methyl groups can 1) reduce water uptake and 2) plasticize standard polymers due to hydrophobicity/branching
- **Bio-based monomers**: methyl muconates/adipates accessible from pyrolysis wastewater bioconversion







Most Common PVC Plasticizer



Diacid	*Loading (wt.%)*	T_g
Adipic	1	90
	5	74
Methyl-Muconate	1	89
	5	67

Functionalized nylons for enhanced flame resistance

Double bonds enable chemical modifications

Outcome: Improvement in flame resistance properties at similar mechanical properties to nylon-6,6

Methyl muconates as plasticizers

Observed dramatic drop in T_g upon incorporation of monomers

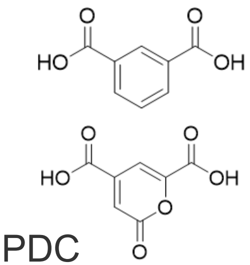
Outcome: Methyl groups can reduce permeabilties and effectively plasticize

Meyers, Rorrer, Hoyt, *et al.* in preparation

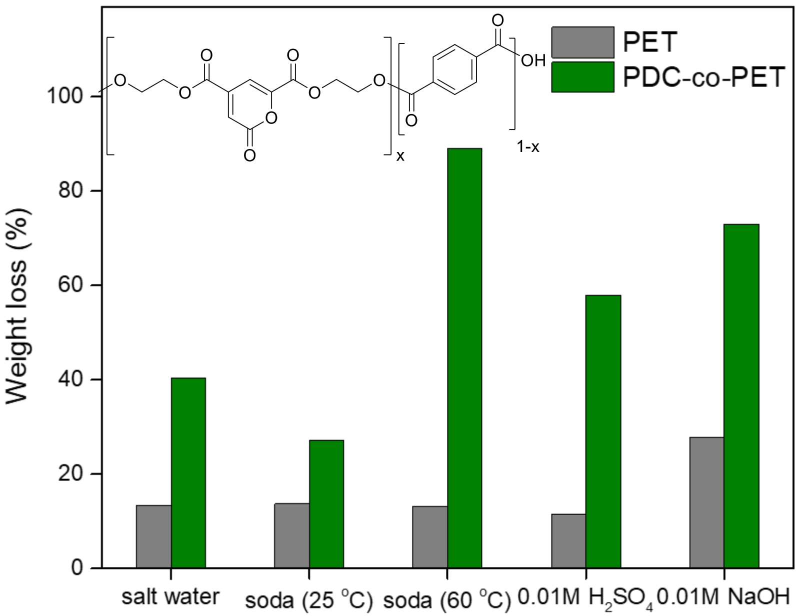
Replacing isophthalic acid in PET and polyaramids

- Isophthalate used to tune PET crystallinity, for thermal barrier in Nomex
- **PABP need (PET): Enabling facile chemical recycling**
- **PABP need (polyaramid): Melt processing is challenging**
- **Hypothesis**: Lactone in PDC can offer route to facile chemical recycling
- **Bio-based monomer**: Pyrone-dicarboxylic acid (PDC) for isophthalate

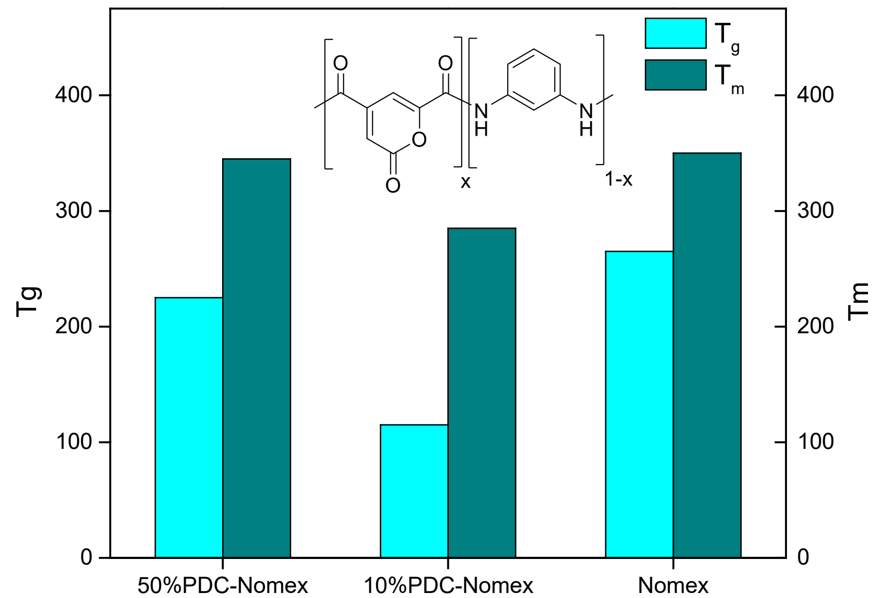
Isophthalic acid



PDC



- Developed PDC polymerization method
- Improved thermal properties of PET
- **Outcome: lower resistance of PET-PDC enables facile recycling at same properties**

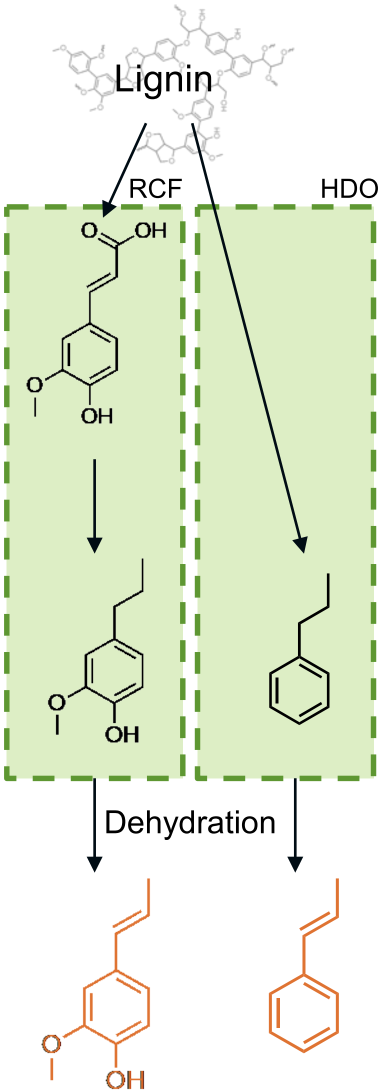


- Consistent thermal properties with Nomex, lower T_g leads to easier processing
- **Outcome: performance-advantaged polyaramid via introduction of PDC**

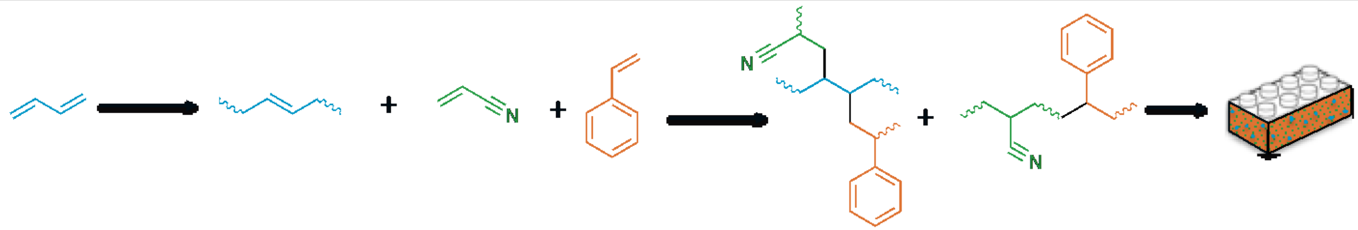
Hoyt *et al.* in preparation

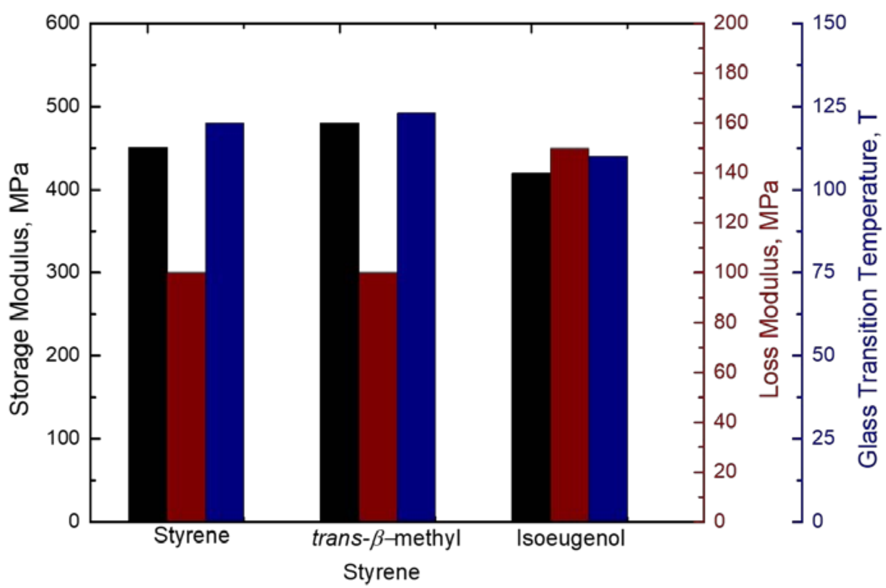
Advantaged styrene replacements from lignin

Stone, Anderson, Rorrer, *et al.* in preparation



- Lignin-first refining enables efficient production of propyl-aromatics
- **PABP need**: Manufacturing with styrene is a toxicological hazard and an energy-intensive separation from ethylbenzene
- **Bio-based monomer**: Propyl-aromatics in place of styrene, e.g., in ABS



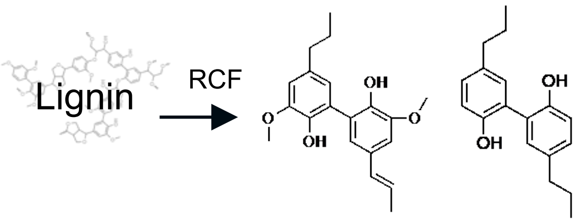


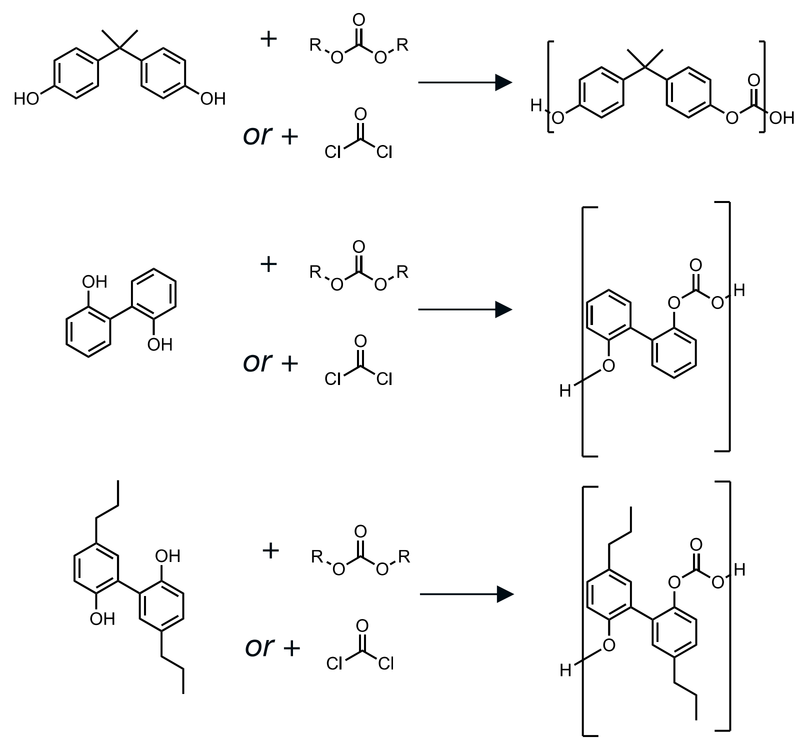
- Tested multiple ABS polymerization approaches with bio-based monomers
- **Outcome**: Trans-ß-methyl styrene exhibits same properties as styrene with reduced toxicological hazards (based on literature reports) and less energy-intensive separations

Advantaged bisphenol A replacements from lignin

- Lignin-first refining enables efficient production of biphenyl compounds
- **PABP need**: Replacing bisphenol A due to endocrine disruption effects
- **Bio-based monomer**: Biphenyl dimers from Lignin-First Biorefinery Development

Rorrer *et al.* in preparation



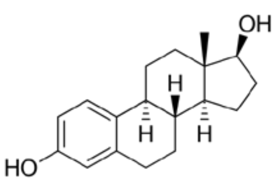


Amorphous T_g ~145°C

Amorphous T_g ~140°C

Amorphous T_g ~110°C

endolytics

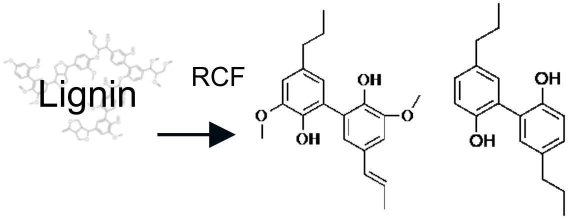


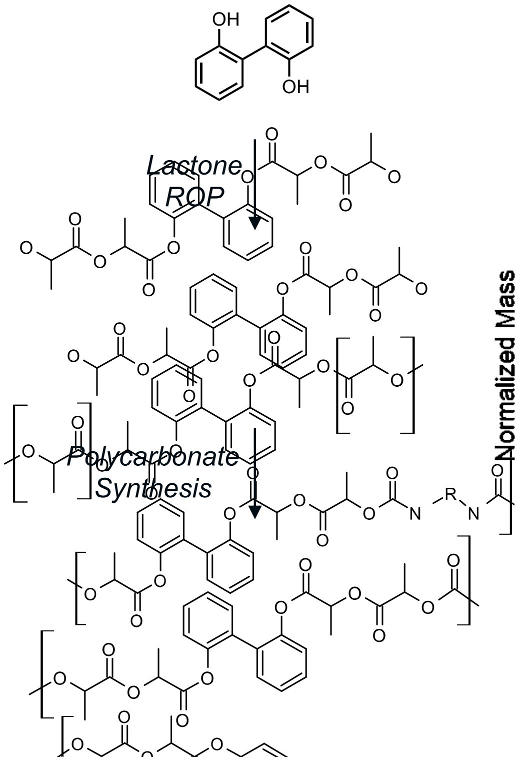
Endocrine disruption tests show no toxicity effects

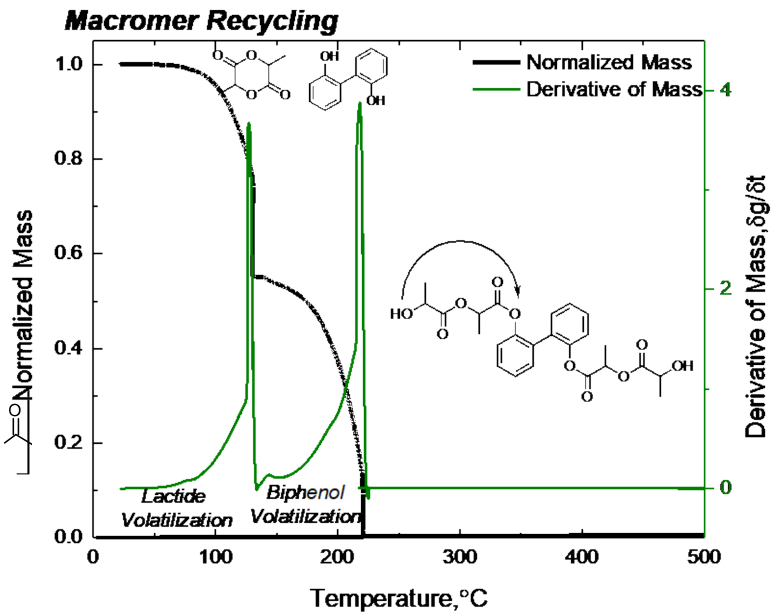
- Endocrine disruption tests show no toxicity effects
- Computational work with Inverse Design project ongoing
- **Outcome**: Biphenyl dimers offer similar thermal properties to standard polycarbonates made with BPA, but with no endocrine disruption effects

Recyclable polycarbonates via biphenyls and lactic acid

- Leveraging biphenyl compounds from lignin-first refining
- **PABP need**: Polycarbonates are not recycled at end-of-life
- **Bio-based monomer**: Biphenyl dimers polymerized with lactide may enable chemical recycling







Clear, Amorphous, T_g ~140°C

- Lactide does not affect polymer properties and can be thermally recycled
- **Outcome**: Biphenyl dimers offer similar thermal properties to standard polycarbonates made with BPA, but with no endocrine disruption effects

Rorrer, Anderson, *et al.* in preparation

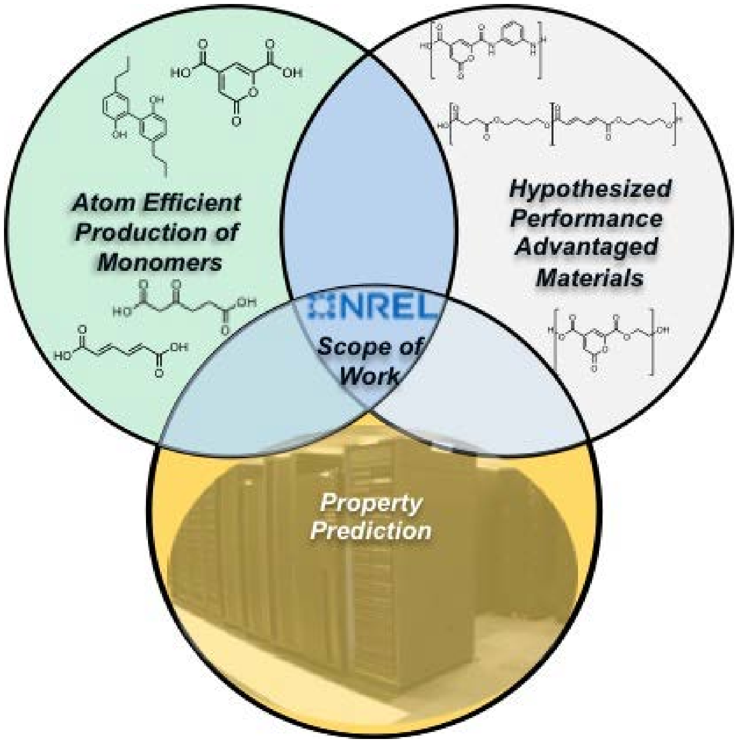
Summary of technical accomplishments

Petroleum Polymer	*Bio-based Monomer*	*Metric*	*Property Change*	*Formulations*
Polyamines/Polyaramids				
Nylon 6,6	BKA	Permeability	20% Reduction	4
		Tg	110% Increase	
	BKG	Tg	105% Increase	4
	Muconic	Td/Flame Resistance	10% Increase	4
	Methyl-muconates	Permeability	15% Reduction	4
Nomex	PDC	Processability	Reduction in T_g	4
Polyesters				
PET *(amorphous)*	PDC	Tg	10% Increase	4
		Biodegradability	Acid/Base Reduction Increased	
Polycarbonates				
BPA-PC	5-5’ Linked Dimers	Endocrine Disruption	Currently Testing	2
	Lactide	Recyclability	Enabled	6
Styrenic Polymers				
ABS	Lignin Monomers	Toxicity Reduction	80% Reduction	6
		Separation Severity	60% Reduction	

38 new formulations developed out of target 50, at least 7 so far are PABPs

Relevance

Goal: Develop PABPs from selective transformations of oxygenates (sugars, lignin, CO_2, etc.)



Why is this project important and what is the relevance to BETO and bioenergy goals?

- Advantaged bioproducts that do not directly compete with petroleum chemicals and exhibit superior properties will catalyze investment
- Highlights new building block molecules for broader R&D community
- Can directly contribute to BETO cost targets for lowering fuel selling prices via novel co-products

How does this project advance the State of Technology and contribute to commercial viability of biofuels production?

- Bioproducts are essential for biofuels
- Produces new bio-based materials beyond the "Top Ten" biochemicals list

Technology transfer activities

- Filing IP applications on compositions of matter
- Publishing findings in peer-reviewed journals
- In talks with industrial partners for new products
- Writing methods documents on chemical recyclability and biodegradability standards
- Energy I-Corps proposal in FY19/FY20

Future work

Petroleum Polymer	*Bio-based Monomer*	*Metric*
Thermosets		
Unsaturated Polyesters	Muconic TBD	Loading Reduction
		Recyclability
Epoxy Resins	5-5’ Linked Dimers, Lactones	Endocrine Disruption
Heteroatom Containing Polymers		
PVC	Modified Muconates	Recyclability
Fluoropolymers		Process Intensity
Coatings		
Polyacrylates	PDC	Recyclability Ease of Modification
Nitriles		
Poly(acrylonitrile)	Multiple Organic Acids	Char Percentage, Loading, Mechanical
Styrenic Polymers/Rubbers		
ABS	PDC Fumaronitrile Muconates	Recyclability
Nitrile Rubbers		Permeability, Toughness
Isoprene Rubbers		Recyclability
Applications Beyond Polymers		
Plasticizers	Methyl-Muconates	Endocrine Disruption
		Loading Reduction
Lubricants	Terpenes	Viscosity Profile
Extraction Solvents	Lignin dimers	Efficiency

- 38 new formulations developed out of target 50, 7 are PABPs
- **Continue development of ongoing portfolio and expand into new materials with same monomers**
- **Introduce new/novel monomers into the portfolio via collaborations**
  - Nitrilation chemistry for N-polymers
  - Lactones via collaborations with CSU
  - Modified PHAs with DTU, BETO projects
  - Terpenes from metabolic engineering efforts in external projects
  - Fatty-acid products via work with algae platform
  - On-board additional lignin dimers and monomers
- **Expand to additional material classes (see table)**
- **Work with Inverse Design Project**

Summary

Overview

– Develop performance-advantaged bioproducts that harness innate oxygen content and chemical handles in bio-derived compounds

Approach

– Leverage novel monomers across BETO portfolio, synthesize and test new materials hypothesized to offer performance advantages, employ computationally-guided R&D

Technical accomplishments

– Developed more robust nylon formulations, new plasticizers based on methyl muconates
– Replacing isophthalic acid with PDC and BPA with lactic acid and biphenyl to enable recyclability in thermoplastics
– Replacing styrene with lignin-based products that are easier to separate and less toxic

Relevance

– Performance-advantaged co-products can enable investment in bio-based materials
– Addresses Whole Barrel of Oil Initiative and bolsters the biomass value chain
– New bio-based building block molecules for the academic and industrial R&D community

Future work

– On-board new bio-based monomers via collaborative efforts
– Expand accessible material classes
– Engage more with both computational and industrial efforts in PABPs

Acknowledgements

BETO: Nichole Fitzgerald, Jessica Phillips

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

BIOENERGY TECHNOLOGIES OFFICE

Contributors

- Jared Anderson
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Collaborators

- Yuriy Roman-Leshkov, MIT
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- Marc Hillmyer, University of Minnesota
- Pablo Nikel, Denmark Technical University
- Eugene Chen, Colorado State University

Collaborators on BETO projects

- Mary Biddy, Analysis in support of novel bio-based products and functional replacements
- Michael Crowley, Inverse Design of Polymers
- Mark Nimlos, Performance Advantaged Bioproducts from Catalytic Fast Pyrolysis
- Andrew Sutton, Los Alamos National Laboratory, Tailored Polymers Through Rational Monomer Development
- Agile BioFoundry (Chris Johnson, Davinia Salvachua), Lignin-First Biorefinery Development (Jake Kruger, Nick Thornburg), Biological Lignin Valorization (Chris Johnson, Davinia Salvachua), Biological Conversion of Thermochemical Aqueous Streams (Alex Meyers)

Milestones

FY18		
Q1	QPM	Incorporate varying levels of ß-ketoadipate in nylons and measure changes in material and thermal properties and extents of water uptake; compare properties to desired properties indicated by industrial stakeholders . [Base case]
Q2	QPM	Conduct at least 15 customer discovery interviews with industrial representatives in targeted areas of composites, polyesters, and nitrile-based materials; prepare a brief report on the most important material property attributes that industry would consider "performance advantaged" in a quantitative manner and use this information to prioritize and baseline materials testing. [Base case]
Q3	QPM	Deployment of GPC-MALLS: Complete commissioning of GPC-MALLS instrument, including purchase of instrumentation, installation, calibration/validation with existing standards of known molecular weight distributions for routine analysis of biopolymer molecular weight. [Base case]
Q4	Annual	We will predict through machine learning, simulate through molecular dynamics, and experimentally synthesize variants of Nylon-6,6 incorporating at least two additional derivatives inspired from bio-derived monomers (e.g. β-keto-adipic acid, β-keto-caprolactam, muconic acid) with at least three loadings. From these results, we will correlate polymer function (gas permeability and water uptake) to structure (degree of crystallinity and side-chain functionality) and down-select two systems with improved functionality (decreased permeability while maintaining base Nylon-6,6 properties) for polymer synthesis. Joint with "Inverse Biopolymer Design through Machine Learning and Molecular Simulation". [Base case]

Milestones

FY19		
Q1	QPM	Produce a lignin-derived styrene replacement for ABS synthesis (in collaboration with Lignin-First Biorefinery Development). Incorporate trans-ß-methylstyrene (a resin derivable from lignin) and at least two other substituted trans-ß-methylstyrene (e.g. eugenol) into an Acrylonitrile-Butadiene-Styrene (ABS) analogue. Report material properties relative to a styrene-based control; compare properties to desired properties indicated by industrial stakeholders, including environmental health and safety metrics of styrene relative to trans-ß-methylstyrene.
Q2	G/NG Annual	Demonstrate incorporation of 5-5 linked lignin dimers into advanced polycarbonates and polyurethanes. We will incorporate 5-5 linked dimers resulting from lignin depolymerization, which are often the most recalcitrant lignin dimers, into non-isocyanate based polyurethanes and polycarbonates via functionalization with other bio-derived co-monomers (g/ng)
Q3	QPM	Demonstrate production of bio-derived advantaged nylons, recyclable elastomers, and improved composites through methyl muconates (in collaboration with the Biological Conversion of Thermochemical Aqueous Streams). Produce 2-methyl and 3-methyl muconic acid from the fermentation of substituted cresols. The methyl-muconic acids will be converted into methyl-adipic acids and all 4 diacids will be implemented into polymers and tested for their properties. Thermal properties will be tested and water permeabilities investigated.
Q4	QPM	Demonstrate bio-derived BPA replacements that do not have endocrine disruption efforts and is recyclable (in collab. with Lignin-First Biorefinery Development). Design and synthesize three epoxy resins that possess recyclable and/or degradable units as well as renewably sourceable units for end-of-life considerations. Characterize the resin relative to a BPA-epoxy resin base case to elucidate how the properties are affected by the incorporation of the additional units. Depending on implemented linkage, degradation and recyclability with be tested and characterized.

Publications

1. 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", in review at ***Energy Env. Sci***.

2. Nicholas A. Rorrer, Scott Nicholson, Alberta Carpenter, Mary J. Biddy, Nicholas J. Grundl, and **Gregg T. Beckham***, "Combining reclaimed PET with bio-based monomers enables plastics upcycling", ***Joule***. (2019) in press.

Presentations

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

Hybrid biological and catalytic processes to manufacture and recycle plastics, IBM Almaden, September 12th, 2018

Hybrid biological and catalytic processes to manufacture and recycle plastics, University of British Columbia, June 20th, 2018

Developing new processes to valorize lignin and sugars to building-block chemicals and materials, RWTH Aachen University, May 28th, 2018

Hybrid biological and catalytic processes to manufacture and recycle plastics, MIT, April 27th, 2018

Hybrid biological and catalytic processes to produce chemicals and materials from biomass, University of Delaware, October 5, 2017