DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

EE0009295

Production of high-performance biodegradable polyurethane products made from algae precursors

April 4, 2023
Technology Area Session

Prof. Michael Burkart
University of California San Diego

Project Overview

- Develop algae-based diisocyanates
- Improve polyols with algae-based and branched chain monomers
- Produce performance enhanced polyurethane products with >80% bio-content
- Measure physical characteristics of bio-based polyurethanes
- Biodegradation of bio-based polyurethanes

Participants:

Michael Burkart, PI, UC San Diego, Chem/Biochem

Stephen Mayfield, UC San Diego, Molecular Biology

Alissa Kendall, UC Davis, Civ/Env Engineering

Ryan Simovsky, Algenesis Materials

Big Picture Impact

- **Algae-based Polyols** – Algae is the most sustainable means of producing replacements for petroleum-derived fuels and chemicals. High value products, such as polyols and the PUs made from them valorize biomass and biofuel production, as well as replace other uses of petroleum with sustainable sources that pull CO_2 from the atmosphere.
- **Algae-based Isocyanates** – Over 5 billion kilograms of diisocyanates are made annually via reaction with toxic phosgene. No biological sources of diisocyanates currently exist, nor those made without phosgene. Our methods CAN produce isocyanates where all carbons in the molecule come from algae using flow chemistry, which eliminates the use of phosgene. Algae-based isocyanates, along with algae-based polyols, allow us to make 100% algae-derived high-quality PUs.
- **High performance** – For companies to use and adopt these materials, they must be comporable to petroleum chemicals for factory integration and they must perform as well or better than current solutions. Low quality plastics simply will not be adopted – our PUs are high quality polymers that are drop-in replacements for current plastics, they perform as well or better than commercial alternatives.
- **Biodegradable** – Nearly 10 million metric tons of plastic have been made world-wide, less then 5% has been recycled, and nearly 60% has ended up in our environment, with most of that making microplastics that impact human and environmental health. To prevent further pollution & ecological devastation, our PUs must be biodegradable!

1 – Approach

- Purification and separation of azelaic acid from algae source
- Utilizing the flow chemistry method for the production of diisocyanates
- Optimization of flow chemistry conditions to deliver the high yield and high purity isocyanates
- Synthesis of algae-based polyols and compared their physical properties with commercial polyols. Large-scale production of polyols for polyurethane application.
- Test out the algae-derived isocyanate and polyols for polyurethane applications such as making TPUs, foams, adhesives, etc.
- Synthesis of polyurethane products with >80% bio-content
- Measure physical characteristics of bio-based polyurethanes
- Making prototype products such as phone cases, hand watches, etc.
- Determine the biodegradation of bio-based polyurethanes products

Challenges facing the technical approach

- Scaling up the production of isocyanates
- Optimization of flow chemistry conditions to deliver the high purity of and high-yield isocyanate.
- Scaling up the production of algae-based polyols

Go/No-Go Decision Points

GN.1 Go/No-Go Budget Phase 1: Process and Data Validation. If parameter validation fails or site visit team finds that project is not feasible and these obstacles are found to be insurmountable, the project will be terminated.
Outcome: Passed

GN.2 Go/No-Go Budget Phase 2: Based on data from Tasks 1 – 4, highest bio-based content of PUs and capacity for analysis and demonstration of complete biodegradation will be evaluated to determine if subsequent tasks on scaled production and biodegradation are feasible. If the barriers to >80% bio-content and subsequent biodegradation are insurmountable, the project will be terminated.
Outcome: Passed

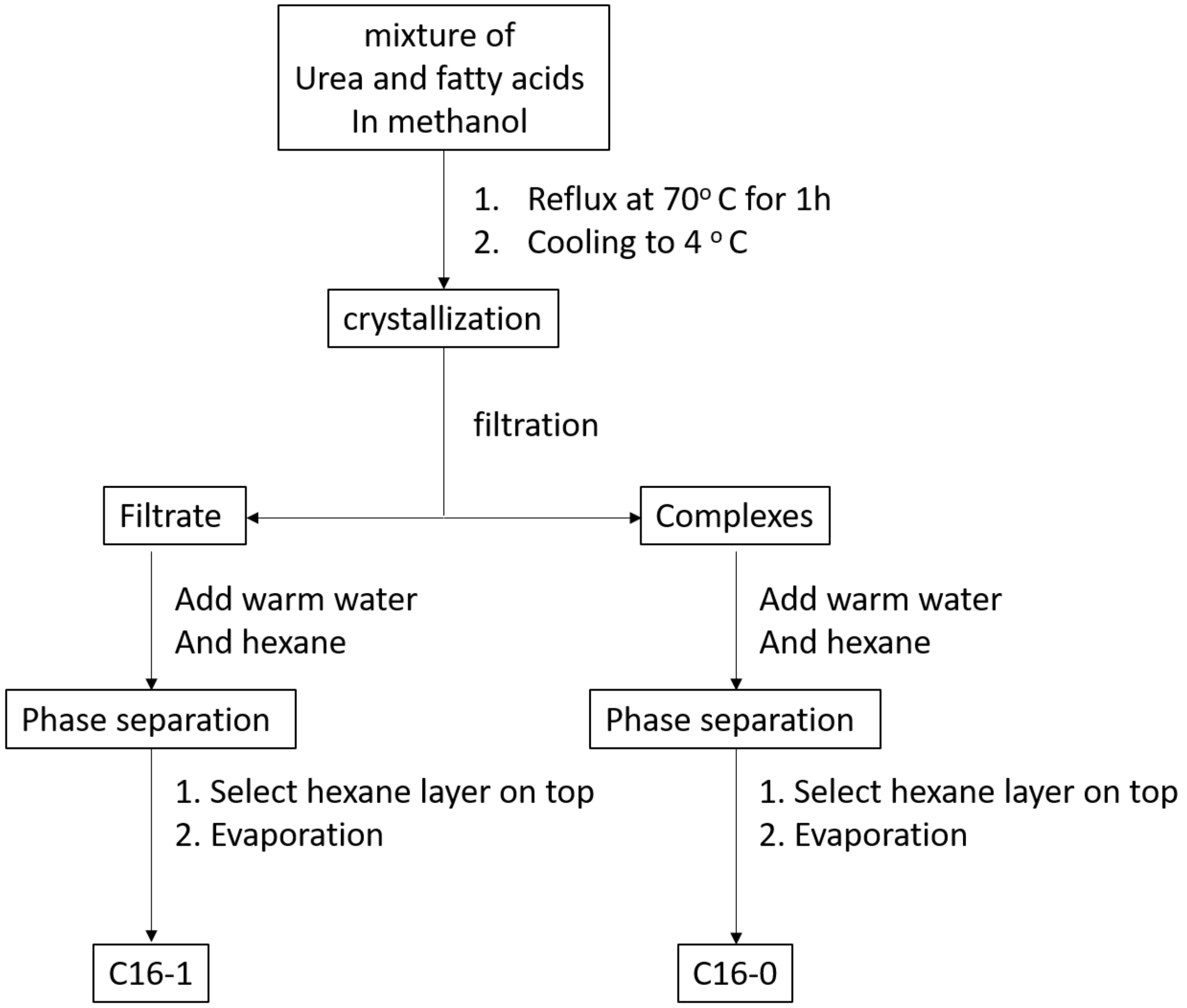
Brief risk analysis and mitigation strategies

- The production of isocyanates involved the explosive intermediate such as azide, so running those reactions in the flow system can avoid any potential explosions.
- The large-scale synthesis of polyols is challenging, but maintaining the desired conditions such as temperature and time can lead to the desired physical properties.
- Production of desired polyurethanes with specific applications requires a good choice of polyols and isocyanates, we will optimize the conditions for the polyurethane formulations to deliver a successful prototype product.

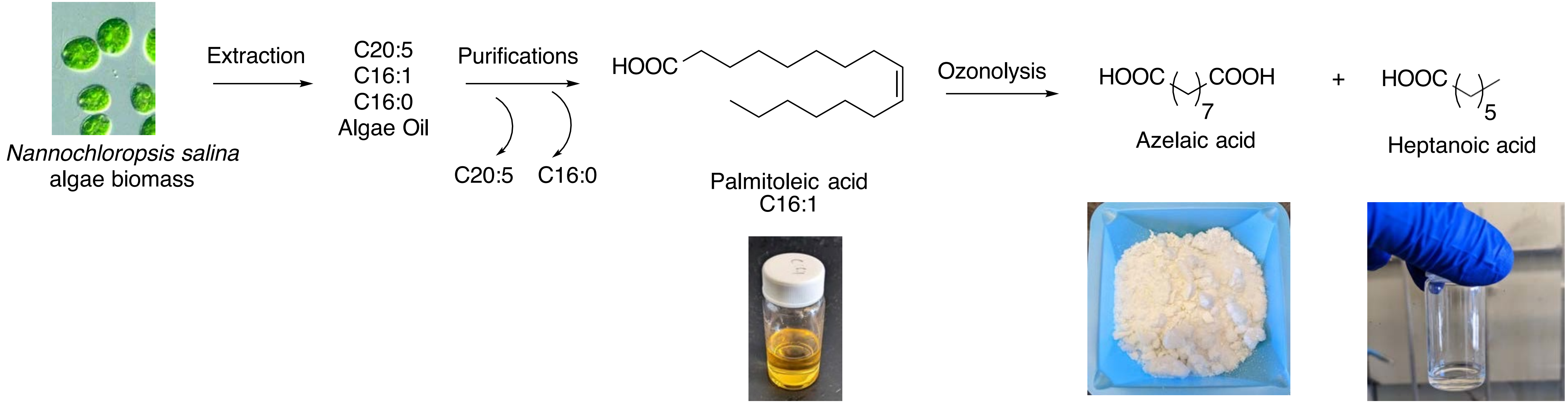
2 – Progress and Outcomes

A)Develop algae-based diisocyanates

Purification of C16-1 by urea complexation



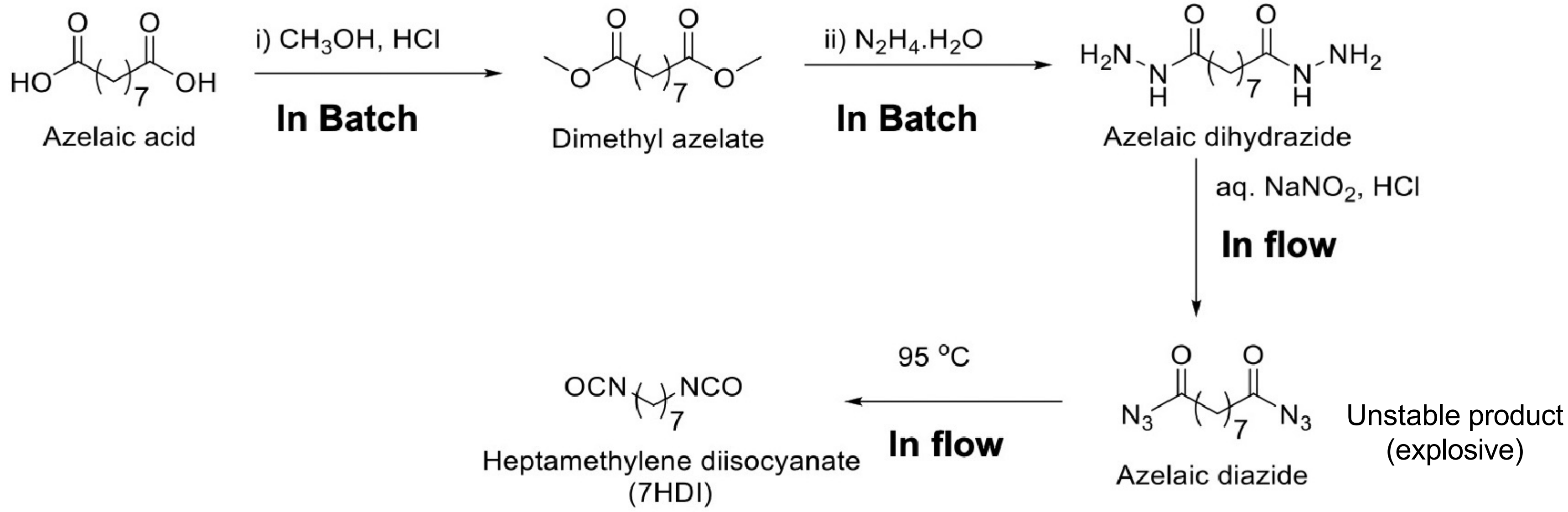
Production of Algae Azelaic Acid



Scheme: Production of algae azelaic acid.

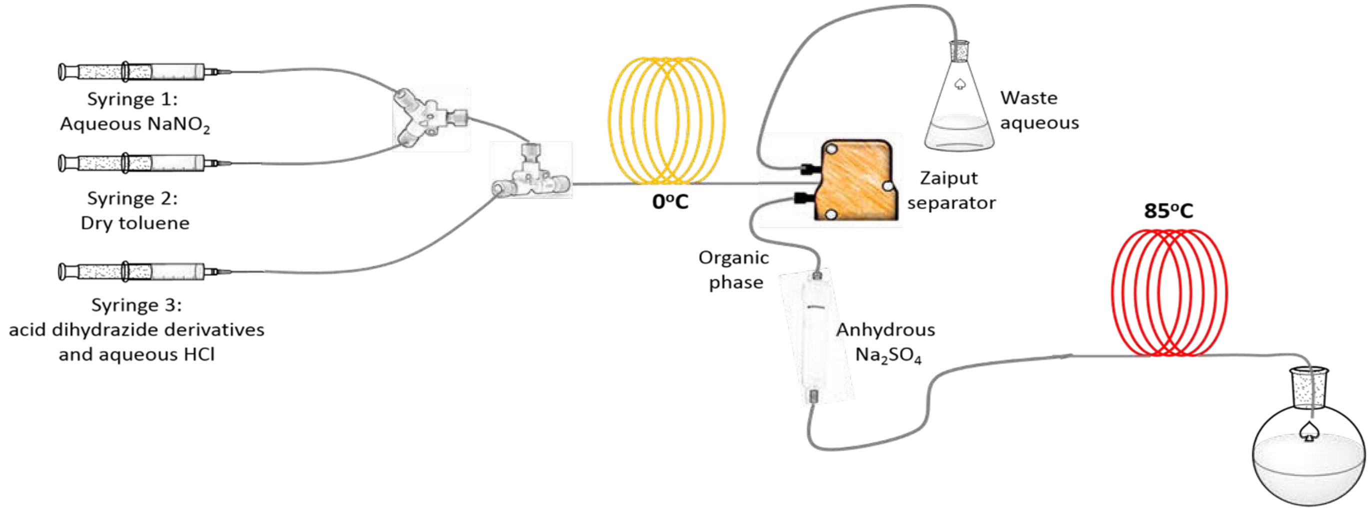
T. A. Phung Hai, N. Neelakantan, M. Tessman, S. D. Sherman, G. Griffin, R. Pomeroy, S. P. Mayfield, M. D. Burkart, *Green Chem.* 2020, 22, 3088.

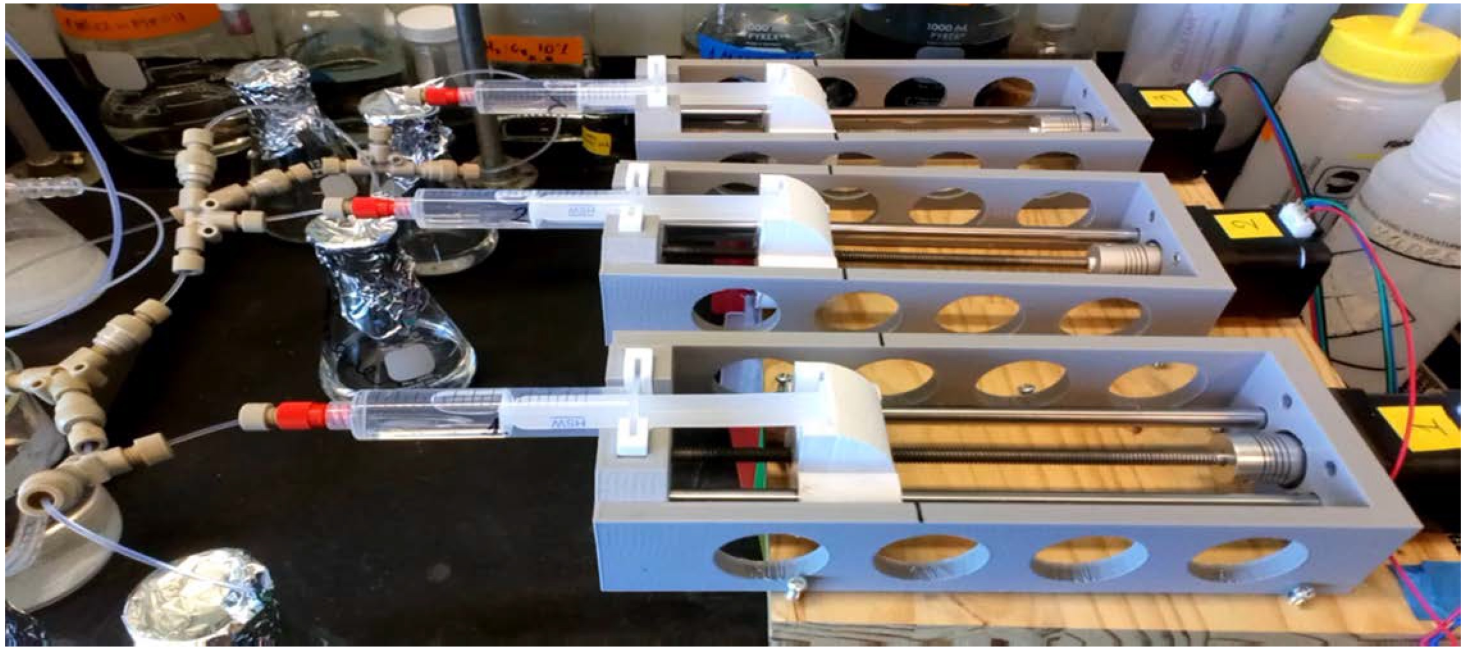
Production of algae based heptamethylene diisocyanate (7HDI)



Scheme: Pathways to algae-derived isocyanate.

Flow Chemistry – Initial Setup



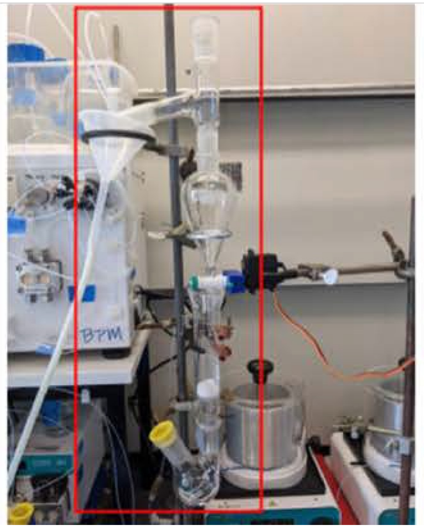


Hai, T. A. P., De Backer, L. J. S., Cosford, N. D. P., Burkart, M. D. *Org. Process Res. Dev.* 2020, 24 (10), 2342-2346.

Flow chemistry set-up for production of 7HDI

There are total **4** pumps and **2 Reactors**

- ✓ Pump 1 deliver the aq. $NaNO_2$ solution
- ✓ Pump 2 deliver the $CHCl_3$
- ✓ Pump 3 deliver the azelaic hydrazide solution
- ✓ Pump 4 deliver the azelaic diazide in $CHCl_3$
- ✓ Pump 1 & 2 are binary pump it can select solvent and reagent
- ✓ Pump 3 & 4 are high pressure HPLC pumps which select and change solvent and reagent by manually



Without contactor/separator

Flow chemistry set-up for production of 7HDI

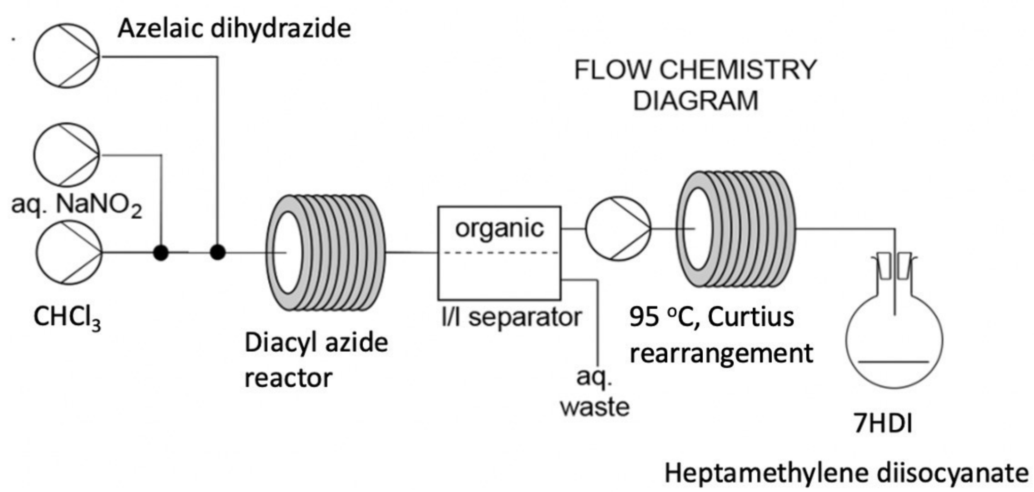


Figure: Flow diagram for production of algae-derived 7HDI.

There are a total of 4 pumps and 2 reactors

- ✓ Pump 1: $NaNO_2$ solution
- ✓ Pump 2: $CHCl_3$
- ✓ Pump 3: Azelaic dihydrazide
- ✓ Pump 4: Azelaic diazide in $CHCl_3$
- ✓ Flow rate: 5 ml/min.
- ✓ Product purity (7HDI) : > 95%

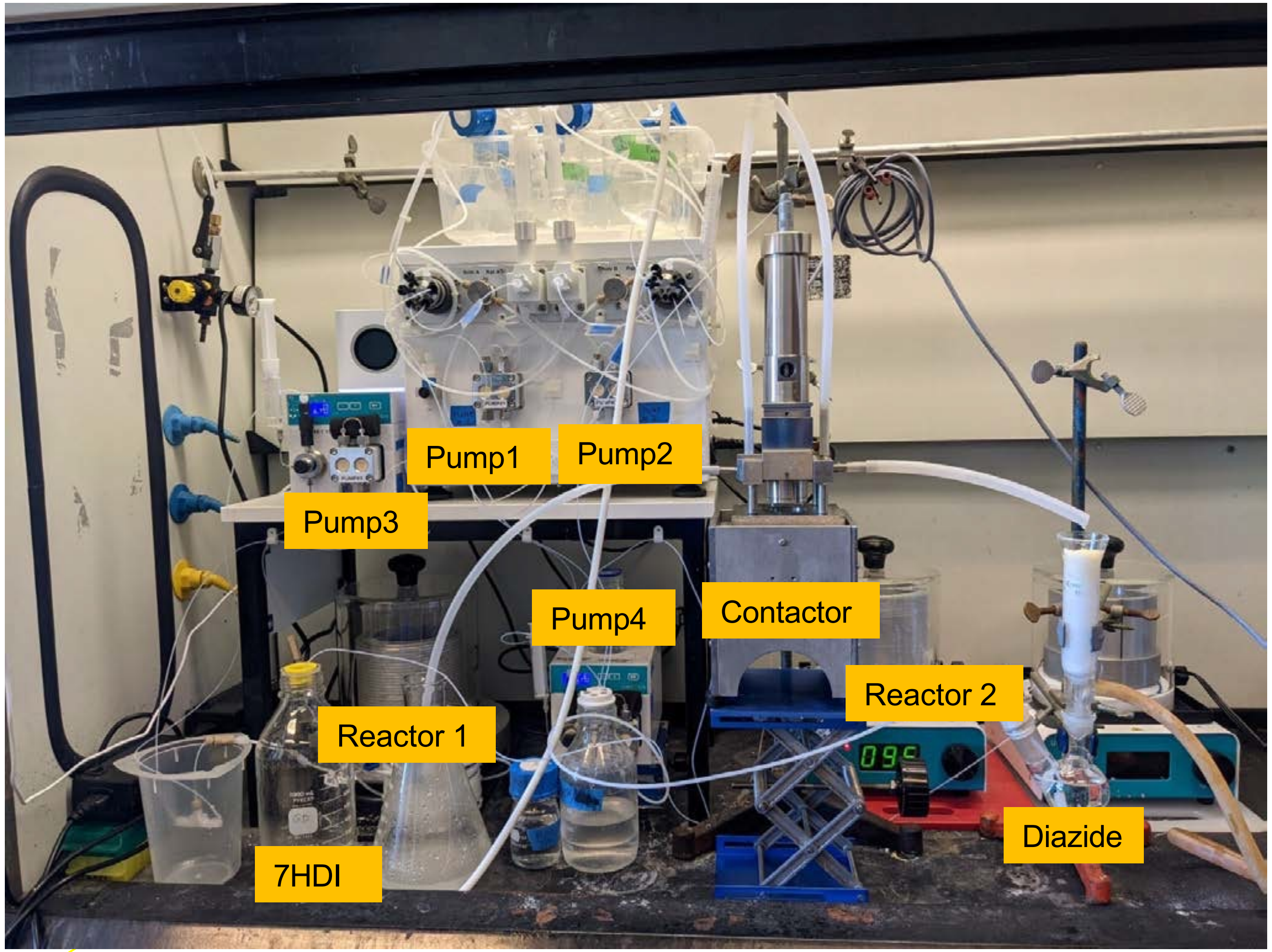
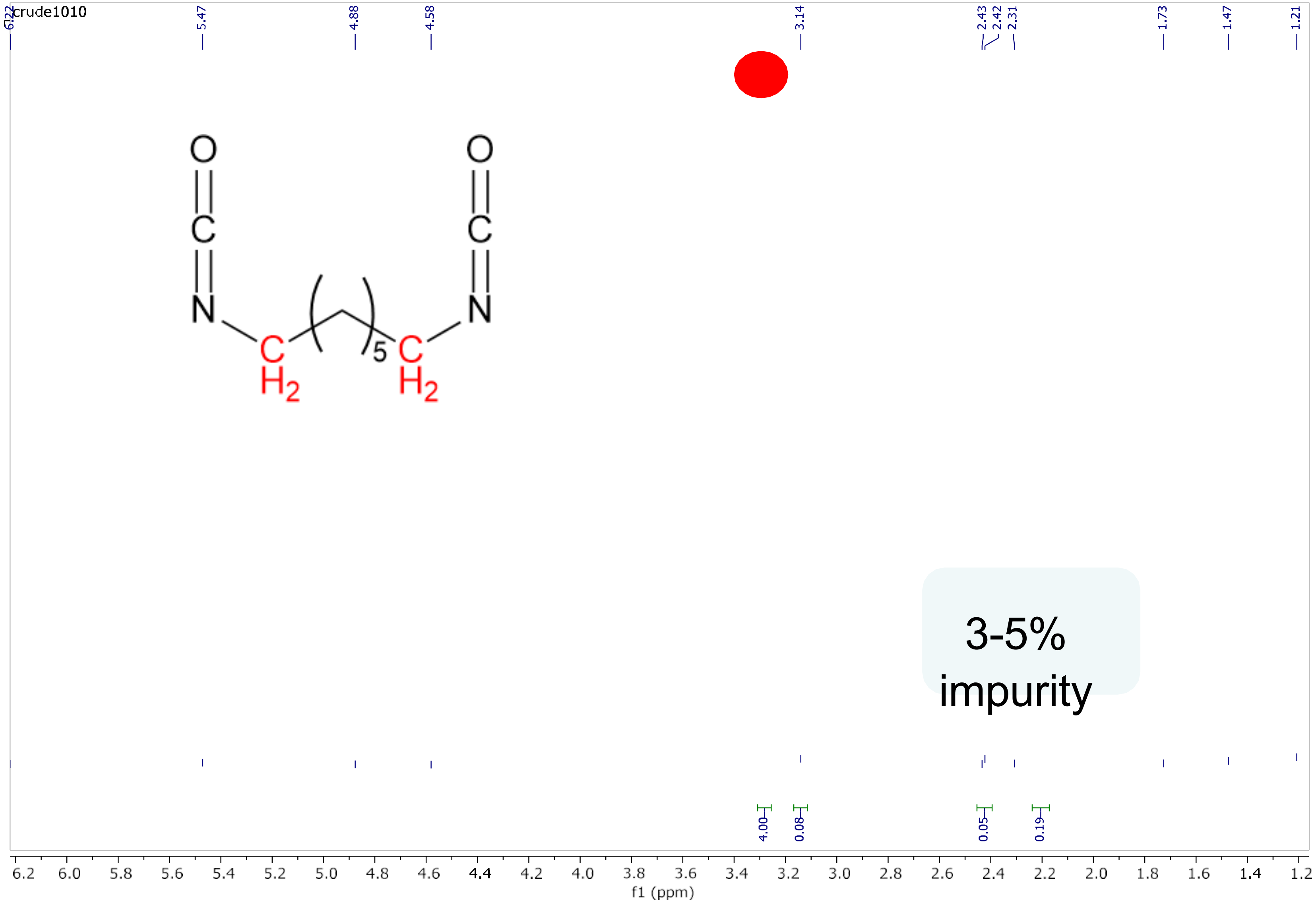


Figure: Flow chemistry set-up for production of algae-derived 7HDI.

With contactor/separator

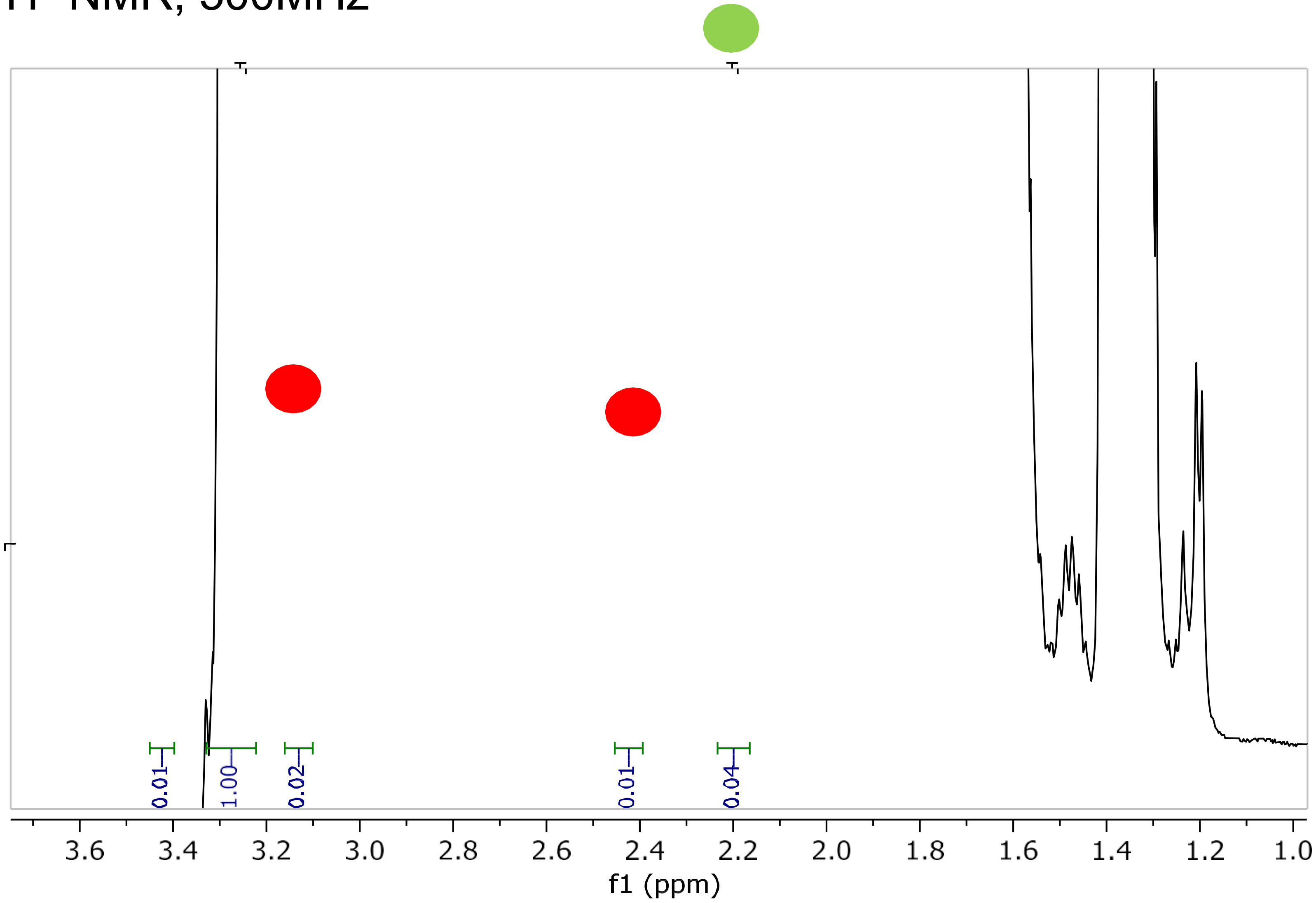
Crude Product- 7HDI

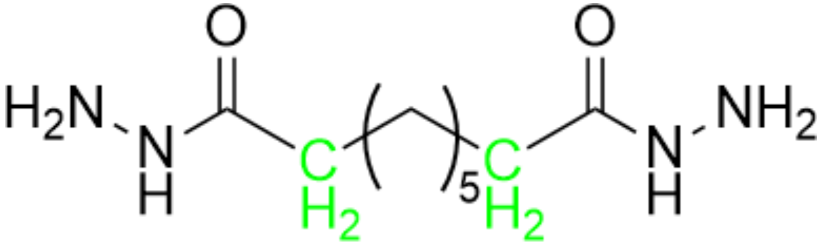
H1 NMR, 500MHz



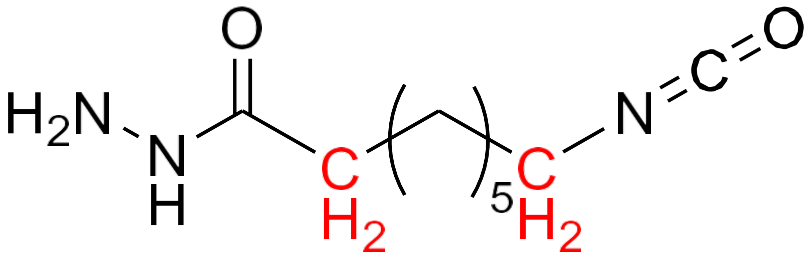
Impurities in 7HDI

H^1 NMR, 500MHz





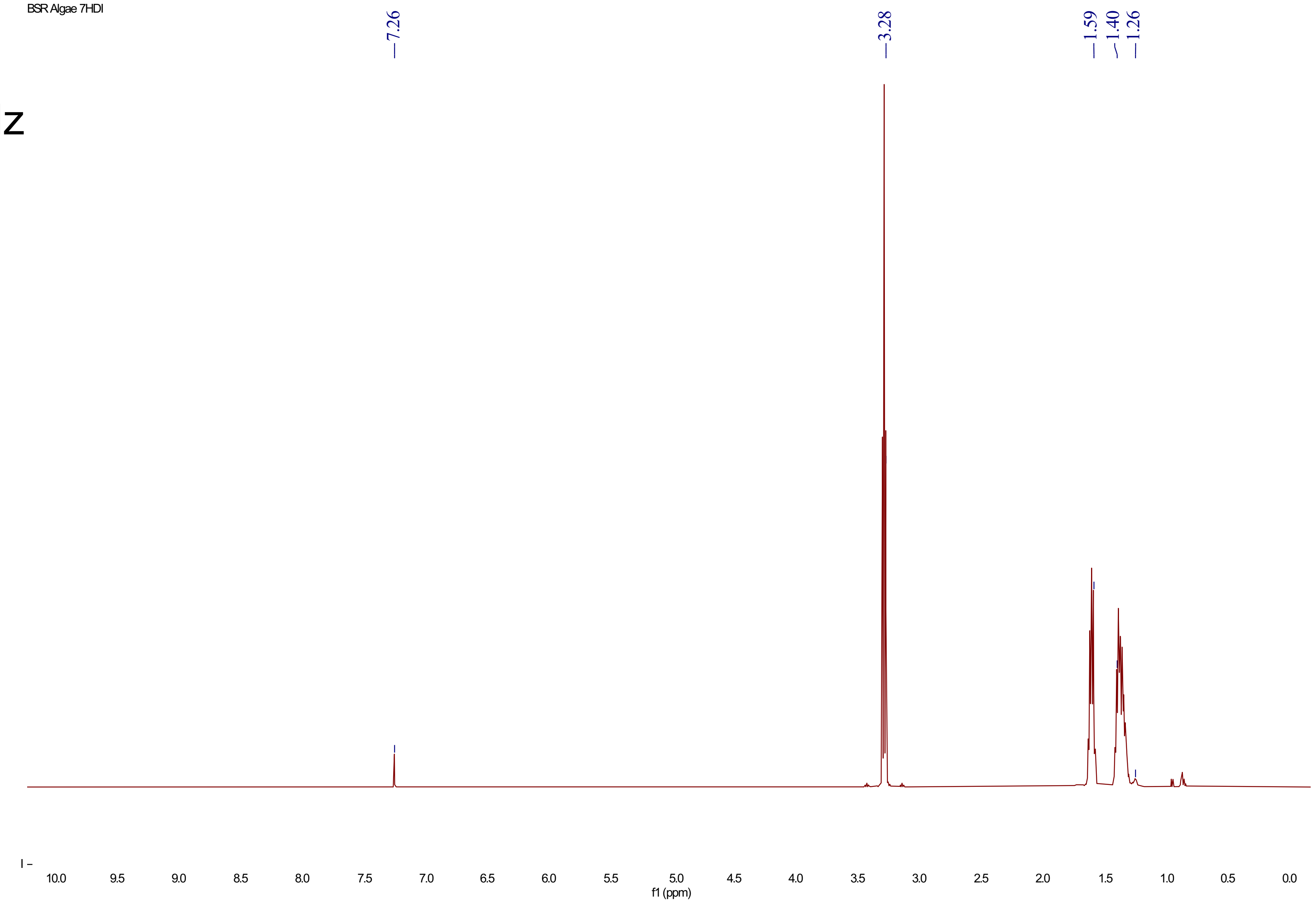
Hydrazide (starting material)



Mono Conversion

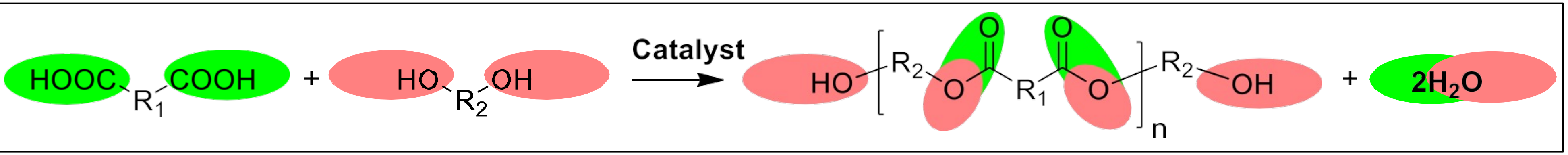
Purified 7HDI

H1 NMR, 500MHz



B- Improve Polyols with Algae-based and Branched-chain Monomers

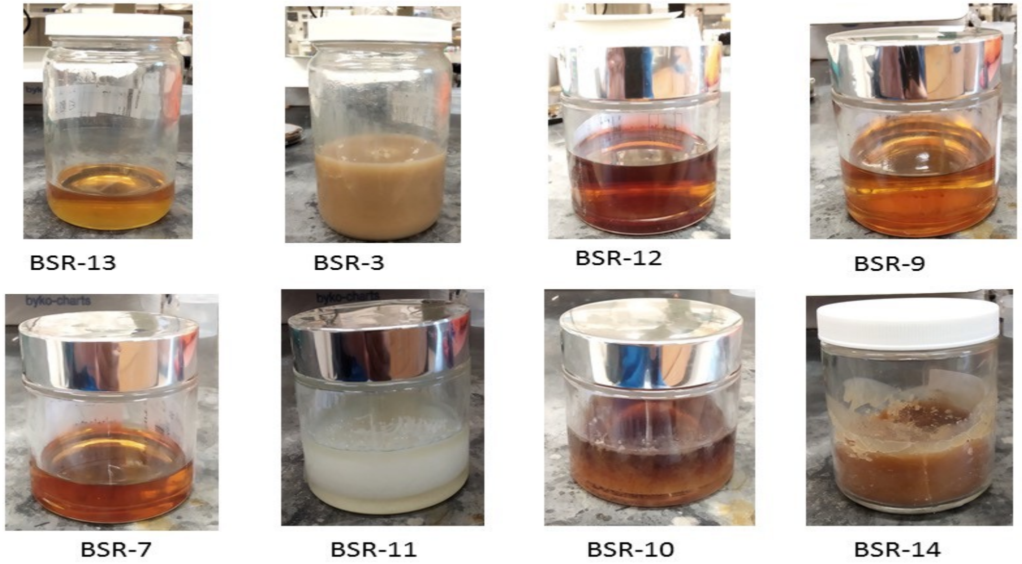
Synthesis of Polyester-Polyols



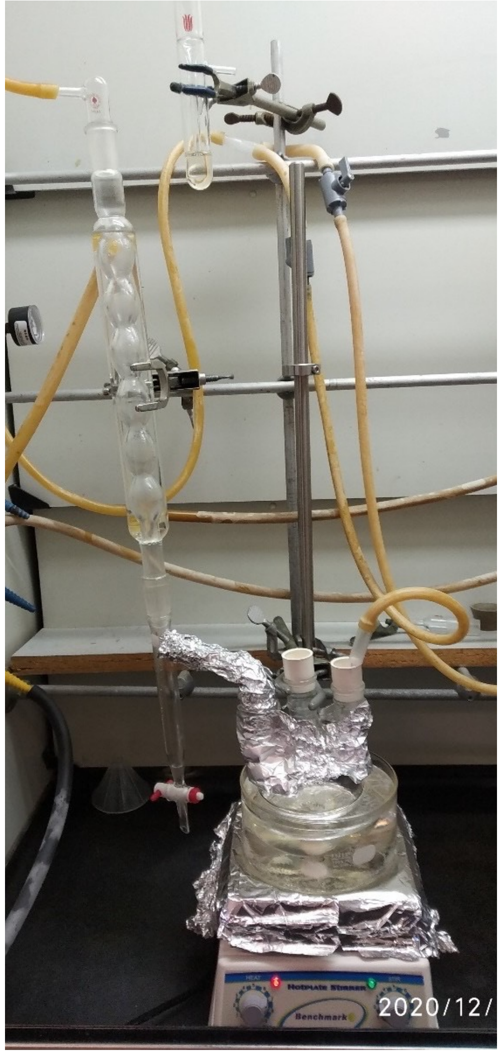
Diacids

Diols

Polyester-polyols

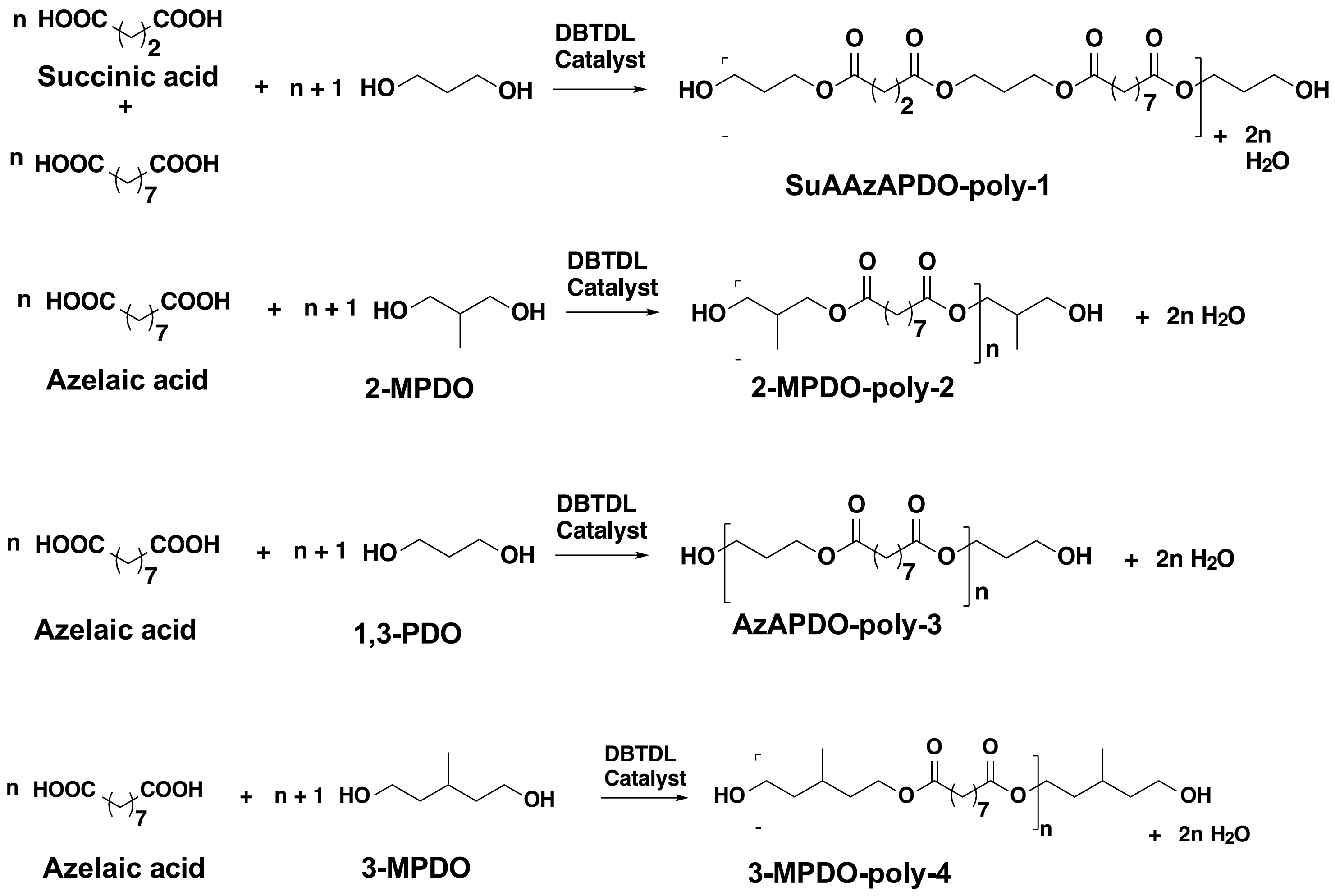


Molecular weight = 2000 g/mol
Acid number = < 2 mg KOH/g



Polyol reaction set-up

Examples of Polyester-Polyols



Scheme: Synthesis of polyester-polyols.

Rajput, B. S., Hai, T. A. P., Burkart, M. D. *Molecules.* 2022. 27 (15), 4885-4897.

Properties of Algae-based polyester-polyols

Table: Properties for polyester-polyols.

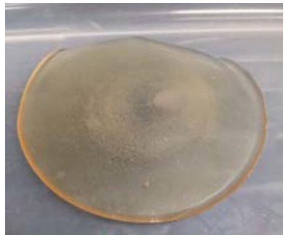
Run	Polyol	Diacids/Diol	Acid value (mg of KOH g^{-1})	OH number (mg of KOH g^{-1})	Molecular weight (by OH number)	Viscosity (55 °C, cP)	Physical state of polyester-polyol at RT (25 °C)	Algae carbon content (%)	Bio-carbon content (%)
01							Semisolid	50	
02		AzA/2MPDO	1.7	53	2100	ND	Liquid	66	
03		AzA/PDO	1.4	56	2000	1188	Solid	73	
04									

SuA = Succinic acid, AzA = Azelaic acid, PDO = 1,3-propanediol, 2MPDO = 2-methyl propanediol, 3MPDO = 3-methyl propanediol.

C- Develop >80% bio-based TPUs

$HO\text{-}(R'')_n\text{-}OH \quad + \quad HO\text{-}R'\text{-}OH \quad + \quad OCN\text{-}R\text{-}NCO \quad \rightarrow \quad TPU$

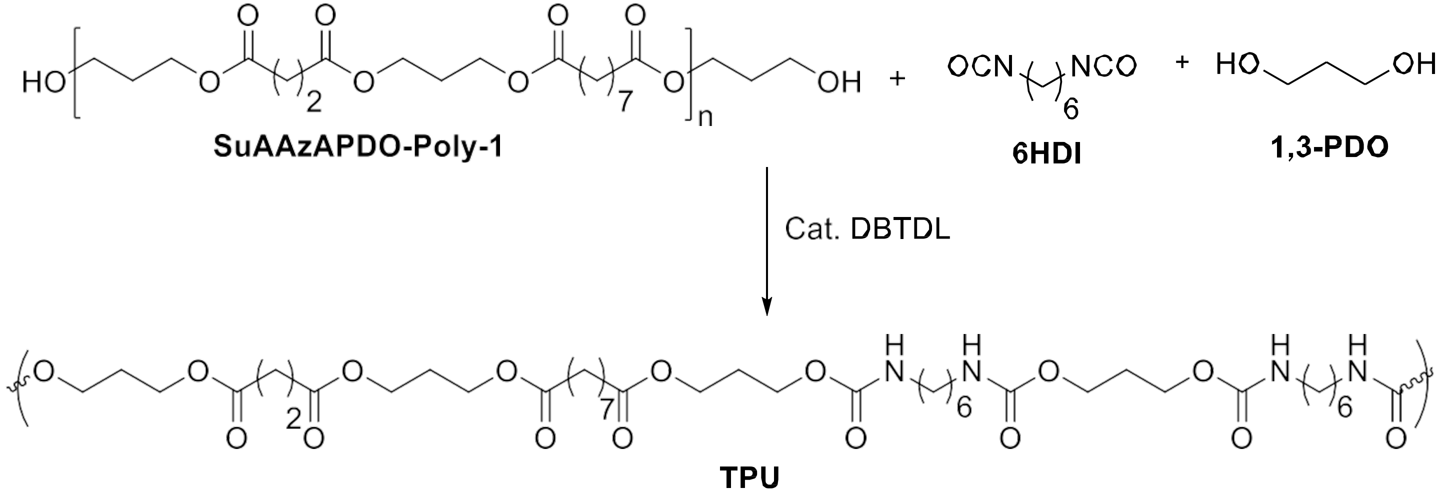
Polyol | Chain-extender | Diisocyanate | Thermoplastic Polyurethane



Conditions: OH/NCO is 1/1.1, with catalyst (DBTDL). The reaction temperature is 75 ˚C, curing temperature is 75 ˚C for 2 days.

Rajput, B. S, Hai, T. A. P., Gunawan, N. R., Tessman, M., Neelakantan, N., Scofield, G. B., Brizuela, J., Samoylov, A. A., Modi, M., Shepherd, J., Patel, A., Pomeroy, R. S., Pourahmady, N., Mayfield, S. P., Burkart, M. D. *J. Appl. Polym. Sci.* 2022, 1-14.

TPU synthesis

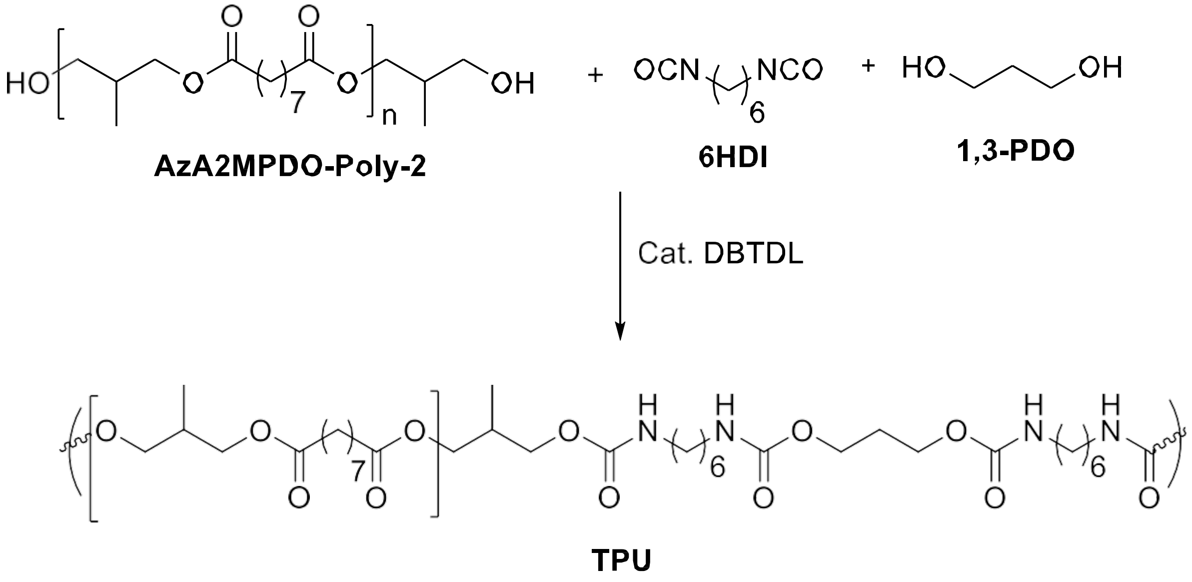


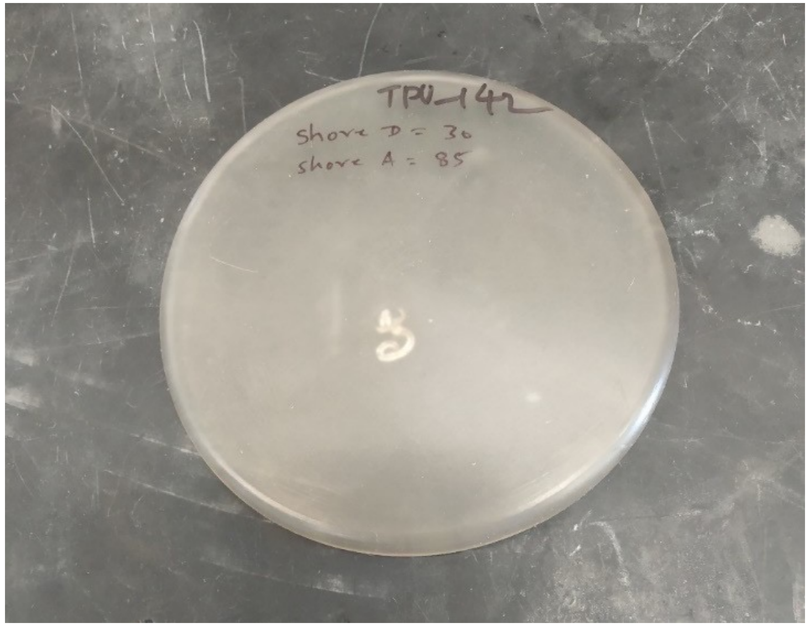
Conditions: Ratio of OH/NCO = 1/1.1; Reaction temperature = 75 °C; Speed mixing = 1 min (after mixing the polyol mixture and diisocyanate); Curing temperature = 75 °C for 2 days.

Algae content = 42 %
Bio-carbon content = 84 %

TPU synthesis

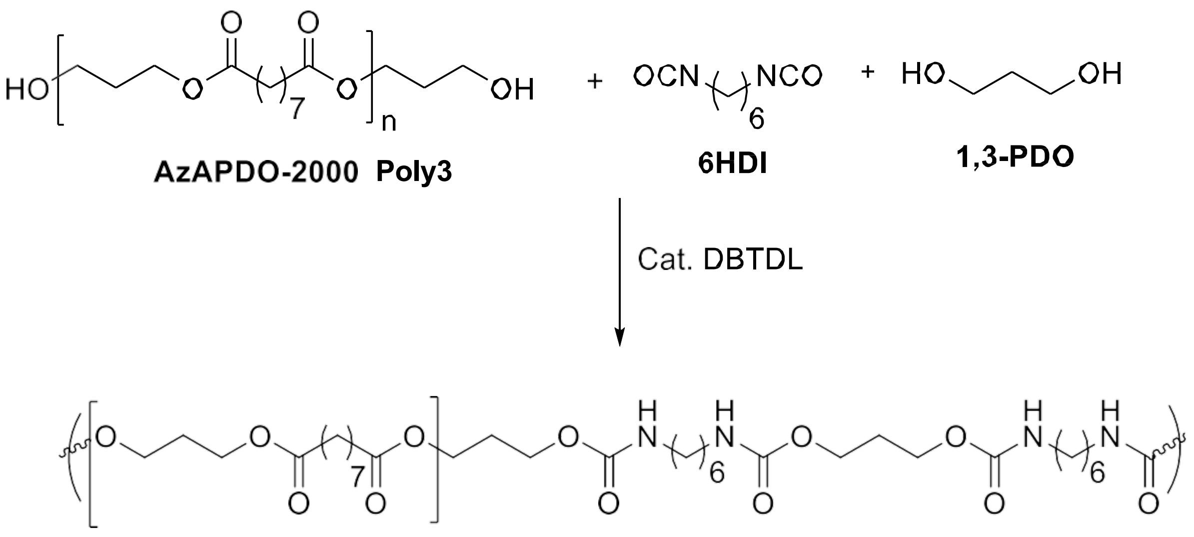
Algae content = 57 %
Bio-content = 65 %





Conditions: Ratio of OH/NCO = 1/1.1; Reaction temperature = 75 °C; Speed mixing = 2 min (after mixing the polyol mixture and diisocyanate); Curing temperature = 75 °C for 2 days.

TPU synthesis



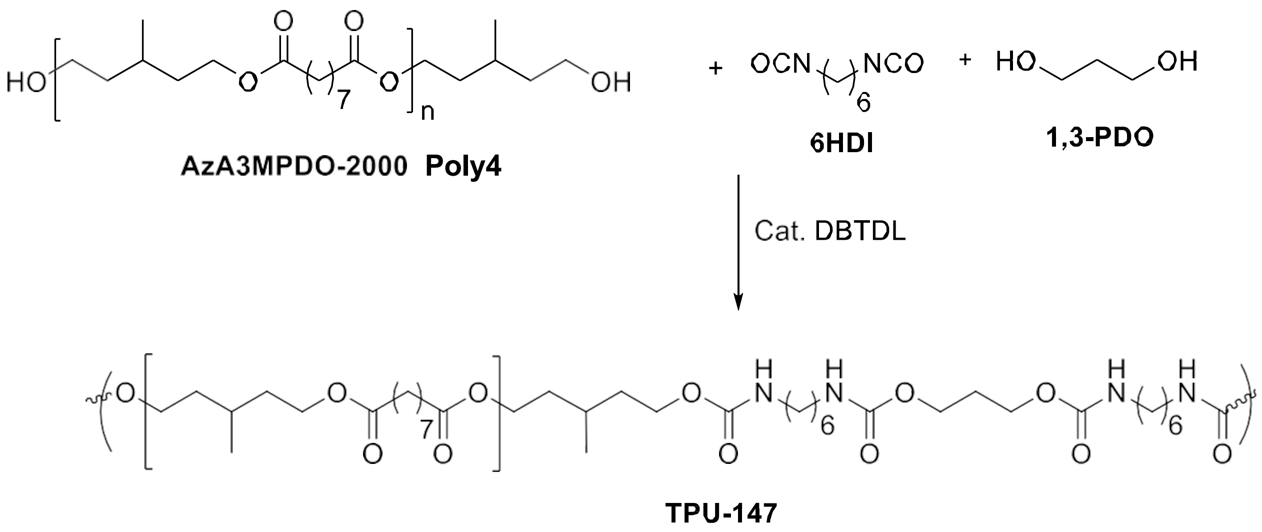
TPU-129

Scheme 3: TPU synthesis.

Conditions: Ratio of OH/NCO = 1/1.1; Reaction temperature = 75 °C; Speed mixing = 1 min (after mixing the polyol mixture and diisocyanate); Curing temperature = 75 °C for 2 days. Tensile testing was carried out after 7 days curing at RT.

Algae content = 61 %
Bio-carbon content = 85 %

TPU synthesis



Conditions: Ratio of OH/NCO = 1/1.1; Reaction temperature = 75 °C; Speed mixing = 1 min (after mixing the polyol mixture and diisocyanate); Curing temperature = 75 °C for 2 days. Tensile testing was carried out after 7 days curing at RT.

Algae content = 47%
Bio-carbon content = 86 %

D-Physical characteristics of >80% bio-based TPUs

Properties	TPU-137 (SuA/AzAPDO, PDO, 6HDI)	TPU-142 (AzA2MPDO, PDO, 6HDI)	TPU-129 (AzAPDO, PDO, 6HDI)	TPU-143 (AzA3MPDO, PDO, 6HDI)	[a]Commercial TPU (Ether-based)
Tensile strength at RT, MPa			48	17	
Elongation at break (RT, %)		881	765	809	
Shore A hardness (RT)		85	95	81	
Shore D hardness (RT)		30	42	30	
Algae carbon content (%)		57	61	47	
Bio-carbon content (%)					

Our bio-based TPUs

Petroleum TPU

Commercial TPU: [a]Huntsman IROGRAN® A 80 P 4699L Ether-Based TPU for Cable Industry.

SuA = Succinic acid, AzA = Azelaic acid, PDO = 1,3-Propanediol, 2MPDO = 2-Methyl propanediol, 3MPDO = 3-Methyl propanediol, 6HDI = Hexamethylene diisocyanate.

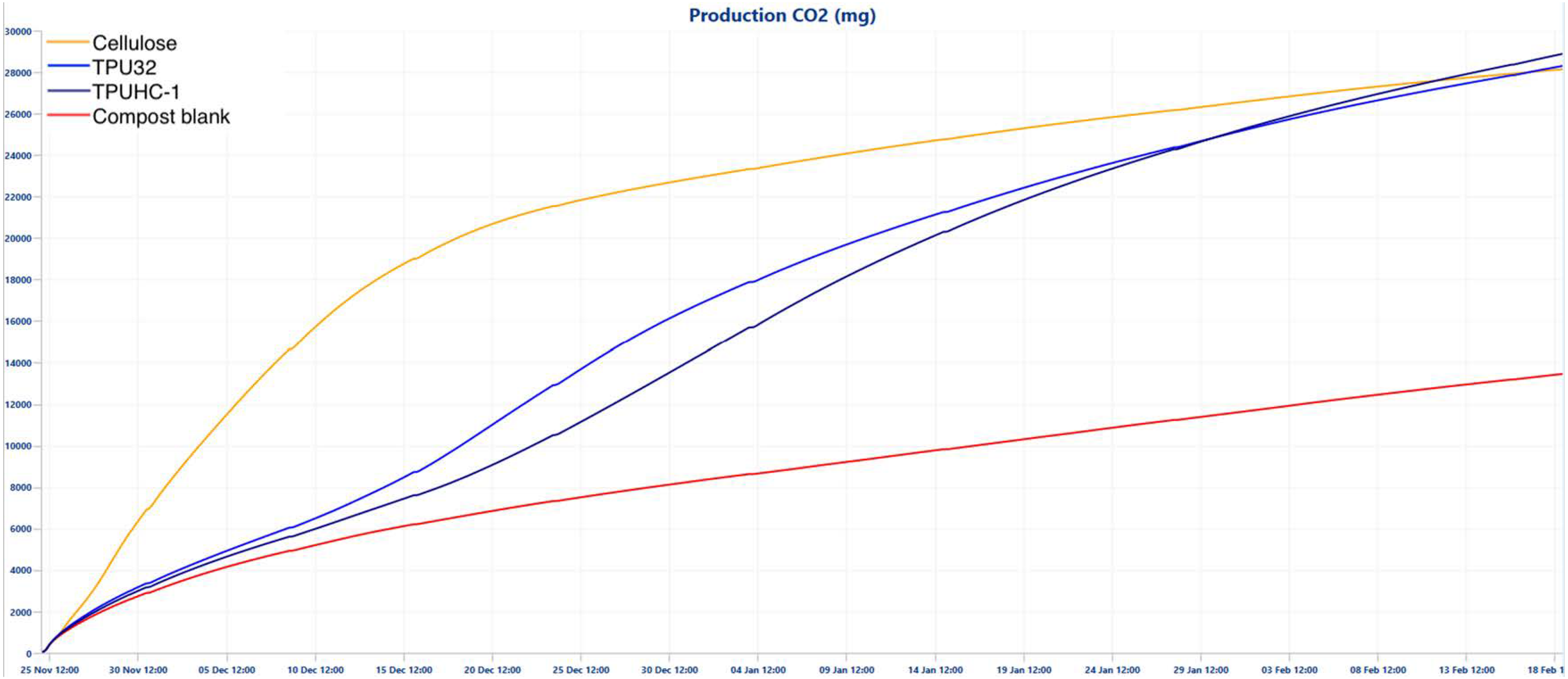
E- Biodegradation of >80% bio-based TPUs

Respirometer for Biodegradation Studies

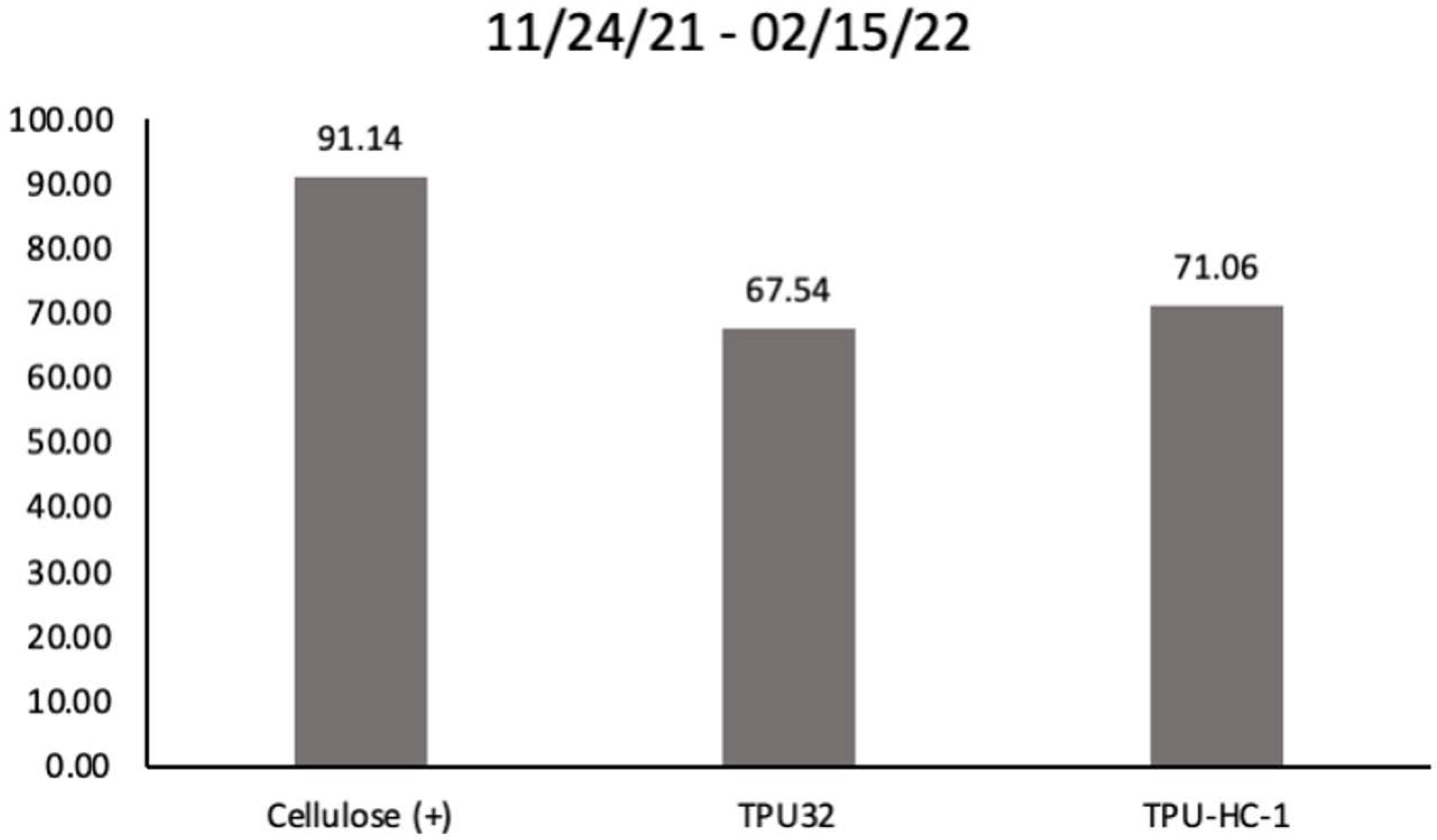
TPU degradation data - raw CO_2 production

Current TPU samples in respirometer: TPU32 (SuA/Sb-PDO-6HDI), TPU-HC1 (SuA/AzA-PDO-6HDI)

- Both TPUs are roughly 85% bio-content, polyol portion is algae-based, 6HDI is not algae-based



3 Month TPU Film Biodegradation %



Biodegradation of thermoplastic polyurethanes (TPUs)

Week 0

Week 2

TPU 129 TPU 142 TPU 147

Conditions: Samples were placed in compost and incubated at 45 °C for 2 weeks. Compost was regularly maintained with the input of DI water to maintain a live and active environment and humidity remained ~85%. Samples were gently rinsed off with DI water before imaging at 2 week time-point.

TPUs after 7 Months in Compost

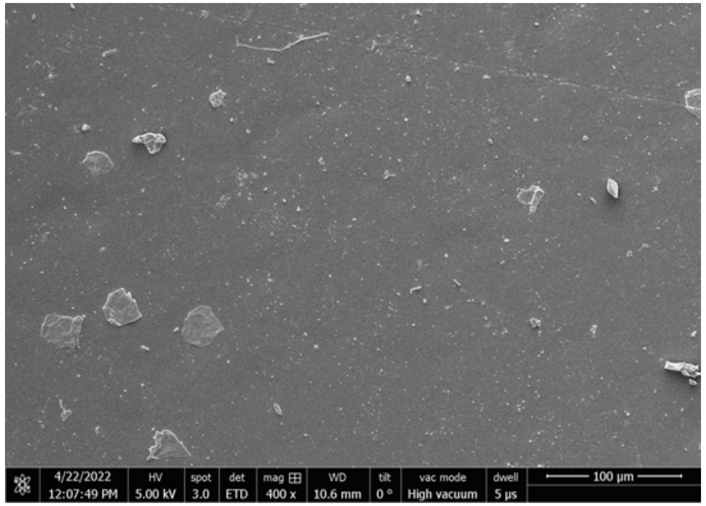
TPU142

TPU17

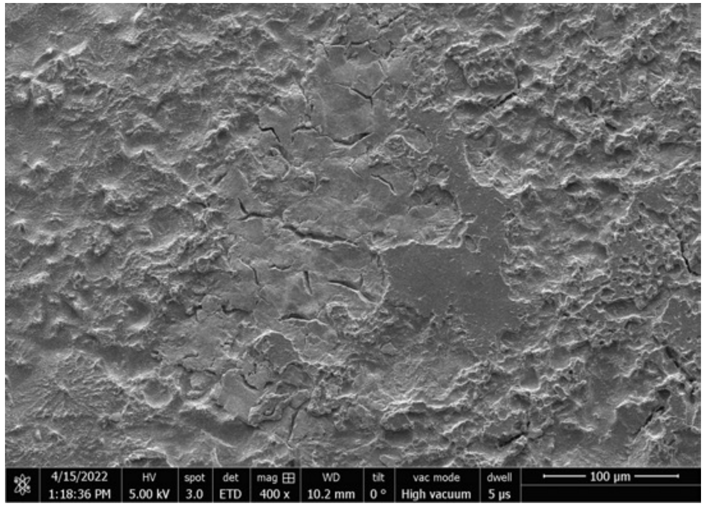
TPU-147 SEM

Run #1 400x Magnification

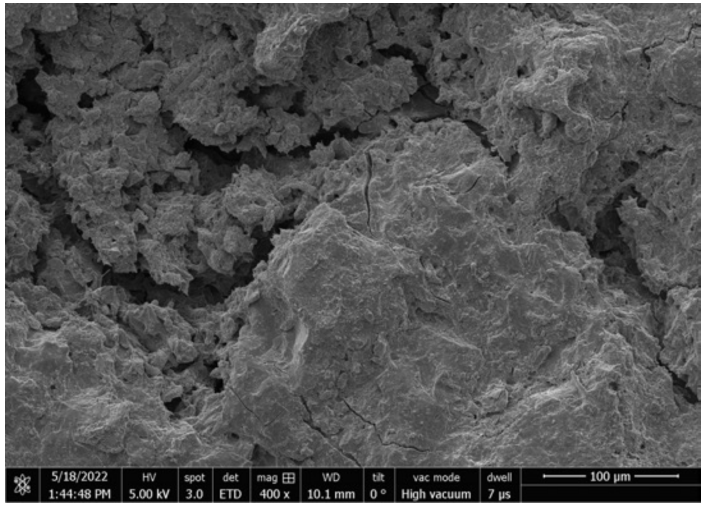
0 Weeks



4 Weeks



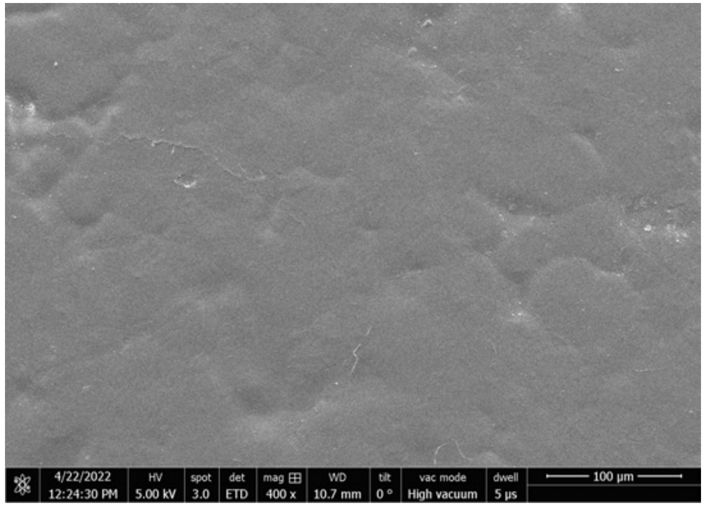
8 Weeks



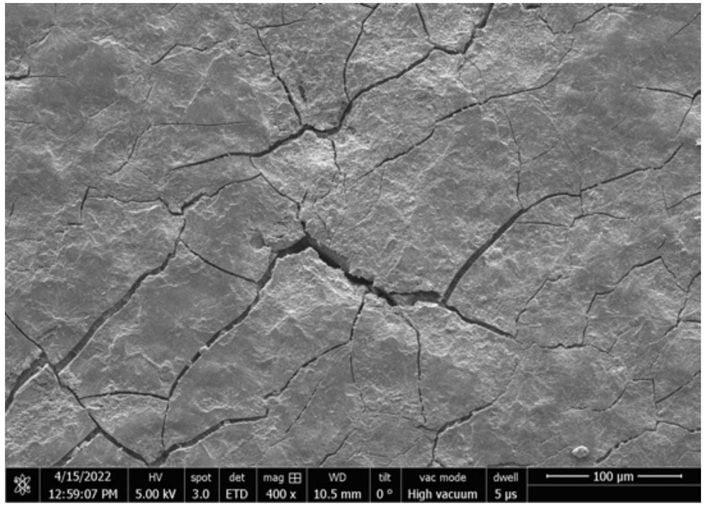
TPU-129 SEM

Run #1 400x Magnification

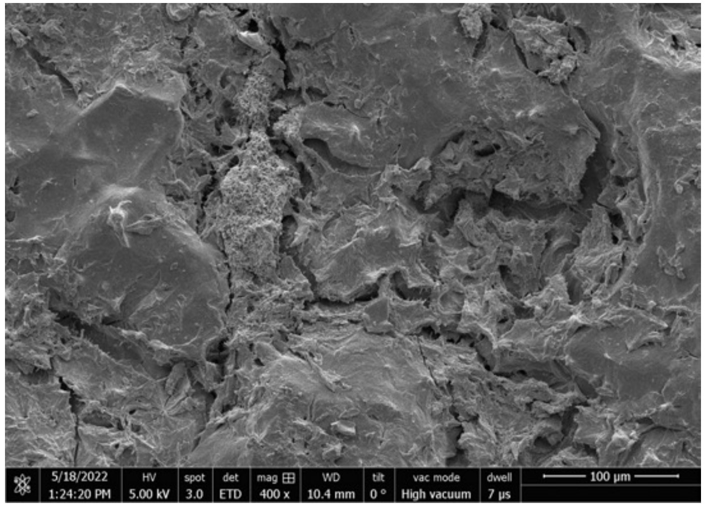
0 Weeks



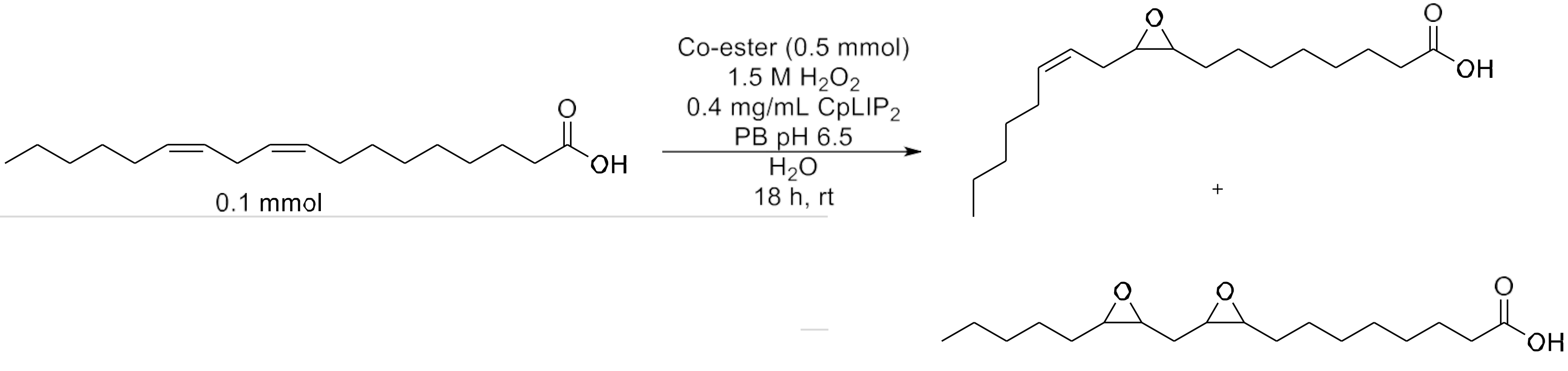
4 Weeks

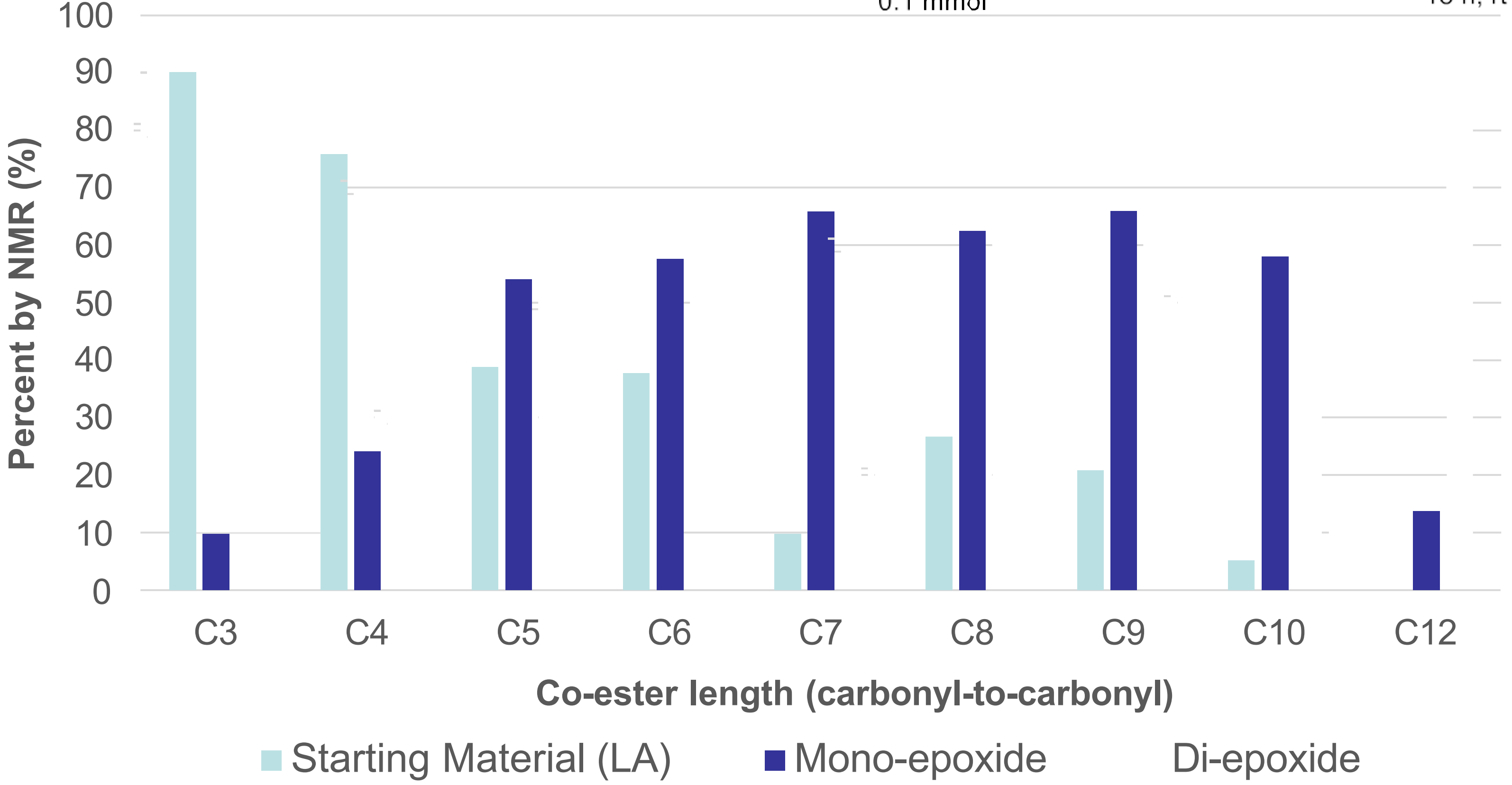


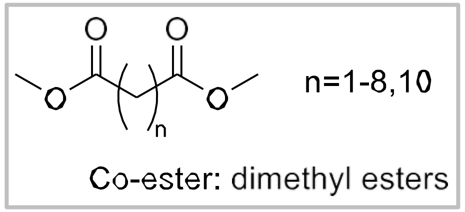
8 Weeks



New Diacid from Algae via Epoxidation



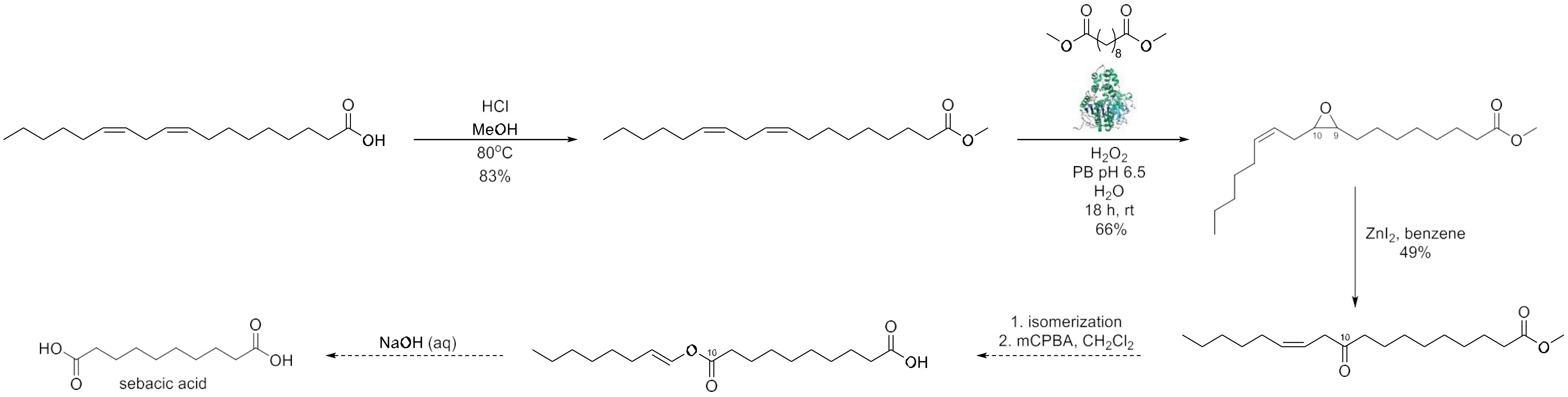




Lipase CpLIP2 of *Candida parapsilosis*

Transforming PUFAs into Sebacic Acid

From



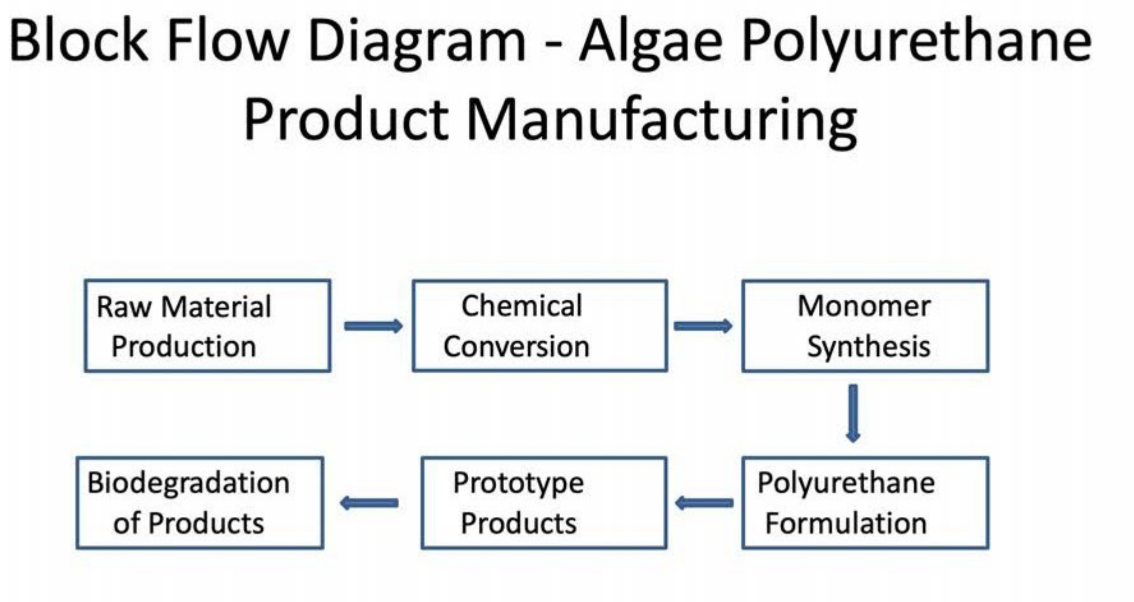
Hai, T.A.P., De Backer, L.J.S, Cosford, N.D.P, and Burkart, M.D. *Org. Process Res. Dev.*, **2020**, *24*, 10, 2342; Re, R. N., Proessdorf, J. C., La Clair, J. J., Subileau, M., Burkart, M.D. *Org. Biomol. Chem.*, **2019**, *17*, 9418; Shaikh, R.R., Khan, R.A., Alsalme, A. *J Ind Eng Chem*, **2018**, *64*, 446.

3 – Impact

- We successfully tested the thermoplastic polyurethane application in making prototypes such as phone cases, hand watches, toys, filaments, etc. See the prototypes images below.
- The provisional patent application has been filed “Renewable Low Viscosity Algae-Based Polyester-Polyols for Biodegradable Thermoplastic Polyurethanes”.
- The potential partner are Algenesis Material, BASF, etc.

Summary

- Production of azelaic acid from algae oil
- Synthesis of heptamethylene diisocyanate using a flow chemistry method
- Synthesis of algae-derived polyester-polyols
- Thermoplastic polyurethanes were made with >80% biocarbon content
- Thermoplastic polyurethanes were successfully tested to make prototypes products
- Biodegradation of thermoplastic polyurethanes



Quad Chart Overview

Timeline

Start of Project: 4/1/2021
End of Project: 3/30/2024

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$768,030*	*(negotiated total federal share)* *$2,000,000*

TRL at Project Start: 3

TRL at Project End: 6

Project Goal

Develop scalable algae-based diisocyanates using flow chemistry and novel algae-based polyols that can be used to increase the bio-based content of our biodegradable PU products to >80% and enhance PU product performance.

End of Project Milestone

1) *Develop new, algae-based diisocyanates and polyols and use these to produce >80% bio-based PU products with improved performance characteristics based on clear material property metrics to provide commercially viable products.*
2) *Demonstrate that these >80% bio-based PU products can biodegrade.*
3) *Prototype a scaled production system for these high bio-content products and perform economic analysis to evaluate the environmental and commercial viability of a circular carbon economy based on our processes and the developed bio-based PU products.*

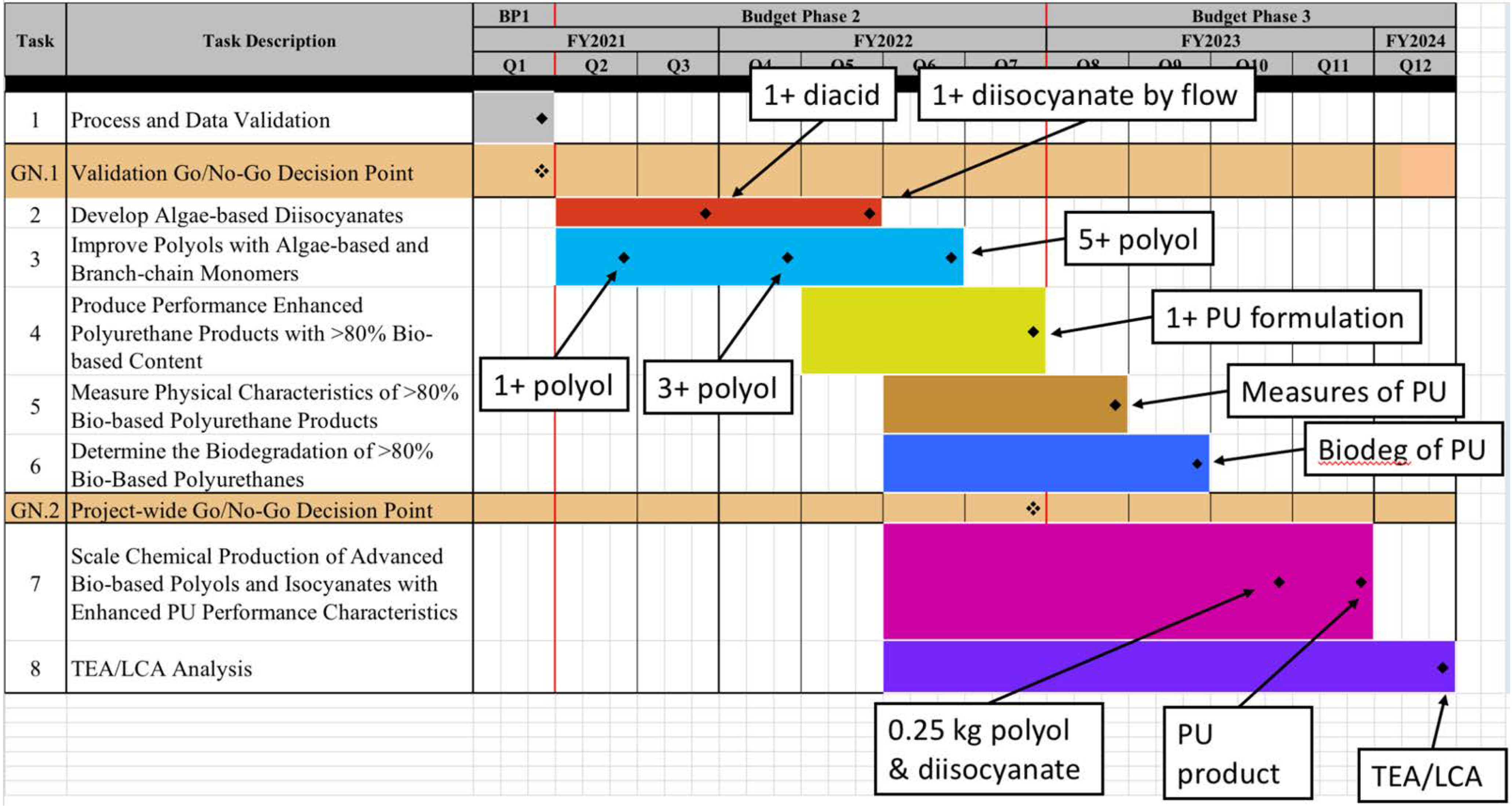
Funding Mechanism

DE-FOA-0002245 – Topic 1a: Novel Bio-Based Plastics: Designing Biodegradable Bio-Based Plastics

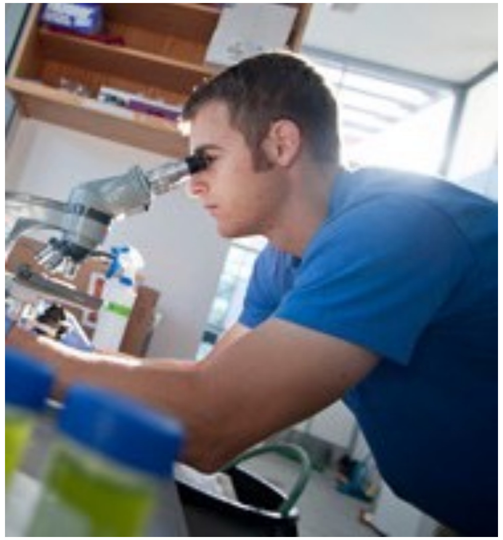
Project Partners*

UC Davis
Algenesis Materials
BASF
REEF Lifestyle
PepsiCo

Project Timeline



Acknowledgements



UCSD

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Nitin Neelakantan
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Ryan Simkovsky
Kaniela Zehn

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