ResIn: Responsible Innovation for Highly Recyclable Plastics

U.S. DEPARTMENT OF ENERGY

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

April 4, 2023

Performance Advantaged BioProducts Review Panel

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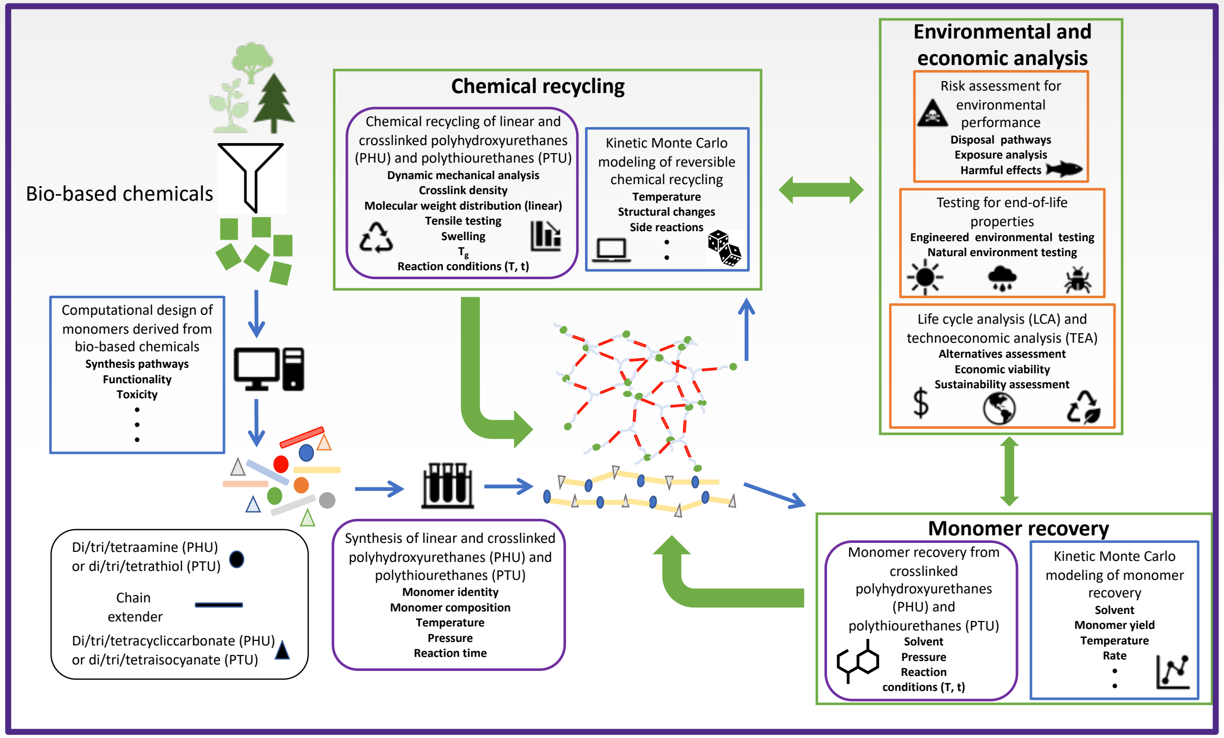
Northwestern University

FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement DE-FOA-000209

Area of Interest: 8a: Designing Highly Recyclable Plastics



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Project Overview

Goals

- Achieve 25% monomer recovery of polyhydroxyurethanes (PHU) and polythiourethanes (PTU)

State of the Art is 0%

- Deliver PHU and PTU materials using a minimum of 50% biobased content

Biomass is not currently used as a PU feedstock

Aligned with BETO's mission of ensuring our nation's competitive advantage in the emerging bioeconomy by funding research and development of technologies to produce advanced bioenergy from terrestrial and algal biomass, biogas, and other waste streams

- Deliver kinetic Monte Carlo (kMC) framework that predicts conditions for chemical recycling/monomer recovery from PHU and PTU
- Demonstrate economic viability and sustainability of approach through TEA and LCA
- Deliver risk assessment framework to enable responsible design of polymers
- Deliver insights into end-of-life fate of polyurethanes in different scenarios

Context

- **Aim:** recover monomers from PHU and PTU replacements for polyurethanes
- **Start of project:** state-of-the-art is 0% recovery of monomers from this important class of materials
- **Important:** design of novel materials that can be recycled considering all aspects of the lifecycle provides potential environmental and economic benefits
- **Risks:** broad range of applications demands specific material properties and end-use may require additives

Approach

- **Synthesize novel PHU and PTU** linear and network materials and test for properties and monomer recovery
- Use **computational approach** to understand monomer recovery and recycling
- Assemble **risk assessment framework** that evaluates environmental performance
- Carry out **end-of-life degradation testing** using standard and newly developed methods
- Build **TEA and LCA** of the bio-based and baseline PU systems supply chain
- Consider the **material flows** of PU associated with its production and use in the U.S. and how these will change as a bio-based, circular economy scales up. Assess the potential economic and environmental effects of highly recyclable PU
- Integrate all stages of the PU supply chain from at least 50% biomass and **generate TEA and LCA results, a** Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (**GREET) module for the PU circular economy, and an evaluation of potential supply chain disruption when PU is designed for 25% monomer recovery**
- Foster **team** environment that values **diverse** perspectives from different **backgrounds, experience,** and **disciplines**

Partner with industrial collaborators for technology impact

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Approach: Challenges and Milestones

Challenges

- Monomer design space is vast, and testing all potential leads from computation is prohibitive

Experimental accessibility can be used as screening metric

Partnering with NREL on machine learning and PolyID

- Standard degradation tests have long feedback cycle and require significant amount of material

Capability for parallel testing and supply by industrial partners

- Risk assessment framework and TEA/LCA advance in absence of knowledge of leading PHU and PTU candidates

Opportunity for TEA/LCA and risk assessment framework to lead

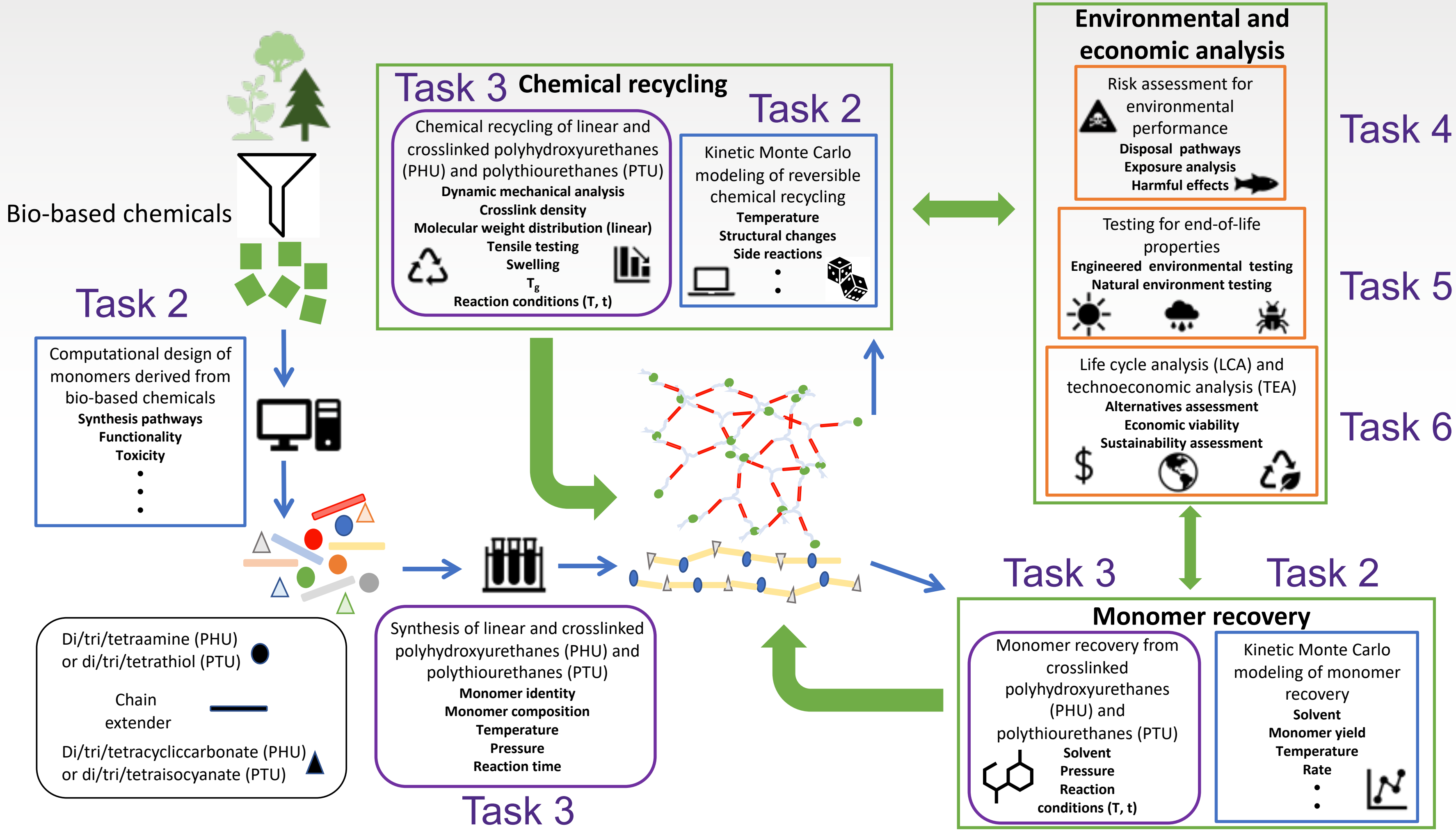
Major milestones, Go/No-Go Decisions

- FY20: Go/No-Go (Initial verification) – synthesis of PHU and PTU with property characterization targets established
- FY21: Major milestone - Identify and quantify disruption of PU supply chain (Task 6)
- FY22: Go/No-Go - Synthesis and quantitative, basic property characterization of one linear and one network PHU or PTU made from model compounds and one biobased monomer identified from Task 2

Technology Impact

- Among all polymers, PU ranks **sixth** in annual **worldwide production**
- Potential to **advance bioeconomy** by moving to bio-based PU replacements
- Focused efforts on responsible recycling of biobased polyurethane (PU)-like materials, namely biobased polyhydroxyurethanes (PHUs) and polythiourethanes (PTUs), that offer the possibility of recovering value and improving sustainability in two ways:
    - **Recovery of monomer** from spent materials, whether thermoplastics or thermosets
    - **Reprocessability** of spent networks with full recovery of crosslink density and associated properties after reprocessing due to the excellent dynamic character of the crosslinks
- In addition, an **overall framework/methodology** for the responsible design of polymers that will be test driven for the case of PHU and PTU will be developed

Project overview and tasks



Management: Task Structure

Task 2.0: Computational Design of Monomers and PHUs and PTUs for Recyclability
Lead: L. Broadbelt (NU)
Milestones: monomer and pathway design, kMC framework development and application

Task 3.0: Synthesis, Testing, Monomer Recovery, and Recycling of Non-Biobased and Bio-based PHU and PTU
Lead: J. Torkelson (NU)
Milestones: synthesis of new materials, monomer recovery studies, property testing

Task 4.0: Risk Assessment Framework
Lead: C. Negri (ANL)
Milestones: quantification of fate and transport in environment, scenarios for risk assessment

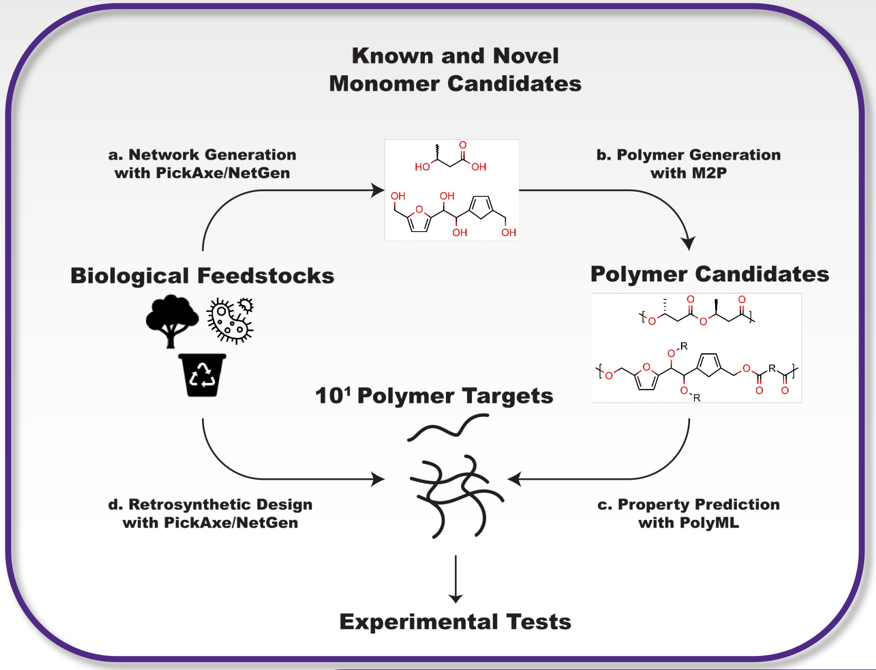
Task 5.0: End-of-Life Property Testing
Lead: M. Urgun-Demirtas (ANL)
Milestones: evaluation of biodegradation, degradation analysis and prediction

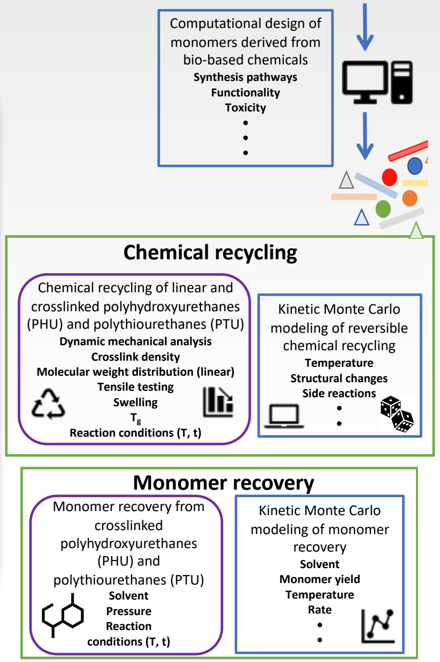
Task 6.0: Systems Economic and Sustainability Analysis
Lead: J. Dunn (NU)
Milestones: material flow analysis, TEA, LCA, GREET^{TM} model enhancement

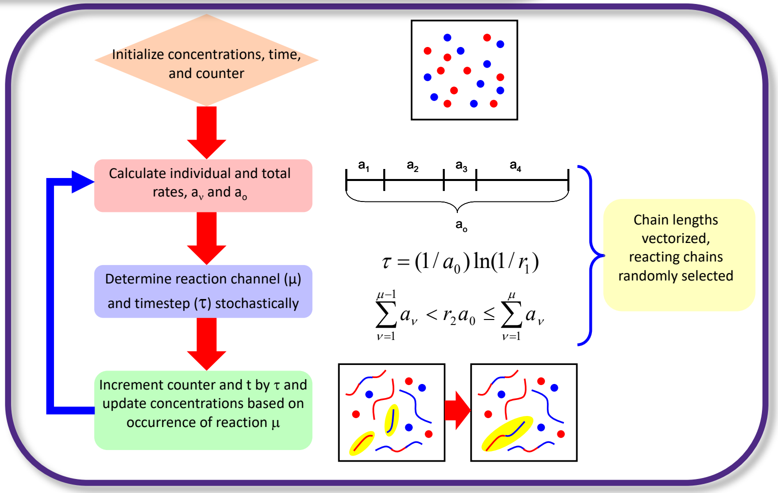
Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

Approach

- Explore design of novel monomers and polymers
  - Identify monomer candidates with desired functionality
  - Leverage related work at NREL using machine learning and PolyID
- Develop kinetic Monte Carlo code for synthesis and degradation of PU
  - Model synthesis of linear and network PHU and PTU
  - Model monomer recovery of same materials



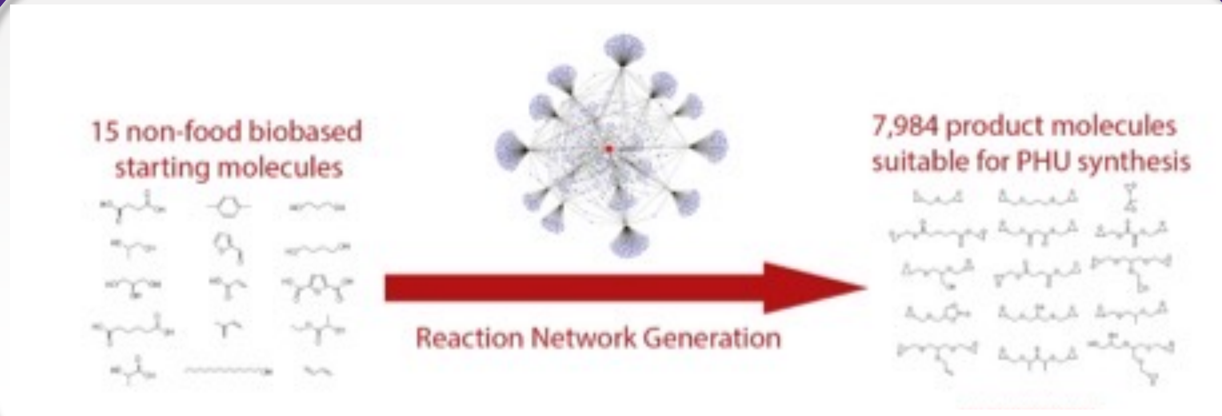


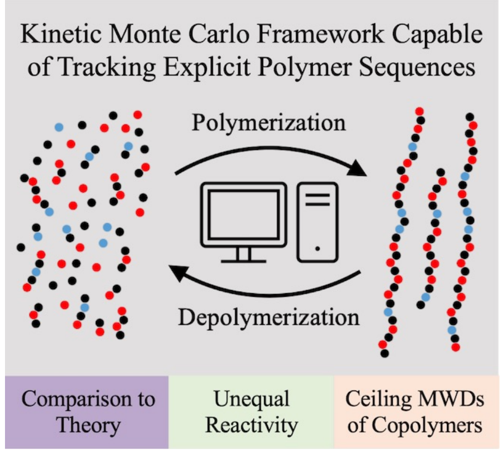


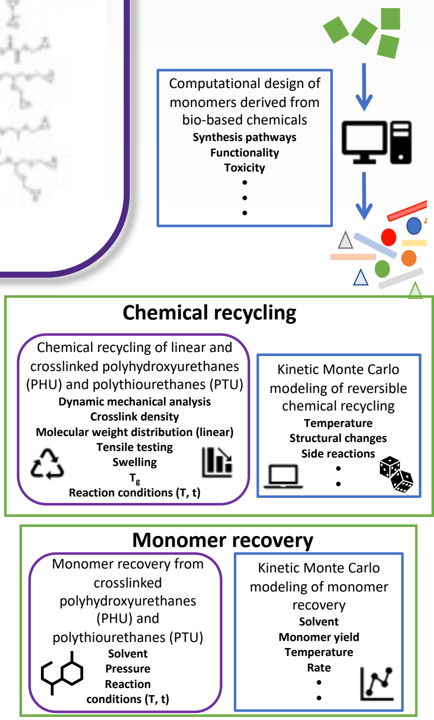
Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

Recent Progress and Outcomes

- Connection of monomer design efforts with experimental synthesis
- Kinetic Monte Carlo code for synthesis and monomer recovery



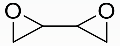
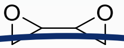
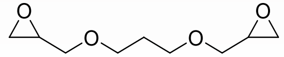
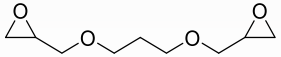
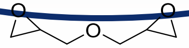
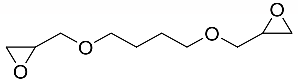
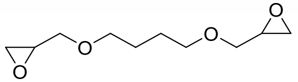
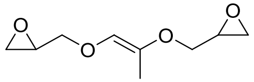
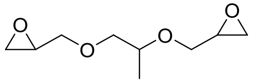
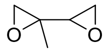
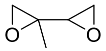
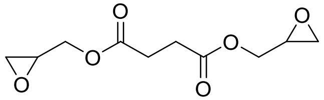
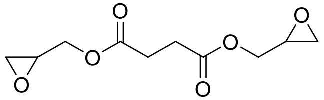
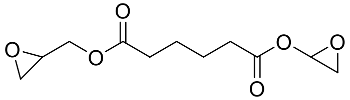
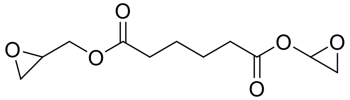


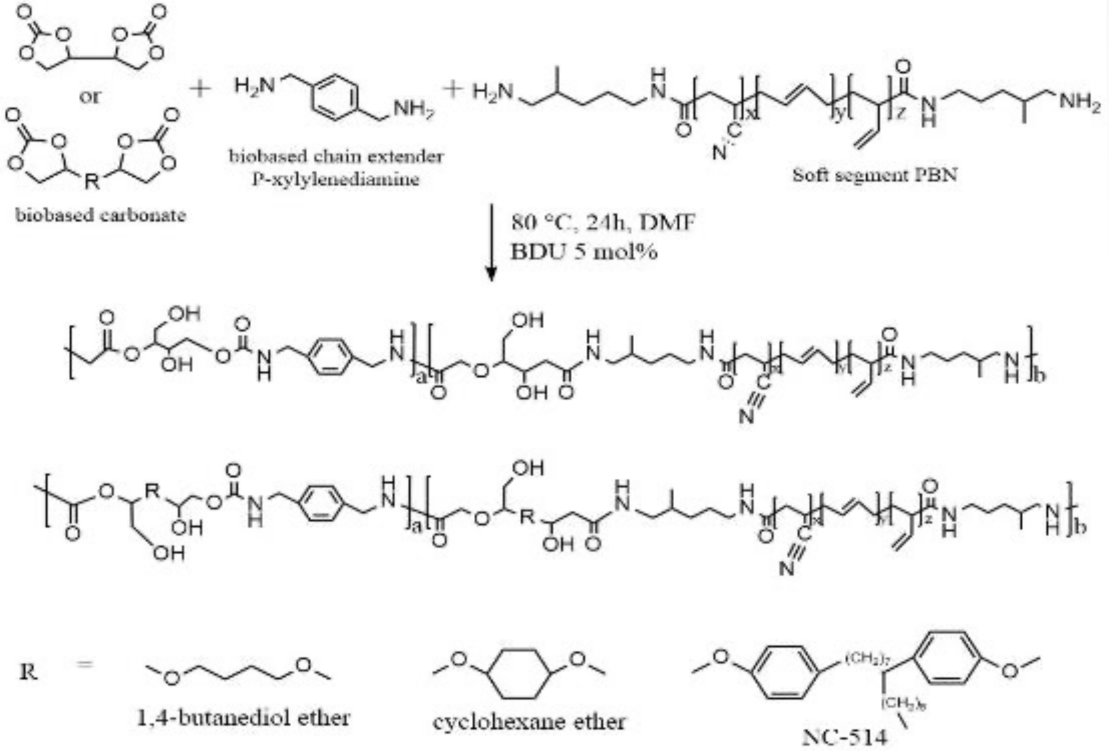


Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

Synthesis of partially bio-based, linear segmented PHUs as a key accomplishment

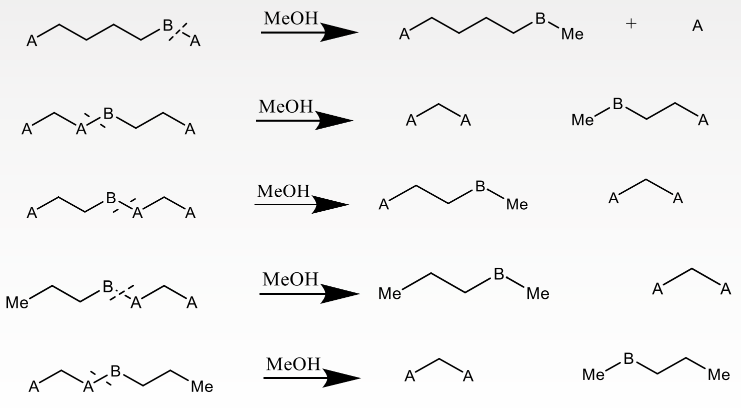
Bio-based epoxies $\xrightarrow{\text{CO}_2\text{ fixation}}$ **Bio-based cyclic carbonate** $\xrightarrow{\text{Cyclic carbonate aminolysis}}$ **Bio-based PHU**

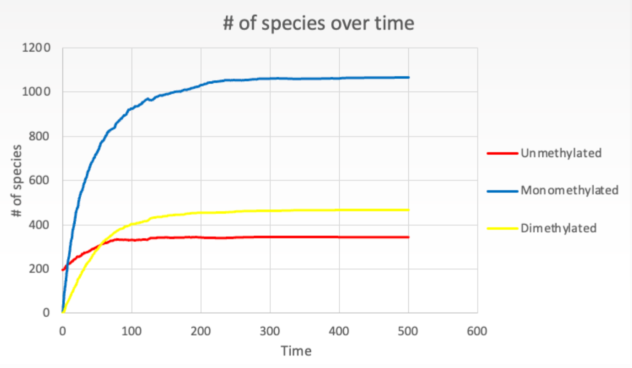
From which 2nd generation candidate	CIS (PubChem ID)	Molecule Structure
	11254	
	3081505	
	16704	
	17046	
	85959	
	22811	
	14440451	
	75987	

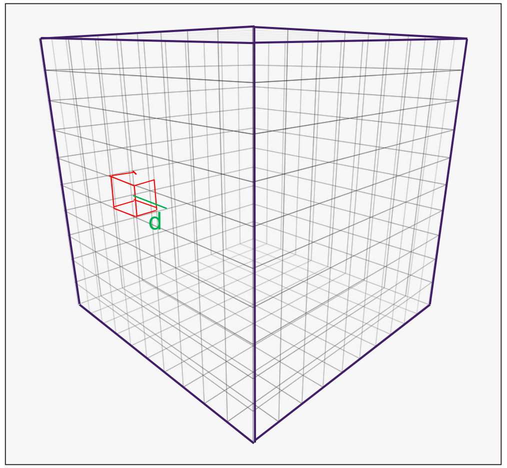


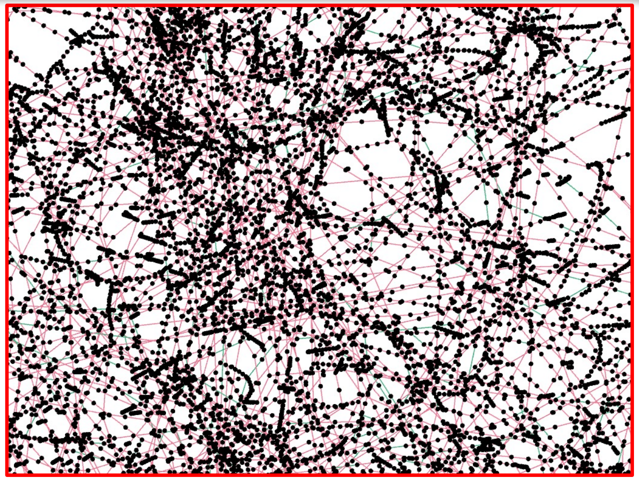
Task 2: Computational Design of Monomers and PHUs and PTUs for Recyclability

- Kinetic Monte Carlo (kMC) code for modeling monomer recovery from linear PHU and PTU materials developed
- kMC framework for modeling synthesis of network materials developed and microkinetic approach for network decomposition underway





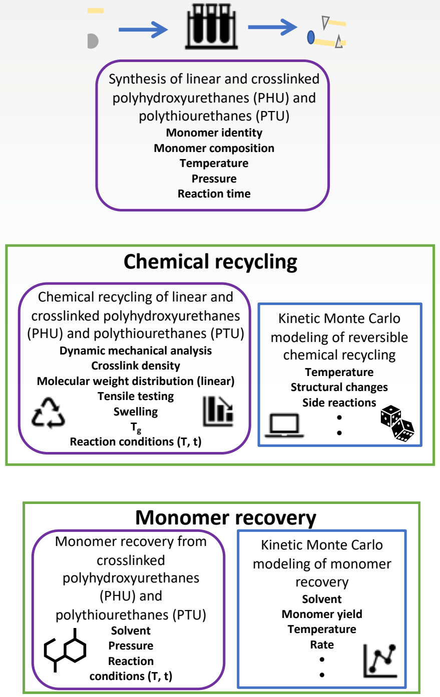




Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of Non-Biobased and Biobased PHU and PTU

Technical Challenges

- Identifying and obtaining or synthesizing appropriate biobased monomers to be used in network or foamed PHU and network NIPTU synthesis
- Overcoming major stumbling blocks for effective synthesis and chemical recycling of network PHU or NIPTU containing dynamic covalent cross-links
  - Slow PHU foaming kinetics lead to long reaction times inferior to PU foaming synthesis
  - Effective chemical recycling of PHU / NIPTU materials without loss of cross-link density
- Going from proof-of-principle monomer recovery to effective, 50%+ recovery



Go/No-Go Decision Points

- Successful syntheses of selected PHUs and PTUs with appropriate properties (completed)
- Monomer recovery from PHU and/or PTU at 10% (in progress & achieved)

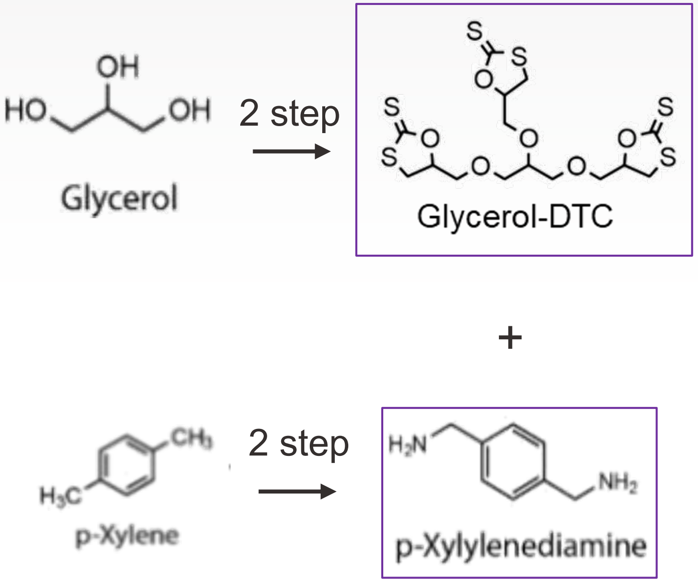
Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

Progress and Outcomes

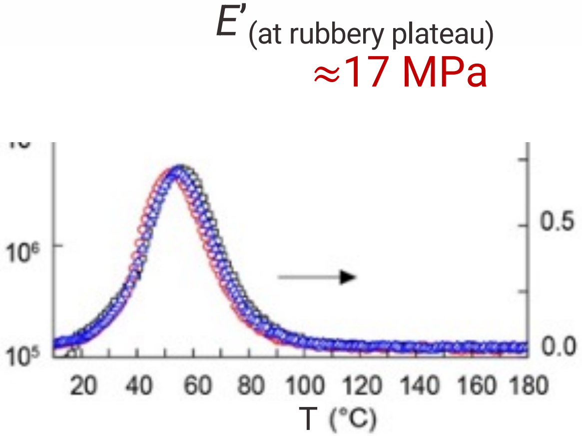
Monomer recovery of biobased NIPTUN, achieving more than 90% monomer yield

Byproduct from biodiesel

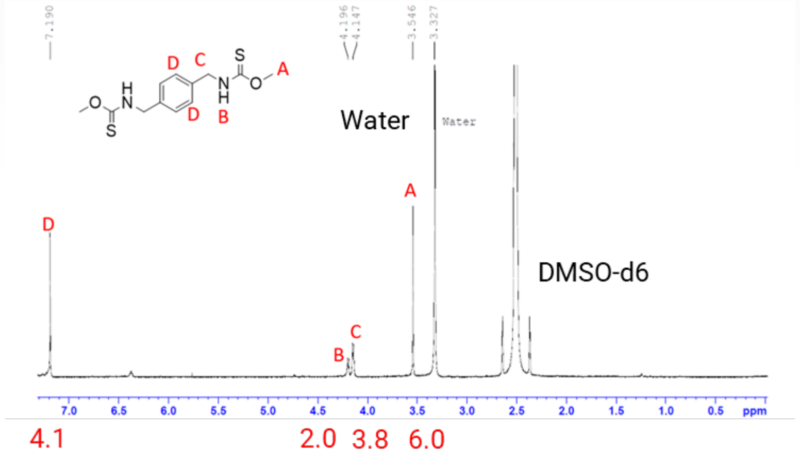
Rice husk



Glycerol-based NIPTUNs with enhanced properties



Recovery of monomer product thiocarbamate



High yield: 93%

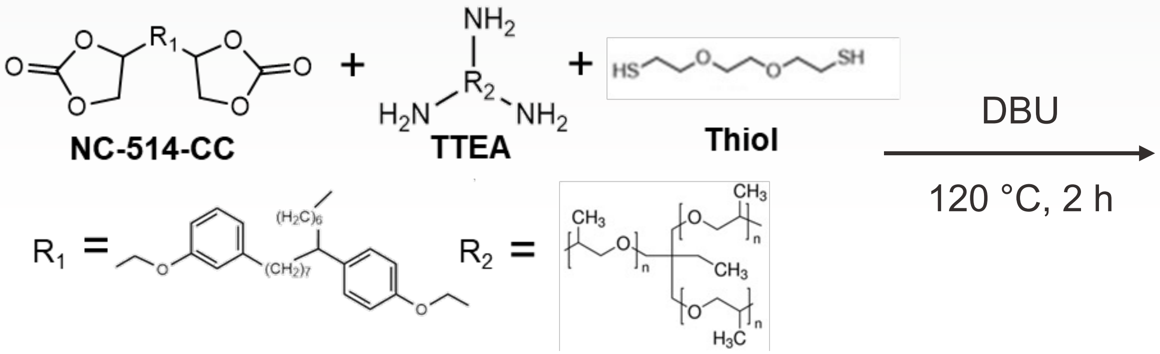
Similarly, monomer recovery from biobased and non-biobased PHU at 52% monomer yield

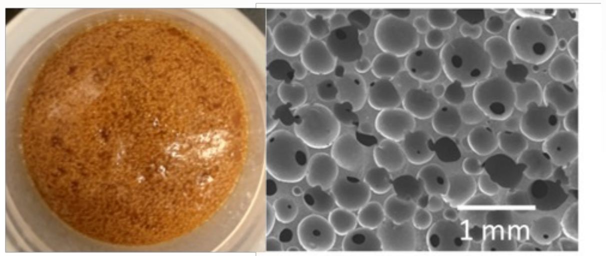
Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

Progress and Outcomes

Synthesis and recycling of biobased PHU foams

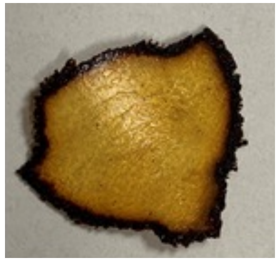
Bio-based epoxies —CO_2 fixation→ Bio-based cyclic carbonate —Cyclic carbonate aminolysis / Thiol decarboxylation→ Bio-based PHU Foams



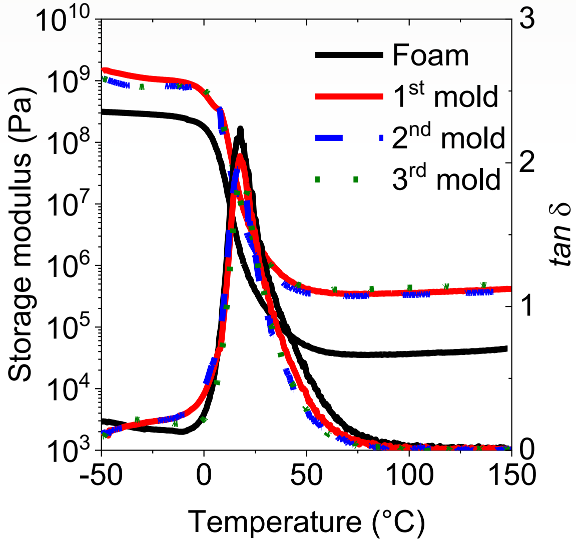


Recycle

140 °C, 2 h, 10 MPa



Recycled PHU foam



Tunable mechanical properties

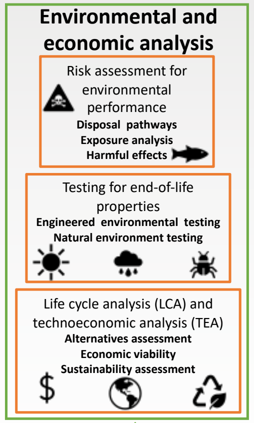
PHU foams provide alternatives to highly relevant PU foams

Tunability of foam properties:

- Mechanical properties: flexible and rigid foams
- Morphology: open- or closed-cells
- Recycling into films with full property recovery

Task 4: Risk Assessment Framework

1. Approach

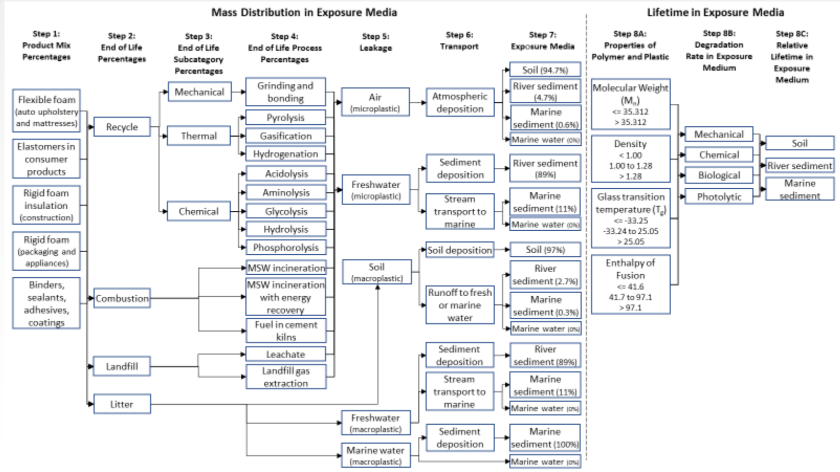


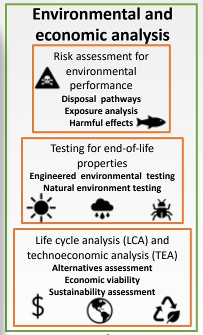
- A risk assessment framework to guide product design balancing environmental impacts with functional performance of PHUs and PTUs (supports responsible innovation)
  - Encompasses polymer use, EOL distribution, leakage, and redistribution in the environmental
  - Uses environmental lifetimes of PHU and PTUs as proxies for environmental risks
  - Uses machine learning of polymer features and degradation rates of all polymer types
- Challenges Facing Technical Approach
  - Modeling polymer uses, EOL distribution, leakage rates, and redistribution
  - Estimating relative and absolute degradation rates
- Decision Points
  - Distribution model predicts realistic distributions in final environmental media
    - Applies published redistribution ratios for polymers based on specific gravity
  - Risk models produce **meaningful estimates of risk** (lifetimes) that respond to **structural differences** in polymers
    - Applies well-established structure activity relationships (SARs) based on published degradation rates for a wide range of polymer structures
- Risks and Mitigations
  - Risk: Degradation rates of PHUs/PTUs not predictable though SARs
  - Mitigation: Measured PHU/PTU degradation rates in Task 5

Task 4: Risk Assessment Framework

2. Progress and Outcomes

- Developed a risk assessment exposure framework
- Implemented the framework in Excel
- Developed/Implemented ML Degradation Models
  - Random Forrest Regressor (developed)
  - Decision Tree Classifier (implemented in Excel)
- Related Degradation Features to Polymer Function
  - Qualitative Structure-Activity Relationships (SARs) found
- Task/Milestone Updates
  - 4.1 Identify 4 EOLs — Complete 12/20
  - 4.2 Environmental Risk 4 EOLs — Complete 7/22
  - 4.3 Correlate PU properties to Risk — Q2FY23
  - 4.4 Functional Properties vs. Risk — Q3-Q4FY 23
  - 4.5 Guidance for Product Design — FY24





Polyurethane Risk Tool

Step 8A: Polymer Attributes

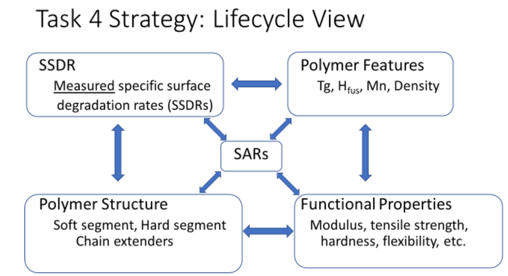
	Select Range
Molecular weight (M_n):	
Density:	
Glass transition temperature (T_g):	
Enthalpy of fusion:	

Step 1: Product Mix Percentages

	Value	Default
Flexible foam (auto upholstery and mattresses):		31%
Elastomers in consumer products:		11%
Rigid foam insulation (construction):		24%
Rigid foam (packaging and appliances):		9%
Binders, sealants, adhesives, coatings:		25%
Total (should equal 100%):		100%

Step 2: End of Life Percentages

	Value	Default
Recycle:		29.0%
Combustion:		12.0%
Landfill:		57.0%
Litter:		2.0%
Total (should equal 100%):		100%



Task 4: Risk Assessment Framework

3. Impact

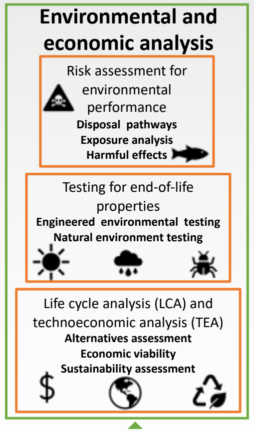
- *Task 4 represents the first prospective risk model for complete lifecycle of new biobased PHUs and PTUs (or for any polymer as far as we know)*
    - *From formulation, through use, EOL, release, redistribution, and degradation*
- *First to explicitly relate environmental and functional performance using SARs*
- *Supports Responsible Innovation*
    - *Allows developers and stakeholders to consider environmental risk in product development*
- *Leverages the results of other RESIN project tasks*

Task 5: End-of-life Property Testing

Approach

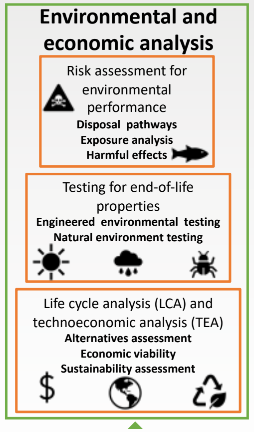
- End-of-life testing scenarios
  - natural environments: soil and freshwater
  - engineered environments: anaerobic digestion and composting facilities
- Test biodegradation of PHU and PTU under different environmental conditions
  - Side-by-side systematic assessment of both synthetic and new PHU and PTU in natural and engineered environments
- Target validation of model results and provision of a more holistic picture of the fate of PHU and PTU in the environment
  - Determine % carbon conversion to CO_2, rate of conversion, and changes in mechanical properties
  - Evaluate PHU and PTU samples before and after exposure to natural and engineered environmental conditions using analytical approaches beyond CO_2 generation evaluation.
  - Conceptual understanding of steps involved in biodegradation

https://www.ieabioenergy.com/wp-content/uploads/2018/10/Standards-and-Labels-related-to-Biobased-Products-2016-to-2018.pdf



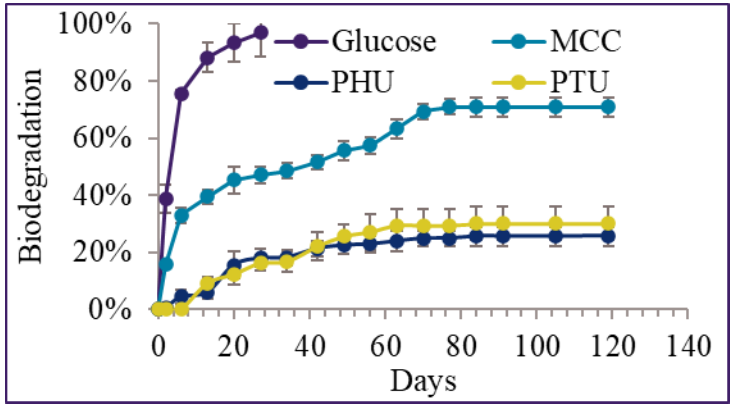
Task 5: End-of-life Property Testing

Progress and Outcomes

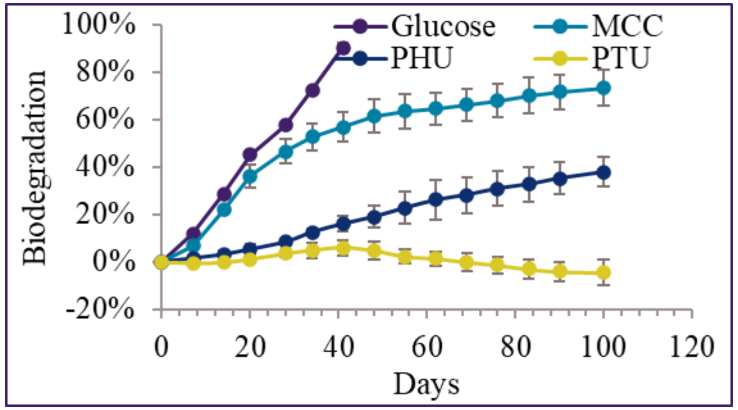


- End-of-life testing:
  - Biodegradation of five samples in natural and engineered environments was analyzed.
    - PHU samples showed 27.91% biodegradation in freshwater (119 days), 39.70% biodegradation in soil (100 days), and 61.30% biodegradation in composting environments (47 days).
    - PTU samples showed 30.25% biodegradation in freshwater (119 days), 4.73% biodegradation in soil (100 days), and 3.18% biodegradation in composting environments (47 days).
  - Estimated lifetime (time to reach 90% biodegradation) for PHU and PTU was predicted using first order kinetics models.
    - PHU: 1519 days in freshwater, 511 days in soil, and 96 days in composting environments.
    - PTU: 799 days in freshwater, 2527 days in soil, and 443 days in composting environments.

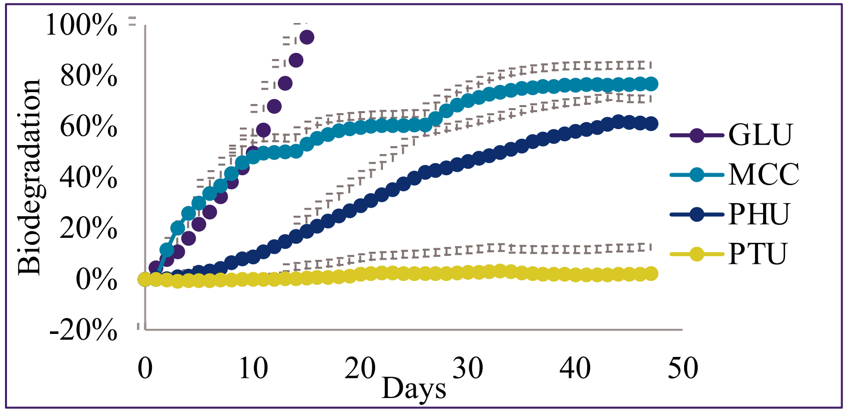
Freshwater



Soil



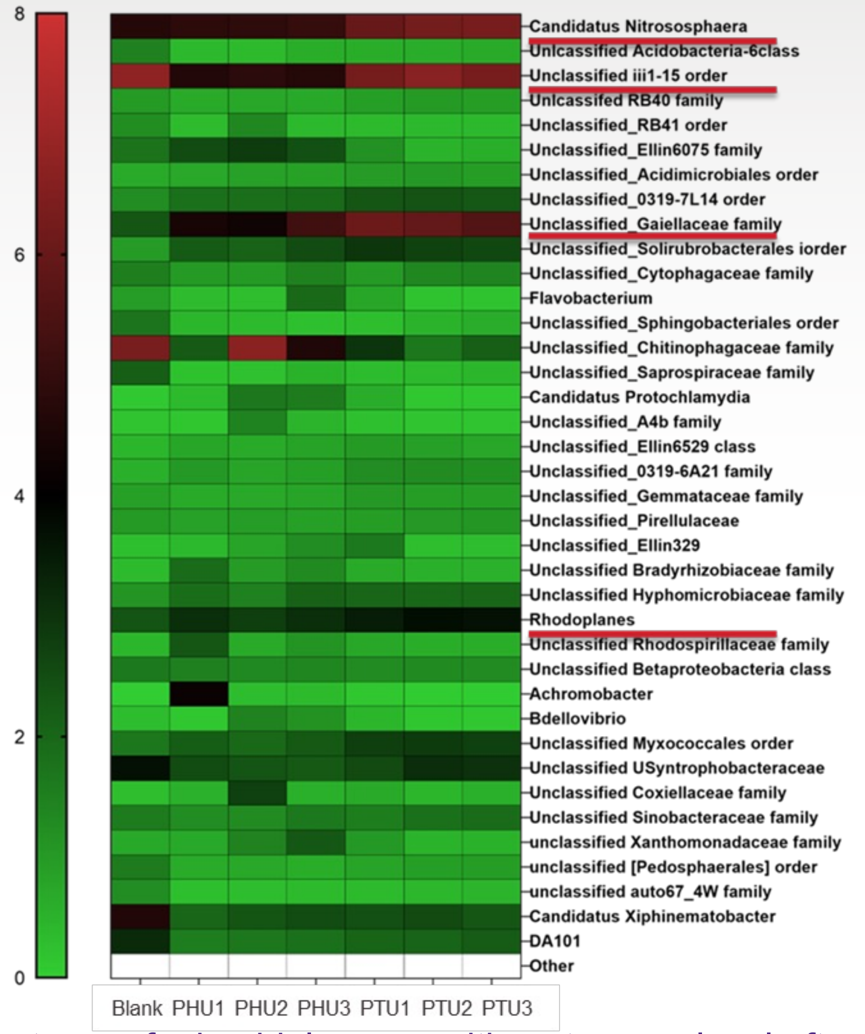
Composting



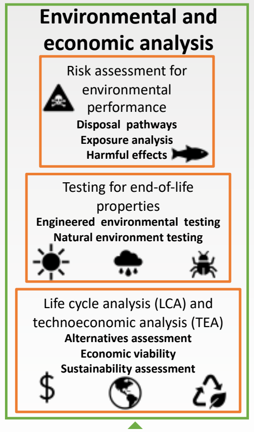
Task 5: End-of-life Property Testing

Progress and Outcomes

- Metagenomic analysis of microbial communities at genus level:
  - Both PHU and PTU showed positive biodegradation in freshwater environment.
  - The enriched genus include *Candidatus Nitrosospharea*, *Rhodoplanes*, *Unclassified Gaiellaceae family*, and *Unclassified iii1-15 order*.
  - *Candidatus Nitrososphaera* has been reported to be enriched during the degradation of PBDEs.
  - *Rhodoplanes* has been reported to have a probable role in degradation of poly aromatic hydrocarbons.
  - No identified function for *Unclassified Gaiellaceae family* but the phylum *Actinobacteria* is related to degradation/decomposition of all sorts of organic substances.
  - No identified function for *Unclassified iii1-15 order* but the phylum *Acidobacteria* is known to be involved in plastic.



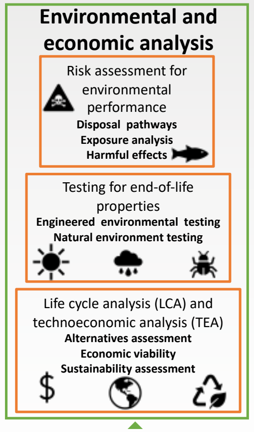
Heatmap of microbial communities at genus level after biodegradation for 3 months in freshwater environments



Task 6: Systems Economic and Sustainability Analysis

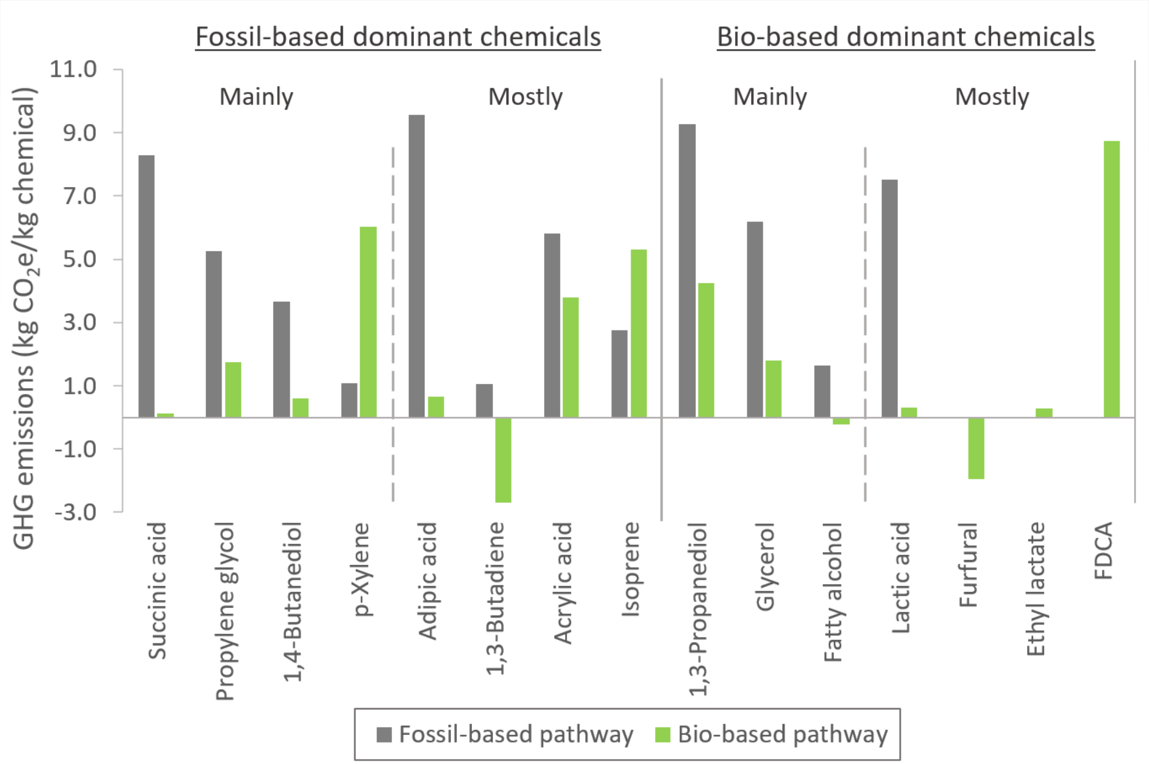
Approach

- Process modeling in AspenPlus that leverages existing BETO design cases, experimental data from ResIn, and prior work.
- Modeling informs techno-economic analysis
- Material and energy flows inform life cycle analysis with Argonne's Greenhouse gases, Regulated Emissions and Energy use in Technologies (GREET™) model
- Material flow analysis used numerous data sources and STAN software for data reconciliation



Task 6: Systems Economic and Sustainability Analysis

Progress and Outcomes



- When both fossil- and bio-based routes are options to produce a chemical, the bio-based route generally offers lower GHG emissions.
- Water consumption may be higher for bio-based routes because of crystallization and fermentation steps. Water optimization in processing is important.
- Replacing fossil fuel-derived chemicals with bio-based chemicals could save 120 million metric tonnes CO_2e – the equivalent of removing 26 million U.S. vehicles from the road
- Changing the production paradigm for 1,3-butadiene, acrylic acid, and adipic acid offers the greatest benefits
- Production pathways for all 15 chemicals will be publicly released in the 2023 GREET™ model.

Northwestern | ENGINEERING

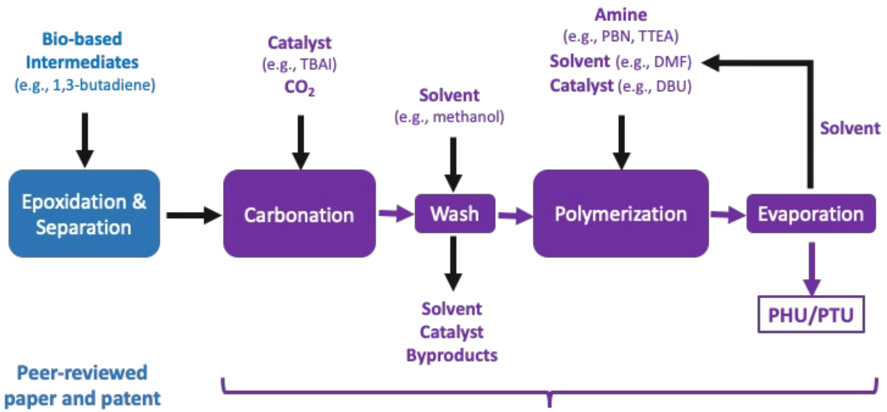
Liang C, Gracida-Alvarez UR, Hawkins TR, Dunn JB. "Life Cycle Assessment of Biochemicals with Clear Near-Term Market Potential." *ACS Sustainable Chemistry and Engineering*. 2023, accepted.

Task 6: Systems Economic and Sustainability Analysis

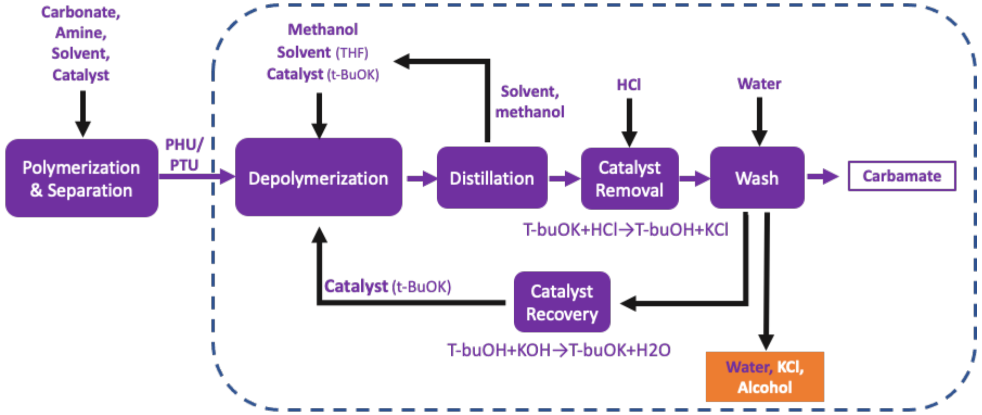
Progress and Outcomes

- In collaboration with Task 3, develop TEA and LCA of PHU and PTU production and monomer recovery
- Preliminary results indicate raw materials drive cost and GHG emissions of PHU and PTU production from bio-based intermediates
- Solvent costs, depolymerization yield are among predominant drivers of monomer recovery costs

Block flow diagram of the modeled PHU/PTU production system



Block flow diagram of the modeled monomer recovery



*Process developed based on the experiments of Task 3

Summary and Key Takeaways

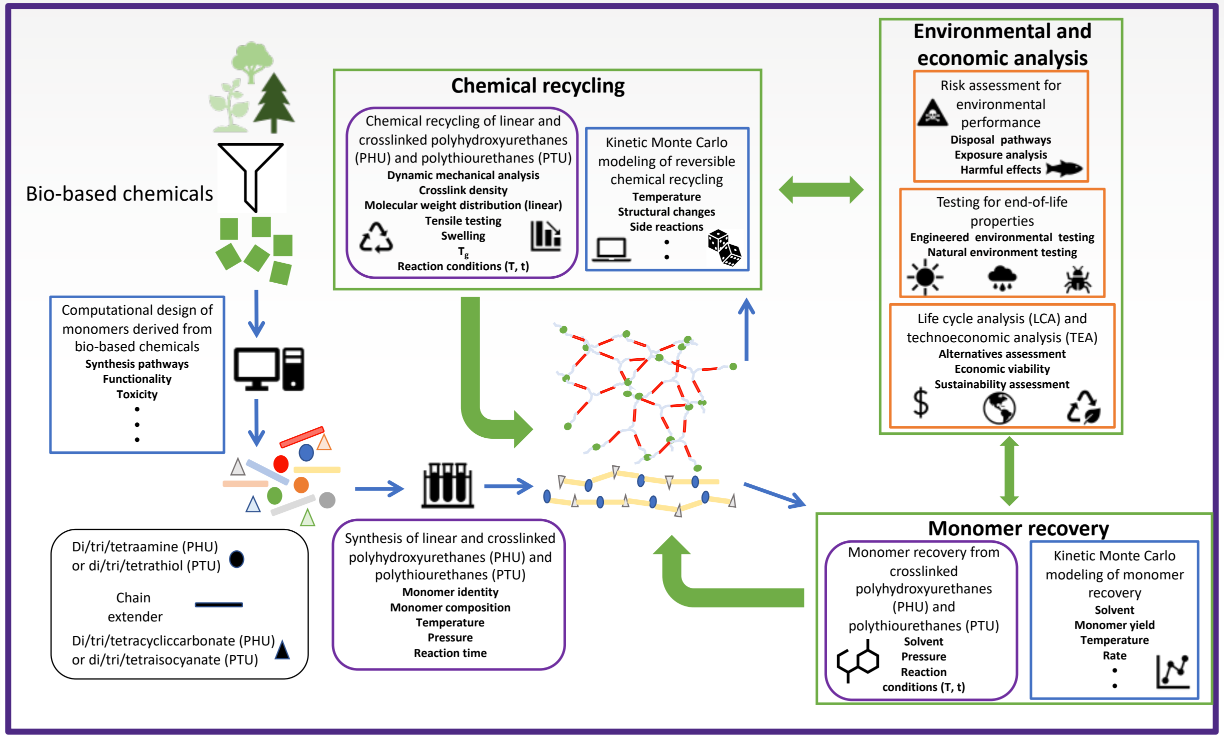
Polyurethanes (PU) are currently not recycled

PU are currently produced from a supply chain originating from fossil fuels

Key deliverables

New bio-based polyhydroxyurethanes (PHU) and polythiourethanes (PTU), linear and crosslinked, that can be recycled to original use or monomer recovery

A design framework that includes kinetic Monte Carlo simulations, LCA, TEA, risk assessment and end-of-life testing



Quad Chart Overview

Timeline
- Project start date: 10/1/2019
- Project end date: 3/31/2024

	FY20 Costed	Total Award
DOE Funding	$239,008	$2,499,998
Project Cost Share	$261,378	$656,485

Project Partners
- Fenner Precision
- The Dow Chemical Company
- Michelin

Project Goal
Our project goal is to achieve chemical recyclability, as measured by 25% or more of recovered monomers, of polyhydroxyurethanes (PHUs) and polythiourethanes (PTUs) through production routes that are economically viable and are at least 50% biomass-derived.

End of Project Milestones
Milestone 2.6: Computational prediction of end-of-life fate as a function of monomer identity, material topology, and chemical recycling conditions

Milestone 3.7: Optimized quantitative details on recovery of crosslink density and recovery of other properties after recycling of spent PHU and PTU networks (from subtasks 3.7 and 3.9) by reprocessing enabled by several dynamic chemistries

Milestone 4.5: Release of complete set of information as report to team members and BETO on critical properties of environmentally benign target products

Milestone 5.4: Definition of key analytical approaches beyond CO_2 generation that correlate with mechanisms responsible for biodegradation of plastics under different environmental conditions

Milestone 5.5: Model results (Task 2) are validated with experimental data

Milestone 6.5: Finalize cost and sustainability metrics for highly-recyclable, 50% bio-based PU (e.g., $/kg, kg CO2e/kg) and characterization of influence of highly-recyclable, 50% bio-based PU on PU and associated supply chains in the United States

Funding Mechanism
FY19 Bioenergy Technologies Office Multi-Topic Funding Opportunity Announcement DE-FOA-000209

Area of Interest: 8a: Designing Highly Recyclable Plastics

Additional Slides

Responses to Previous Reviewers' Comments

- **Application and adoption of ReSIN materials:** The reviewers raised important questions about the application areas for the new ReSIN materials. Overall, the focus is on developing materials with properties that are comparable to polyurethanes that they would replace, and we have four specific properties on which to evaluate these materials and acceptable ranges: strain at break, Young's modulus, tensile strength, and rubbery-plateau tensile strength modulus. In addition, new applications for ReSIN materials have emerged due to properties that were unanticipated at the time of the validation stage of the project; specifically, excellent broad temperature range acoustic noise/vibration damping that is not observed in conventional PU elastomers has been achieved. The industrial partners who are involved in ReSIN are indeed providing regular input about the directions that would lead to industrial applications and adoption. Feedback about the desired properties that informs monomer design efforts is in place based on connections between Task 2 and 3; in addition, it is anticipated that the PolyML efforts in BOTTLE at National Renewable Energy Laboratory may be able to be leveraged for the ReSIN project as they continue to develop.

Responses to Previous Reviewers' Comments

- **Development and dissemination of computational platform and results:** The dissemination of the results of our molecule discovery efforts is an area where we have put recent attention to ensure that the impact goes beyond our own synthesis activities. As part of the recent publication of our first manuscript in molecule discovery related to polyurethane replacements, we provided supplementary information of all pathways to target molecules, which any reader can download and cultivate to identify molecules that may be of interest to their own development efforts related to polyurethanes or other polymer classes. While the Bio-JET project mentioned by the reviewers focuses on molecules for different applications than the ones considered in ReSIN, there may indeed be some synergies. In our own related work focusing on bioprivileged molecules, we have provided supplementary information to a recently submitted manuscript in the form of a JSON file that can be accessed by readers to explore novel molecule space for their own applications. A MongoDB database as a repository for multiple efforts in molecule discovery is in development.

Responses to Previous Reviewers' Comments

- **Considerations of post-consumer processing and impact:** Although the strategies for post-consumer collection, sorting and processing are beyond the specific scope of ReSIN, we acknowledge that these are important considerations and in part depend on the application areas (see above). Using our frameworks for materials flow analysis and risk assessment, we will be well positioned to address the other considerations raised, including what happens to mass that is not recovered as monomers, safe disposal routes of materials, and assessment of the safety of products of biodegradation.

- **Clarification of systems economic and sustainability analysis:** The systems analysis progress presented in the peer review presentation was a completed material flow analysis (MFA) tracking the current production, use, and end of life of today's polyurethanes. The completion of this MFA marked the completion of an FY21 milestone. A reviewer requested further information about treatment of polyester and polyether polyols in this analysis and upcoming techno-economic analysis (TEA) within ReSIN. The MFA illustrates that as polyether polyols and polymeric methylene diphenyl diisocyanate (MDI) are currently the most dominant polyurethane starting materials, producing these two compounds from biomass would be the most disruptive to the supply chain, reducing fossil fuel use to the greatest extent. In upcoming technoeconomic analyses, we will adopt multiple polyurethane products (reaching back to both polyether and polyester polyols) as baselines given the diversity of polyurethane products and uses.

Responses to Previous Reviewers' Comments

- **Management of tasks, risk, and progress:** Although COVID presented some challenges towards progress on specific areas of the project, there is a robust risk mitigation strategy in place that is related to other comments that the reviewers raised. In our own anticipation of obstacles to the research itself, the multi-pronged approach we have adopted with different material classes (i.e., polyhydroxyurethanes and polythiourethanes (PTU)) and balanced efforts on reprocessing and monomer recovery provide opportunities for advances that do not rely on only one project moving forward successfully. The comment about the appearance of distinct multiple threads in two tasks, 2 and 3, is appreciated. We will focus future communication efforts on the design cycle as the overarching focus of both tasks, which has multiple components in order to make them successful. Monomer recovery efforts and synthesis of PTUs will have greater emphasis, now that laboratories have ramped back up more fully and the team is fully staffed, and we will have better metrics of scale and productivity across a broader set of monomer combinations. For the kinetic Monte Carlo simulations that are part of this cycle in Task 2, the ease of formulating models based on this method, as opposed to continuum models in which we have also have expertise, will become more apparent in future communications when we present results on network materials. In addition, we will include the timeline that we have for advancing and measuring progress of the ReSIN team as guided by our milestones in future presentations.

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- Liang C, Gracida-Alvarez UR, Gallant ET, Gillis P, Marques YA, Abramo GP, Hawkins TR, Dunn JB. "Material Flows of Polyurethane in the United States." *Environmental Science and Technology.* 2021, 55: 14215-14224
- Liang C, Gracida-Alvarez UR, Hawkins TR, Dunn JB. "Life Cycle Assessment of Biochemicals with Clear Near-Term Market Potential." *ACS Sustainable Chemistry and Engineering*. 2023, accepted.
- Coile, Matthew W., Rebecca Harmon, Guanhua Wang, Sribala Gorugantu, and Linda J. Broadbelt (Mar. 2022). "Kinetic Monte Carlo Tool for Kinetic Modeling of Linear Step-Growth Polymerization: Insight into Recycling of Polyurethanes". In: Macromolecular Theory & Simulations, p. 2100058. doi: https://doi.org/10.1002/mats.202100058, 2022.
- Wang, Guanhua, Lauren Lopez, Matthew Coile, Yixuan Chen, John M. Torkelson, and Linda J. Broadbelt (Mar. 2021). "Identification of Known and Novel Monomers for Poly(hydroxyurethanes) from Biobased Materials". In: Industrial & Engineering Chemistry Research 60.18, pp. 6814–6825. doi: 10.1021/acs.iecr.0c06351, 2021.
- Chen, Y.; Chen, B.; Torkelson, J. M. Reprocessable, Biobased, Non-Isocyanate Polythiourethane Networks with Thiourethane and Disulfide Crosslinks: Comparison with Polyhydroxyurethane Analogs. Manuscript submitted, 2023.
- Purwanto, N. S.; Chen, Y.; Wang, T.; Torkelson, J. M. Rapidly-synthesized, Self-Blowing, Non-Isocyanate Polyurethane Network Foams with Upcycling to Bulk Networks via Hydroxyurethane Dynamic Chemistry. Manuscript submitted, 2022.
- Hu, S.; Chen, X.; Rusayyis, M. A. B.; Purwanto, N. S.; Torkelson, J. M. Reprocessable polyhydroxyurethane networks reinforced with reactive polyhedral oligomeric silsesquioxanes (POSS) and exhibiting excellent elevated temperature creep resistance. Polymer 2022, 252, 124971. https://doi.org/10.1016/j.polymer.2022.124971

Publications, Patents, Presentations, Awards, and Commercialization

Presentations

- Dunn JB "Evaluating Polymer Sustainability with Life Cycle Assessment." APS Physics Division of Polymer Physics Short Course: Sustainable Polymers: Physics of New Materials, Design for Sustainability and End-of-Life. March 13-14, **2022**. Chicago, IL.
- Dunn JB "Informing laboratory-based research in upcycling with systems analysis." ACS Fall Meeting. August 21-25, **2022**. Chicago, IL.
- Liang, C., Gracida, U. R., Gallant, E., Hawkins, T. R., & Dunn, J. B. (November 16–20, 2020). The Influence of Increasing Polyurethane Recyclability and Renewable Content on Material Flows [Conference presentation]. 2020 Virtual AIChE Annual Meeting.
- Dunn, J. B., Liang, C., Gracida, U. R., Gallant, E., Hawkins, T. R. (December 10, 2020). Materials flow analysis in support of circular plastics economy development: Polyurethane in the United States. Northwestern University Institute on Sustainability and the Environment Program on Plastics, Ecosystems, and Public Health Seminar Series. https://isen.northwestern.edu/materials-flow-analysis-supporting-a-circular-plastics-economy
- Torkelson, J.M., "Transforming Thermosets into Thermoplastics: Dynamic Covalent Bonds Enable the Sustainable Chemical Recycling of Traditionally Non-recyclable Polymer Materials", Inaugural Seminar Series for the Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, Arizona State University, October 15, 2020.
- Coile, M. "Kinetic Monte Carlo Framework for Kinetic Modeling of Linear Step Growth Polymerization: Insight into Recycling of Polyurethanes", Polyurethanes Technical Conference, Poster presentation, 2021.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations, cont'd

- SriBala, G.; Coile, M.; Kebadireng, R.; Broadbelt, L.J. A KMC Based tool to understand the chemical recycling of polyurethanes. AIChE Annual Meeting, Phoenix, AZ, 14 Nov. 2022.
- SriBala, G.; Rorrer, N.A.; Buss, B.L.; Morais, A.R.C.; Beckham, G.T.; Allen, R.D.; Broadbelt, L.J. Kinetic Monte Carlo based tool to unravel solvolysis chemistry of step-growth polymers. ACS Fall Meeting, Chicago, IL, 21 Aug. 2022. [Invited Talk]
- SriBala, G.; Morais, A.R.C.; Rorrer, N.A.; Buss, B.L.; Beckham, G.T.; Allen, R.D.; Broadbelt, L.J. A mechanistic tool to understand depolymerization chemistry of step-growth polymers for monomer recovery. ISCRE 26 (virtual), 6 Dec. 2021.
- SriBala, G.; Morais, A.R.C.; Rorrer, N.A.; Buss, B.L.; Beckham, G.T.; Allen, R.D.; Broadbelt, L.J. Understanding chemical recycling of step-growth polymers using Kinetic Monte Carlo approach. AIChE Annual Meeting, Boston, MA, 8 Nov. 2021.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations, cont'd

- L.J. Broadbelt, "Discovery of Novel Compounds and Pathways through Identification of Bioprivileged Molecules", CoMSEF Spotlight Talk, AIChE Annual Meeting, Boston, MA, November 8, 2021.
- L.J. Broadbelt, "Developing Strategies for Polymer Redesign and Recycling Using Reaction Pathway Analysis", Donald L. Katz Lecture, University of Michigan, April 2022.
- L.J. Broadbelt, "Developing strategies for polymer redesign and recycling using reaction pathway analysis", ACS CATL Lecture Series, online, March 2022.
- L.J. Broadbelt, "Developing Strategies for Polymer Redesign and Recycling Using Reaction Pathway Analysis", Gordon Research Conference on Polymer Physics, South Hadley, MA, July 2022.
- L.J. Broadbelt, "Developing Strategies for Polymer Redesign and Recycling Using Reaction Pathway Analysis", 25th Anniversay Celebration of the Catalysis and Reaction Engineering Division of AIChE, AIChE Annual Meeting, Phoenix, AZ, November 2022.
- L.J. Broadbelt, "Developing Strategies for Polymer Redesign and Recycling Using Reaction Pathway Analysis", Polymer Reaction Engineering XI, Scottsdale, AZ, December 2022.
- L.J. Broadbelt, "Developing Strategies for Polymer Redesign and Recycling Using Reaction Pathway Analysis", FOCAPO/CPC, San Antonio, TX, January 2023.

Publications, Patents, Presentations, Awards, and Commercialization

Presentations cont'd

- Chen, Y.; Chen B.; M. Mielke, N.; LaPorte, M.; Torkelson, J. M. Non-food biobased, isocyanate-free linear and network polyhydroxyuthane and polythiourethane: Recyclability with cross-link density recovery and excellent elevated-temperature creep resistance. 2022. American Physical Society March Meeting 2022. Chicago, IL. Poster Presentation
- Laporte, M.; Chen, Y.; Torkelson, J. M. Monomer Recovery from and Recycling of Biobased Polyhydroxyurethanes. 2022. American Physical Society March Meeting 2022. Chicago, IL. Poster Presentation
- Mielke, N.; Chen, Y.; Torkelson, J. M. Chemical Recycling of Isocyanate-Based and Non-Isocyanate, Bio-Based Polythiourethane Vitrimers. 2022. American Physical Society March Meeting 2022. Chicago, IL. Poster Presentation
- Chen, Y.; Purwanto, N.; Chen, B.; Torkelson, J. M. Employing non-food biobased building blocks in various non-isocyanate PU-like materials with different architectures and properties. 2022. American Chemistry Society August Meeting 2022. Chicago, IL. Poster Presentation
- Chen, Y., Chen, B., Mielke, N., Torkelson, J.M. Biobased, Non-isocyanate Polythiourethane (NIPTU) Networks: Reprocessability, Enhanced Performance by Inter-chain Disulfide Linkages and End-of-Life Monomer Recovery. 2023. American Physical Society March Meeting 2023. Las Vegas, NV. Oral Presentation

Publications, Patents, Presentations, Awards, and Commercialization

Presentations cont'd

- Purwanto, N. S.; Chen, Y.; Wang, T.; Torkelson, J. M.; Biobased, Self-Blowing Polyhydroxyurethane Foams: Improved Synthesis, Tunability of Properties, and Facile Reprocessing. 2022. American Chemical Society Fall Meeting 2022. Chicago, IL. Oral Presentation
- Purwanto, N. S.; Fenimore, L. M.; Chen, Y.; Torkelson, J. M. Biobased Self-Blowing Polyhydroxyurethane Foams: Improved Synthesis, Tunability of Properties, and Reprocessability Studies. 2022. American Physical Society March Meeting 2022. Chicago, IL. Poster Presentation
- Purwanto, N. S.; Chen, Y.; Fenimore, L. M.; Li, L.; Chen, X.; Jin, K.; Torkelson, J. M. Effective Routes to High-Performance, Elastomeric, Cross-linked Polyurethane-like Mtaerials That are Recyclable with Full Cross-link Density and Property Recovery. 2023. Polyurethane Manufacturer Association Meeting 2023. Tampa, FL. Conference Proceedings & Oral Presentation.

Publications, Patents, Presentations, Awards, and Commercialization

Acronym guide

PHU: polyhydroxyurethane
PTU: polythiourethane
PU: polyurethane
kMC: kinetic Monte Carlo
TEA: technoeconomic analysis
LCA: life cycle assessment
NU: Northwestern University
ANL: Argonne National Laboratory
GREET^{TM}: Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies
EOL: End of life
AD: anaerobic digestion
ISO: International Organization for Standardization
ASTM: American Society for Testing and Materials
BOD: biological or biochemical oxygen demand
STAN: subSTance *flow* ANalysis

Material Flow Analysis Data Sources

Name	Time	Source	Summary
Trade Data	2016	USITC, CCC	Import and export data of raw materials for PU, PU products, end-use products, PU wastes
PU Concentration Data	2016	ISOPA, WRAP, PlasticsEurope, peer-reviewed literature, market report, experts' estimates	Content of PU in end-use products and wastes (kg PU/kg commodity)
Production Data	2016	PU Magazine, ICIS	PU production amount
Transfer Coefficient Data	2016	PU Magazine, ACC, peer-reviewed literature	Distribution of PU by end use, distribution of PU by product type
Waste Data	2016	EPA, CCC, peer-reviewed literature, experts' estimates	PU waste amount
Raw Material Data	2014, 2018	ACC, ISOPA, market report	Isocyanate, polyols, and additives production amount, distribution of raw materials to PU products

USITC: United States International Trade Commission
ACC: American Chemistry Council
ISOPA: European Diisocyanate & Polyol Producers Association
CCC: Carpet Cushion Council
EPA: Environmental Protection Agency
ICIS: Independent Commodity Intelligence Services

Project Partners

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SUSTAINABILITY AND ENERGY

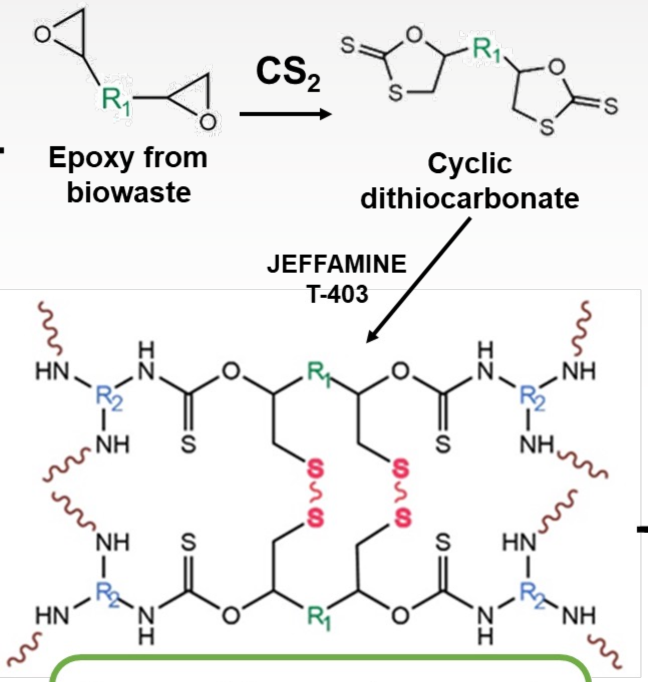
Additional Technical Details

Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of Non-Biobased and Biobased PHU and PTU

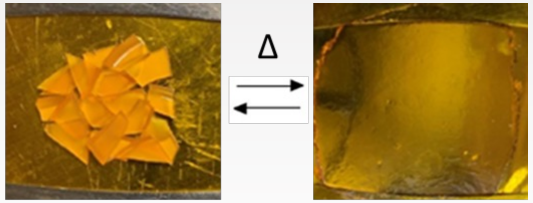
Progress and Outcomes

Synthesis and reprocessability of biobased non-isocyanate PTU (NIPTU)

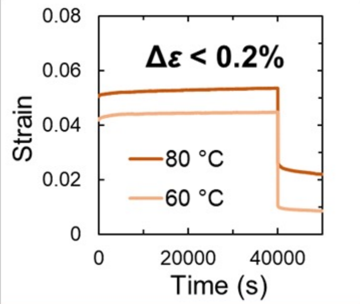
Biowaste



Renewable non-isocyanate polythiourethane (NIPTU) with dual crosslinks



Full reprocessability



Elevated-T creep resistance

Performance superior to PHU analogs

......

Task 3: Synthesis, Testing, Monomer Recovery, and Recycling of non-Biobased and Biobased PHU and PTU

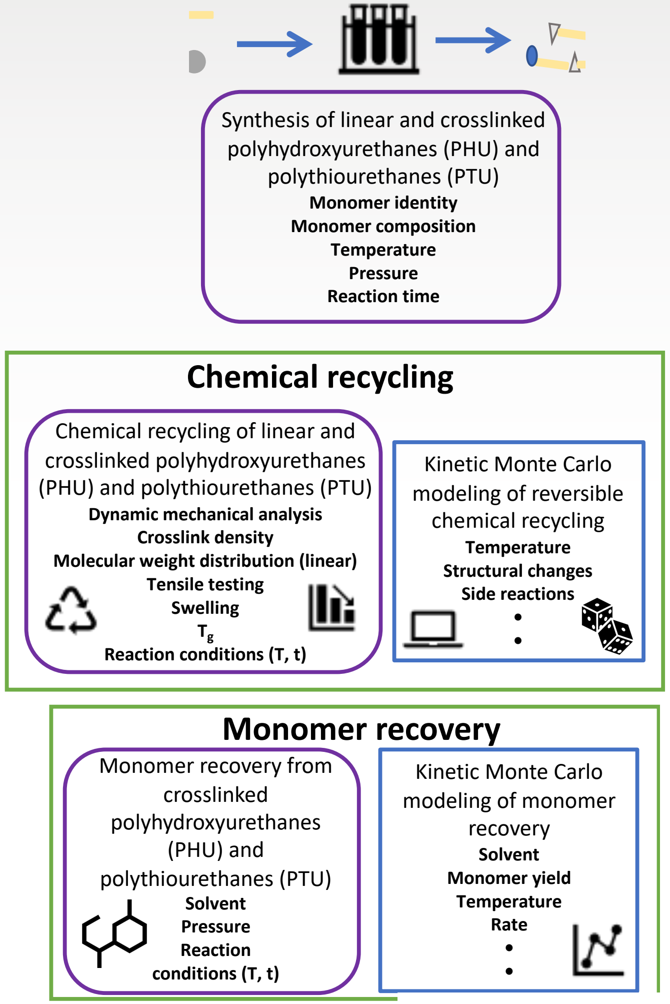
Other accomplishments

1. Successful synthesis of NIPTU networks that exhibit **reprocessability with full cross-link density recovery**.

2. NIPTU networks have advantages in **reactivity, mechanical properties, and water resistance** relative to PHU networks, making them good choices for water-resistant coatings. If **foams** are desired, PHU networks have the advantage.

3. **Collaboration with Task 5**: Provided PHU/NIPTUN samples for biodegradability studies

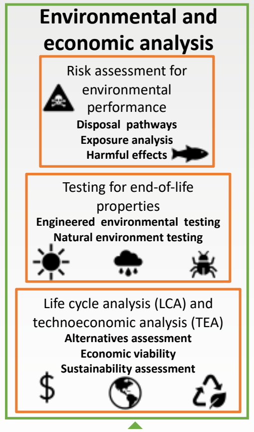
4. **Collaboration with Task 6**: Provided flow diagram of PHU/NIPTUN monomer recovery for end-of-life evaluation.



Task 5: End-of-life Property Testing

Approach: Standard Methods Used for Biocertification

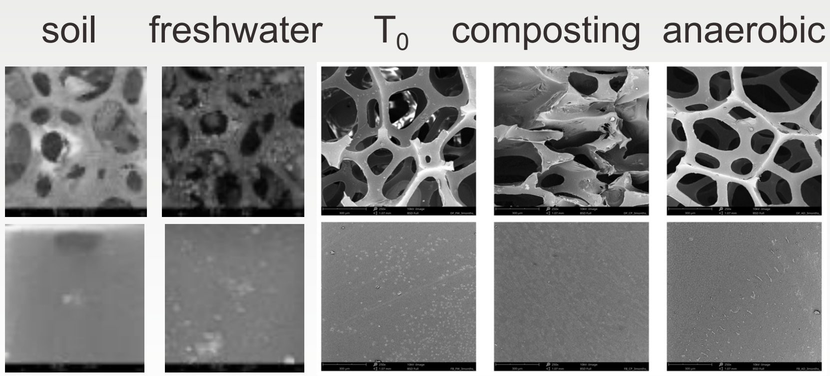
Method Name	Temperature	Inoculum	Sample Size	Reactor size	Duration	Measurement
ISO 14851 - *Aerobic biodegradability of plastic materials in an aqueous medium*	23 °C ± 2 °C	Activated sludge taken from a WWTP	25 mg	300 mL	Min 28 days	BOD over time or CO_2
ASTM 5988 - *Aerobic Biodegradation of Plastic Materials in Soil*	23 ± 2 °C	Natural Soil	1 g	2 L	Max 2 years	Volume of CO_2
ASTM 5338 - *Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions*	58 ± 2 °C	Mature compost	5-6 g	500 mL	Min 45 Days	Volume of CO_2
ASTM 5511 - *Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic Digestion Conditions*	37 ± 2 °C	Activated sludge taken from a stand-alone food waste digester	5-6 g	500 mL	15-30 Days	Volume of CO_2 and CH_4



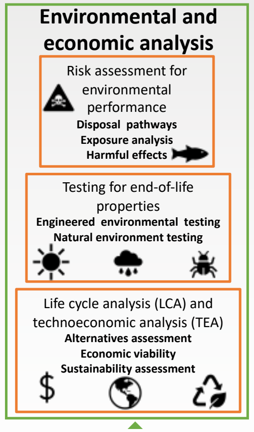
Task 5: End-of-life Property Testing

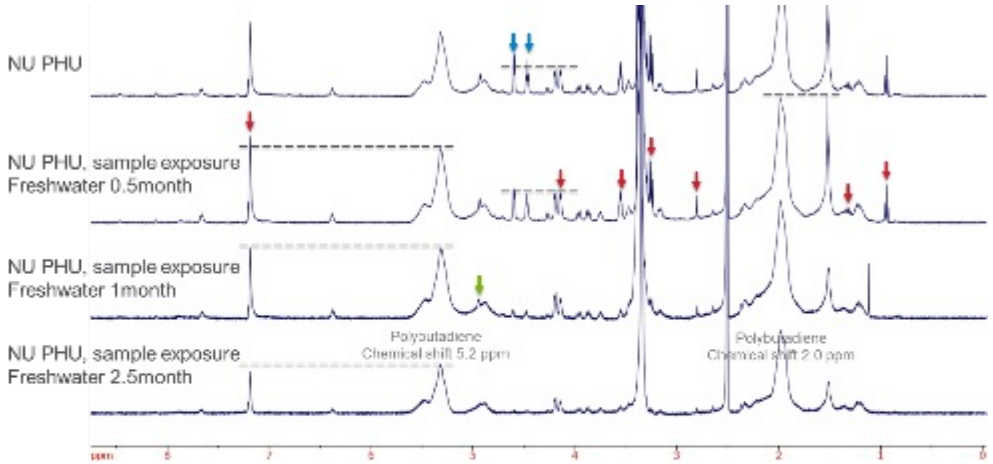
Progress and Outcomes

- Understanding the mechanism of PHU, PTU biodegradation beyond CO_2 capture:
  - SEM graphs showed the breakage of microstructure of polyurethane and formation of small porous structure in the surface in multiple environments.
  - NMR spectra of PHU degradation in freshwater environments overtime showed more than 70% decrease in relative intensity of peaks related to the bio-based cyclic carbonate segments.
  - The bio-based cyclic carbonate segments were biodegraded faster relative to the nondegradable polybutadiene segments.



SEM of PU samples after 3 months exposure.
Top: flexible foam, 300 μm. Bottom: PU





NMR of PHU samples in freshwater environments overtime

Task 6: Systems Economic and Sustainability Analysis

Progress and Outcomes

- Increasing bio-based content of PU and other polymers requires bio-based building blocks
- We applied a consistent life cycle assessment framework to15 bio-based building blocks with near-term commercial potential.[1]
- These building blocks served as the starting points for Task 2 and could play valuable roles as co-products at biorefineries

Green-shaded compounds are predominantly produced from biomass.

Adipic Acid	**Propylene glycol**	**Isoprene**	**1,3-Propanediol**	**Furfural**
Succinic Acid	**1,4-Butanediol**	**p-Xylene**	**Lactic acid**	**Ethyl lactate**
Acrylic Acid	**1,3-Butadiene**	**Fatty alcohol**	**Glycerol**	**2,5-furanedicarboxylic acid**

1. Biddy, M. J.; Scarlata, C.; Kinchin, C. *Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential*; NREL/TP--5100-65509, 1244312; 2016; p NREL/TP--5100-65509, 1244312. DOI 10.2172/1244312

Task 6: Systems Economic and Sustainability Analysis

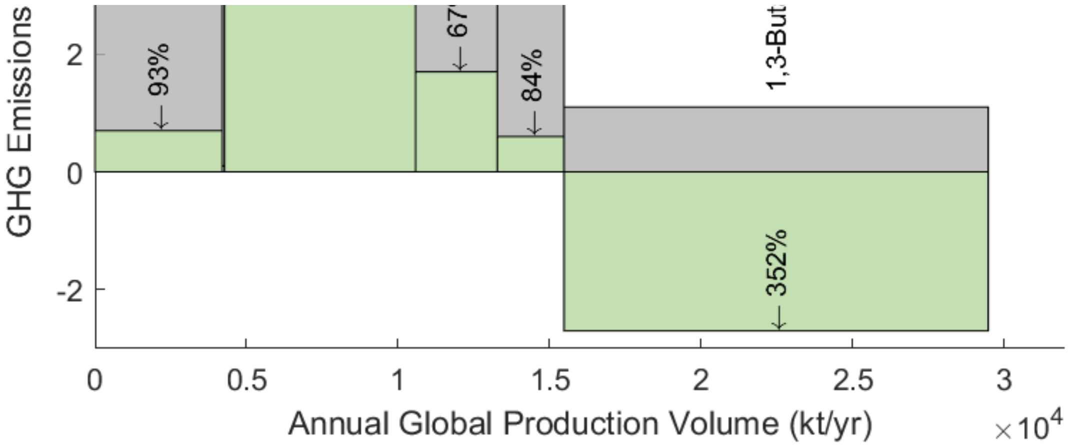
Progress and Outcomes

Gross GHG emissions of:

\+ Fossil-derived chemicals

Bio-based chemicals

Fossil-to-bio transition



- Replacing fossil fuel-derived chemicals with bio-based chemicals could save 120 million metric tonnes CO_2e – the equivalent of removing 26 million U.S. vehicles from the road
- Changing the production paradigm for 1,3-butadiene, acrylic acid, and adipic acid offers the greatest benefits

Liang C, Gracida-Alvarez UR, Hawkins TR, Dunn JB. "Life Cycle Assessment of Biochemicals with Clear Near-Term Market Potential." *ACS Sustainable Chemistry and Engineering*. 2023, accepted.