Recyclable Polyesters Made From CO_2

2024 FECM/NETL Carbon Management Research Project Meeting

US DOE STTR Phase II
DE-SC0022839

Ian A Tonks, PhD
CSO, LoopCO2
Professor, University of Minnesota – Twin Cities

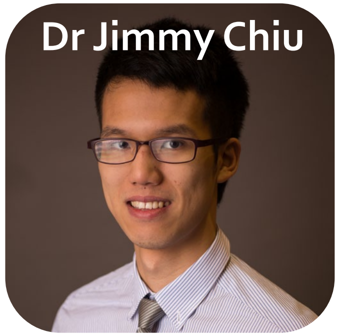
loop CO2

UNIVERSITY OF MINNESOTA
Driven to Discover℠

Company Overview

CEO

CSO



CTO

FOXCONN

DUPONT

NSF Center for Sustainable Polymers

Background

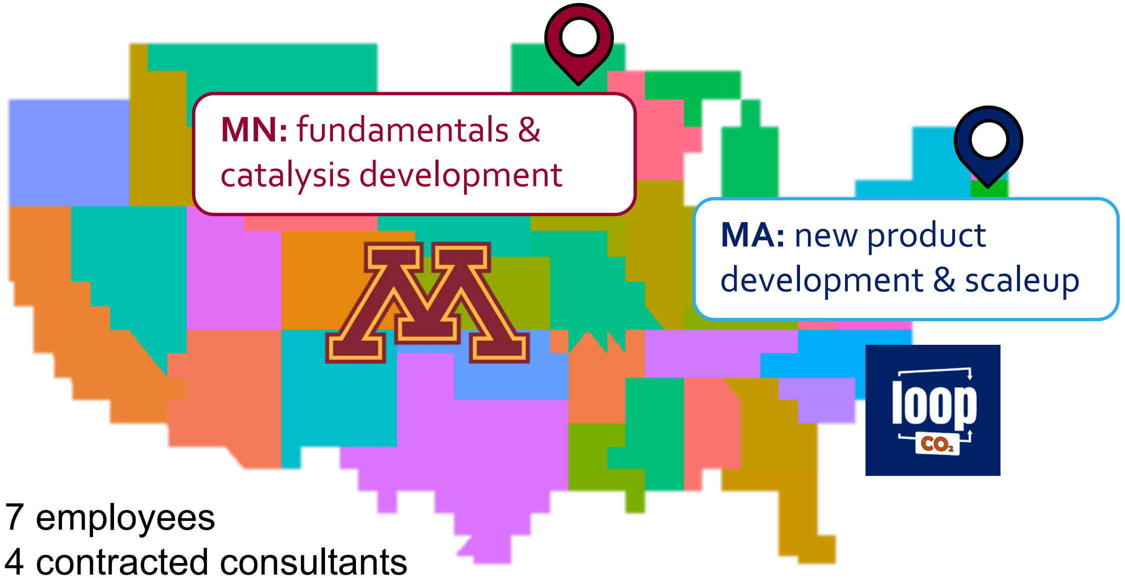
- Spin-out from UMN & CSP in 2022
- HQ at Massachusetts with UMN collaboration
- Seed funded by DOE STTR Phase II & MassVentures

Vision

- Reduce the carbon footprint and promote circular economy in the material industry.

Mission

- Develop a wide coverage of CO_2 and biomass – derived products which have chemical recyclability, biodegradability, negative carbon emissions



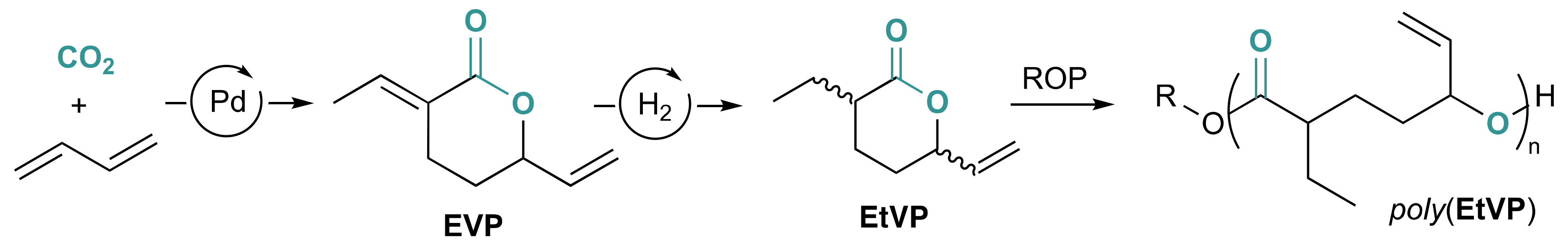
7 employees
4 contracted consultants

SBIR · STTR America's Seed Fund

MASS VENTURES

Technology Background

Core tech: lactones and polymers derived from CO_2 and butadiene



WO2022187490A1

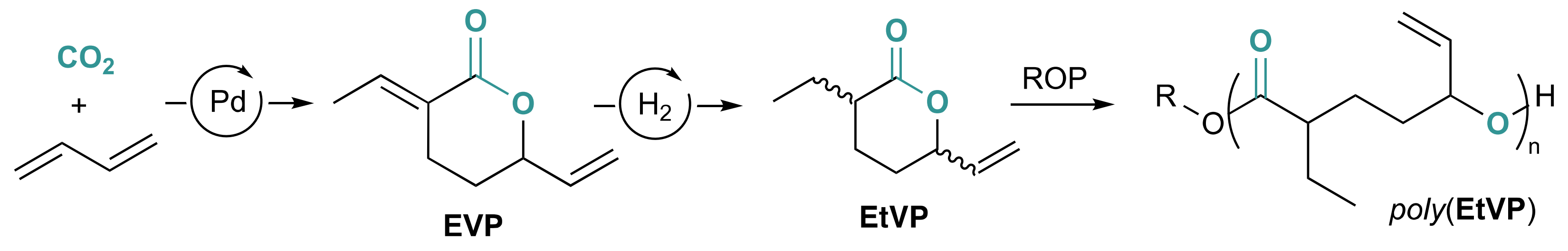
- only polyester from CO_2 and olefins ever made. Almost 30% by weight CO_2
- combines a commodity olefin feedstock (butadiene)
- near the thermodynamic limit of CO_2 fixation by olefins (dG = -0.6 kcal/mol)
- low ceiling temperature, chemically recyclable
- quantitative chemical recycling through reactive distillation at 130 °C
- biodegradable according to OECD-301B (wastewater)

SBIR · STTR America's Seed Fund

MASS VENTURES

Technology Background

Core tech: lactones and polymers derived from CO_2 and butadiene



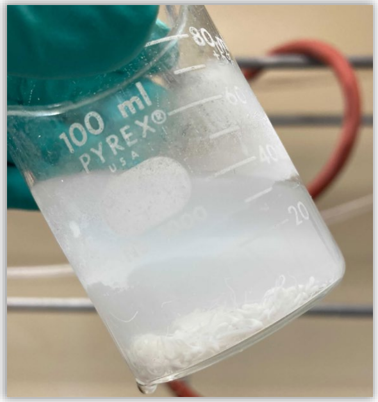
WO2022187490A1

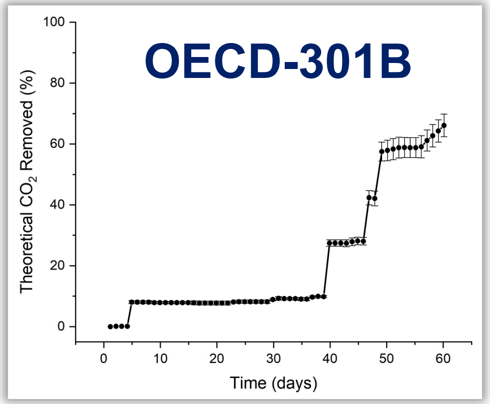
Article | Published: 27 June 2022

Tunable and recyclable polyesters from CO_2 and butadiene

Rachel M. Rapagnani, Rachel J. Dunscomb, Alexandra A. Fresh & Ian A. Tonks

Nature Chemistry **14**, 877–883 (2022) | Cite this article





SBIR · STTR
America's Seed Fund

MASS VENTURES

Value Proposition of Our Polyesters

Sustainable Raw Materials
Harness bio-butadiene and CO_2 to create a carbon-negative material

Circularity
Efficient and gentle chemical recycling, transforming waste back into virgin monomers even from copolymers

Low Viscosity
Maintaining low viscosity at ambient temperatures to streamline processing

Drop-in co-monomer
Easily copolymerizes with lactone monomers for diverse applications, enhancing your product sustainability

Project Objectives

US DOE STTR Phase II Grant (DE-SC0022839)

$1,600,000 ($480,000 to U Minnesota)

Recyclable Polyesters from CO_2 • August 2023 – August 2025

Project Objectives

US DOE STTR Phase II Grant (DE-SC0022839)
$1,600,000 ($480,000 to U Minnesota)

Recyclable Polyesters from CO_2 • August 2023 – August 2025

- Optimize synthetic process of CO_2-derived polyesters and copolymers
- Develop proprietary applications for refined polymers
- Improve the overall lifecycle profile/emissions profile of CO_2-derived lactone monomers
- Develop a pilot plant for scalable, commercially viable CO_2-derived polyesters
- Engage in customer outreach and marketing to identify potential customers/partners

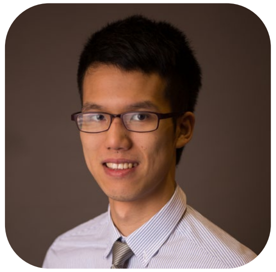
Approach and Team

Fundamental catalysis R&D, initial scale-up
University of Minnesota

Ian Tonks
PI

Arron Deacy
Postdoc

Development of polymer applications
LoopCO2



Jimmy Chiu
PI

Evan Smith

Anuja Tamhane

Research Assistants

LCA and TEA
WAP Sustainability

WAP SUSTAINABILITY CONSULTING

Engineering, pilot reactor design and scale-up
Hickory Run Consulting

Tony Cartolano
Engineering Consultant

SBIR·STTR America's Seed Fund

MASS VENTURES

Project Schedule

First 6 Months:

- Optimize monomer syntheses with LCA feedback loop (complete)
- Deep exploration of polymer properties for key applications (ongoing)

Second 6 Months:

- Optimize CO_2-based polymer synthesis (ongoing)
- Pilot plant design and construction (ongoing)

Year 2:

- Scale up, commission plant, ship test samples to partners
- Continue to design and test products/polymer properties
- Identify partners for continued development/licensing/sales

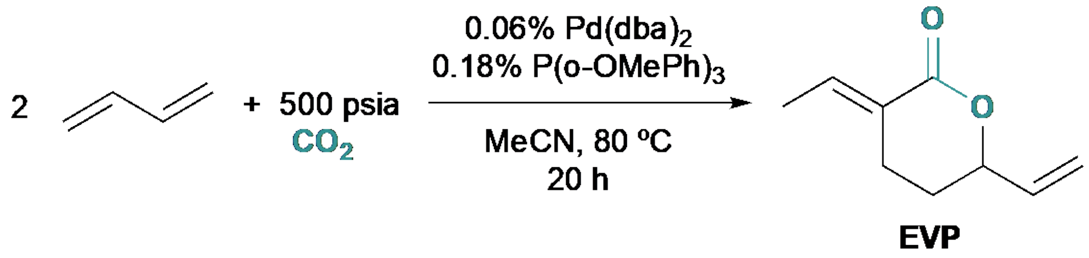
SBIR · STTR America's Seed Fund

MASS VENTURES

Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

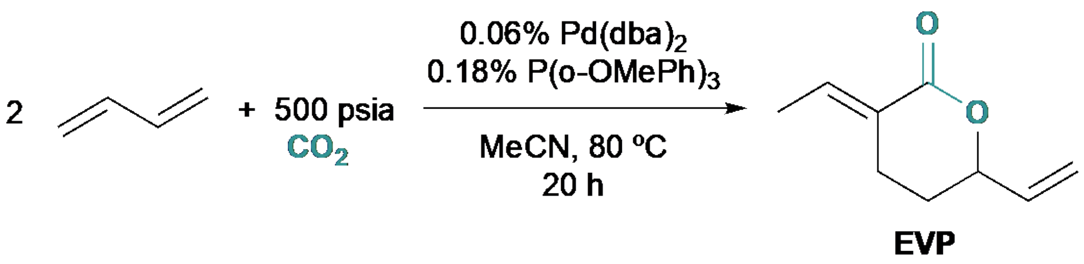
step 1: telomerization



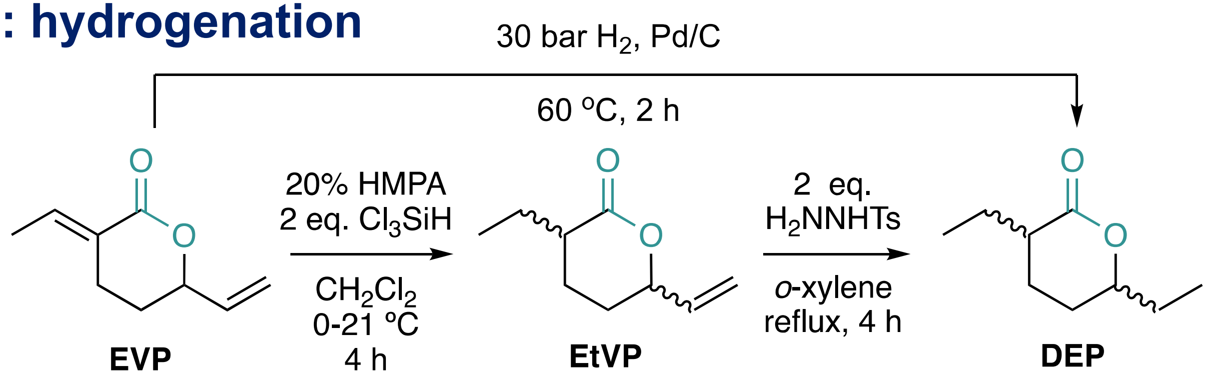
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

step 1: telomerization



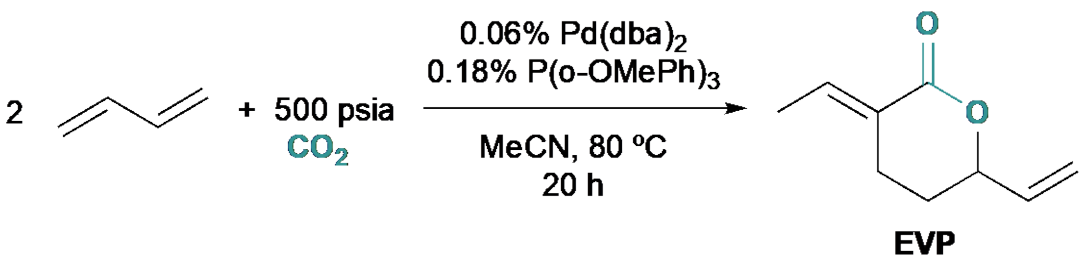
step 2: hydrogenation



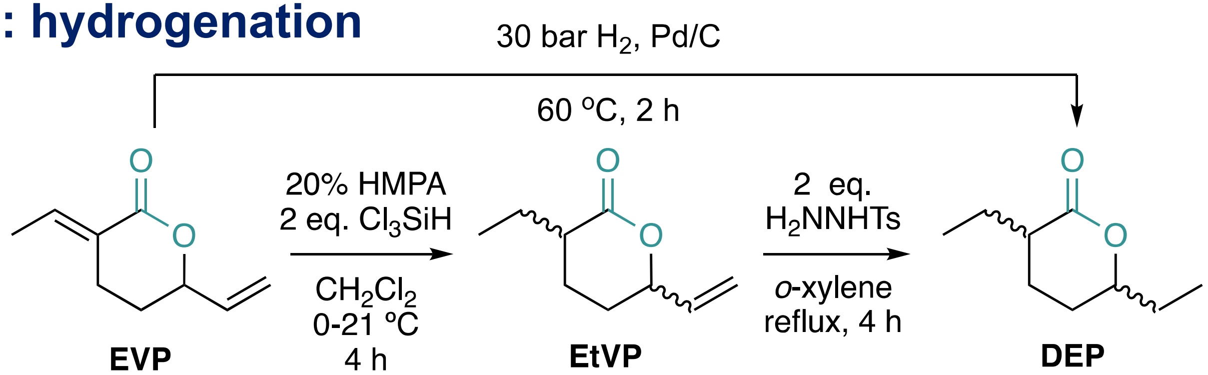
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

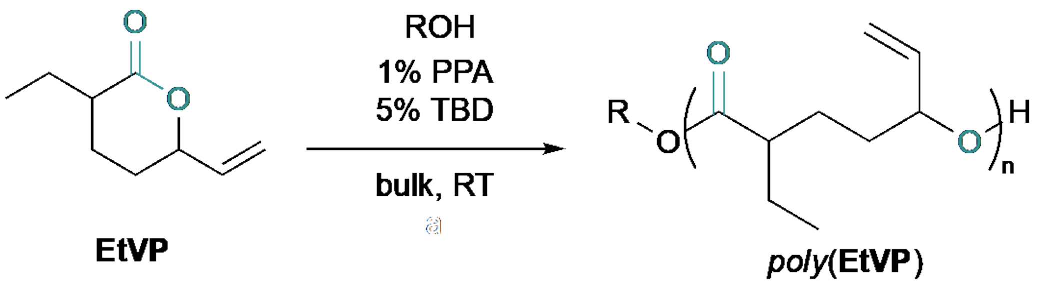
step 1: telomerization



step 2: hydrogenation



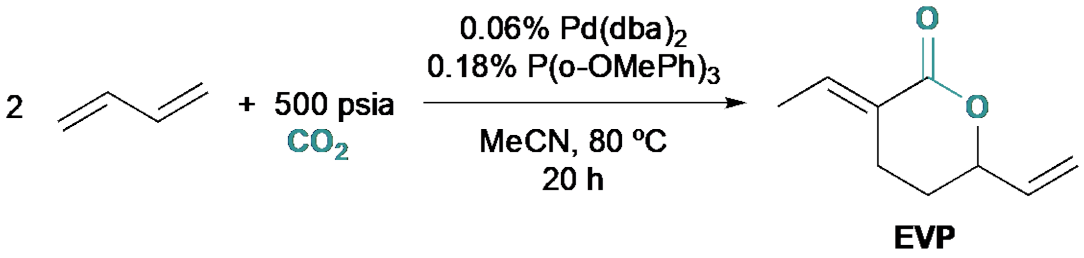
step 3: polymerization



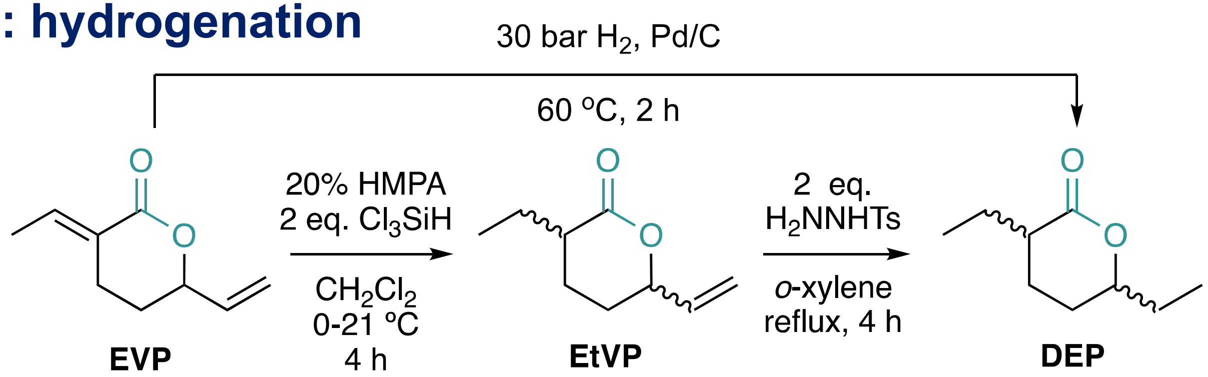
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

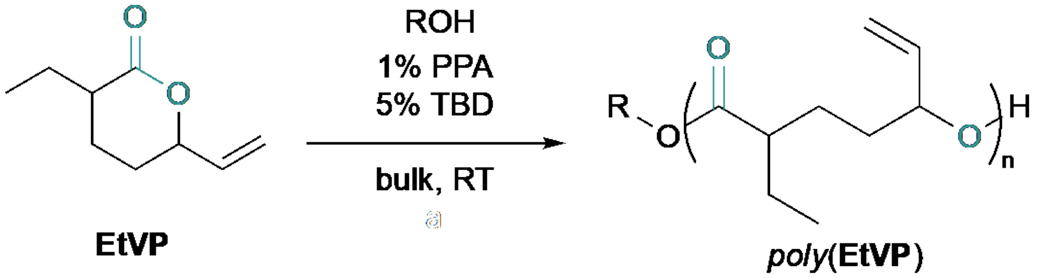
step 1: telomerization



step 2: hydrogenation



step 3: polymerization



major challenges:

- **reactions not scalable beyond ~5 g**
- **costly catalyst system**
- **reduction to EtVP very expensive**
- **overall LCA impractically bad – 200 kg CO_2 per kg polymer**

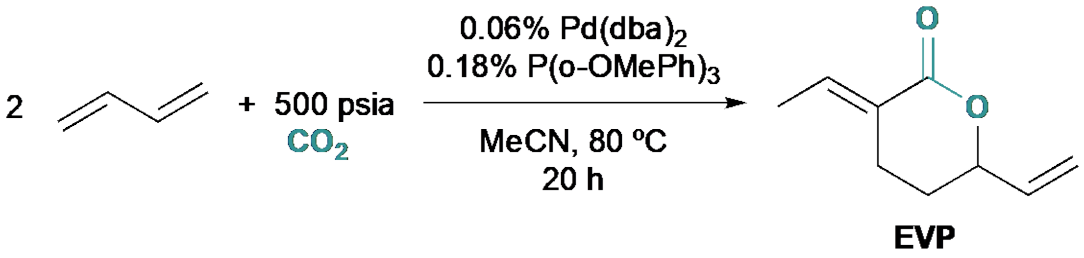
SBIR · STTR America's Seed Fund

MASS VENTURES

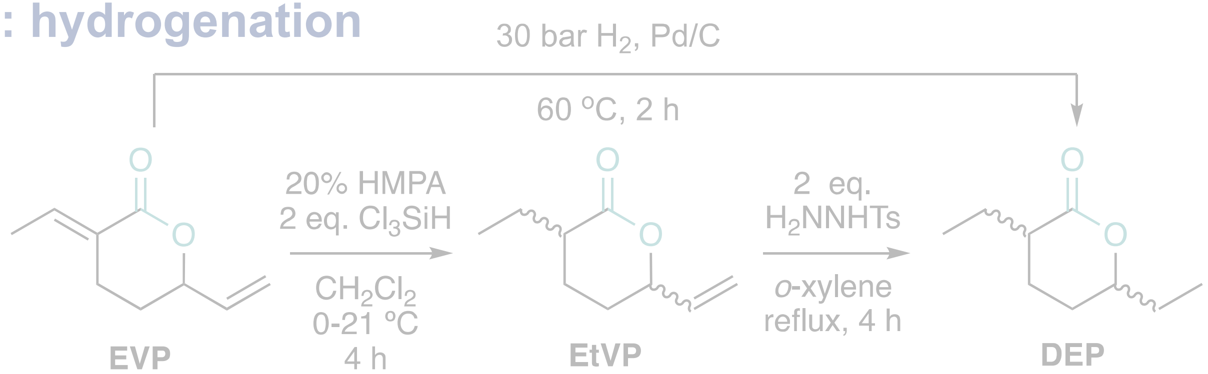
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

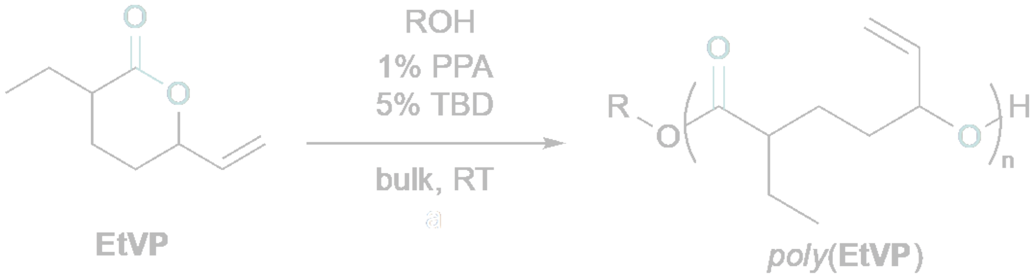
step 1: telomerization



step 2: hydrogenation



step 3: polymerization



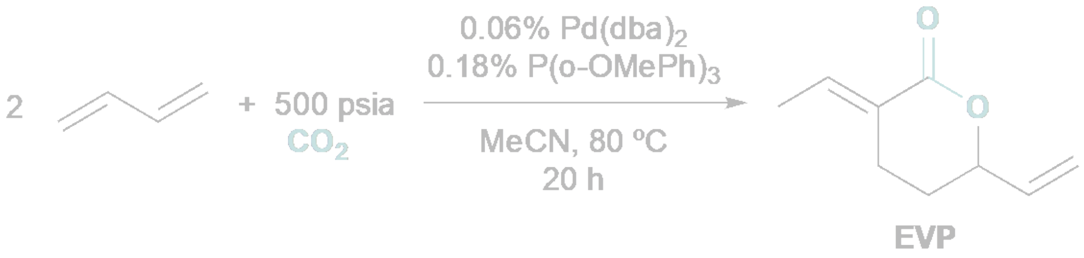
Milestones toward optimization:

- **replaced expensive Pd catalyst with simpler, cheaper system based on $PPh_3/Pd(acac)_2$**
- **developed strategies for solvent, catalyst, and butadiene recycling**
- **scaled reaction to 1 L Parr reactor (0.5 kg yield of EVP per 24 h cycle), distillation purification**

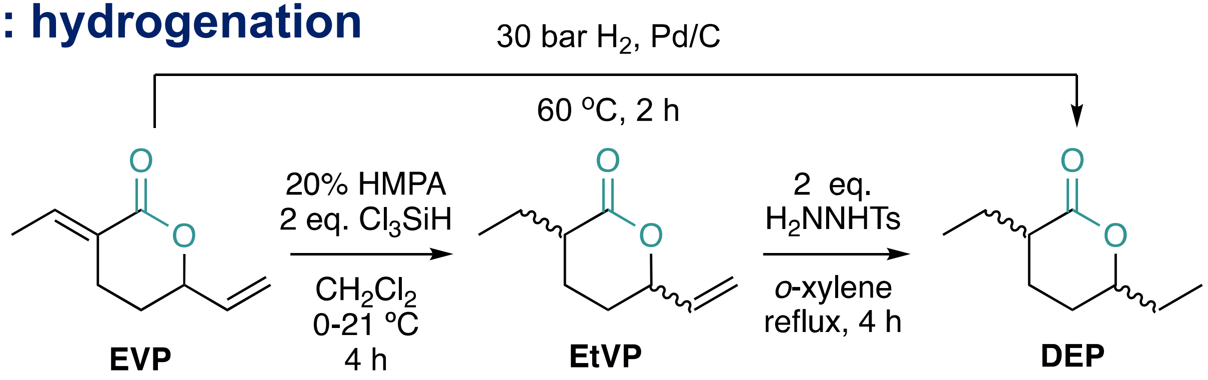
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

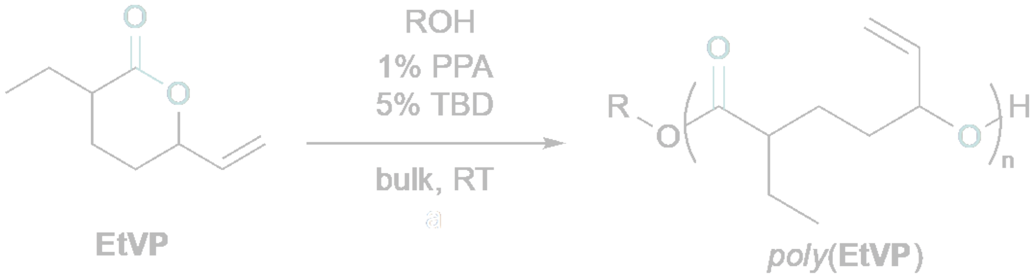
step 1: telomerization



step 2: hydrogenation



step 3: polymerization



Milestones toward optimization:

- **developed Mg/MeOH reduction to EtVP**
- **researching electrocatalytic reductions**
- **scaled to 1 L Parr reactor (0.3-0.5 kg DEP per 24 hr cycle)**

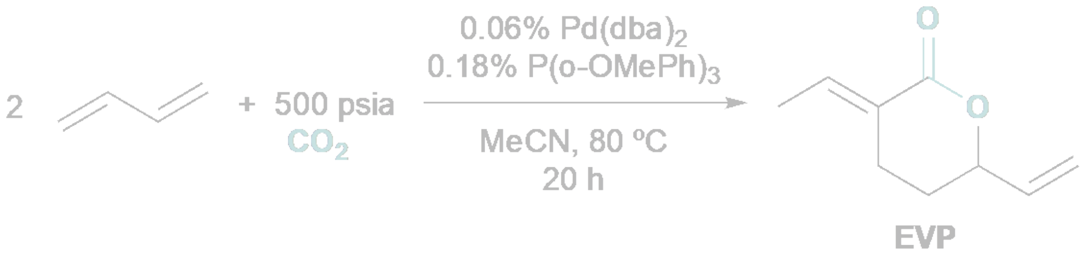
SBIR·STTR America's Seed Fund

MASS VENTURES

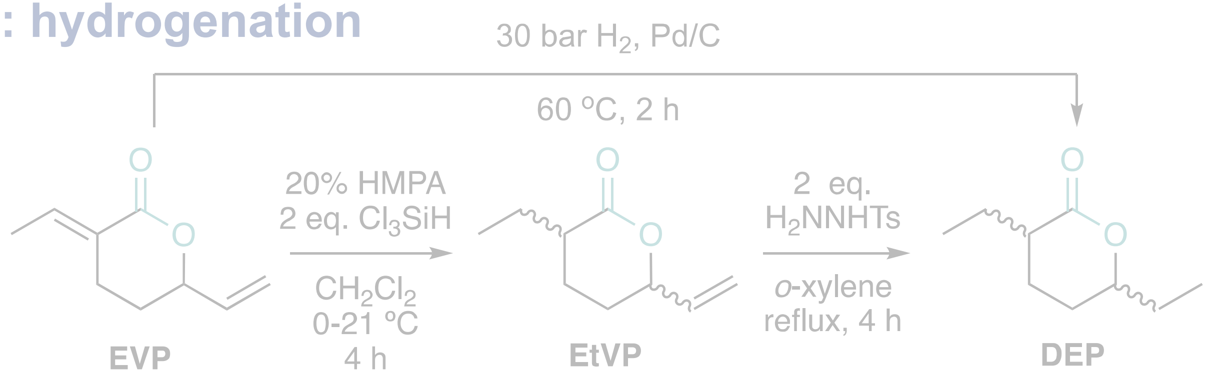
Objective 1 & 3: Optimize Lactone Synthesis

initial gram-scale synthesis from UMN team:

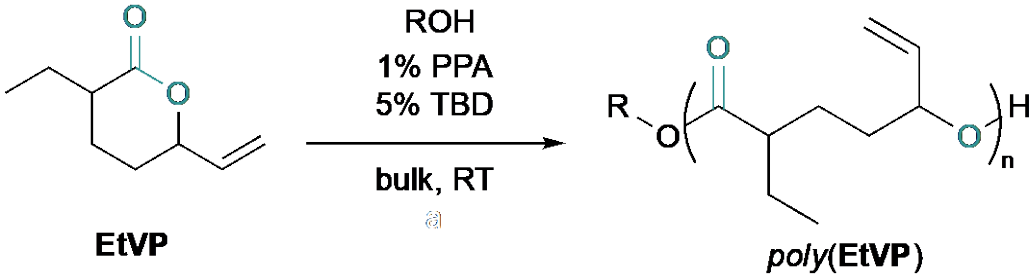
step 1: telomerization



step 2: hydrogenation



step 3: polymerization



Milestones toward optimization:

- **replaced TBD catalyst with inexpensive urea catalysts, which are more active and lead to higher molar mass polymers**
- **now have access to multi-hundred gram scale polymerization reactions for applications research!**

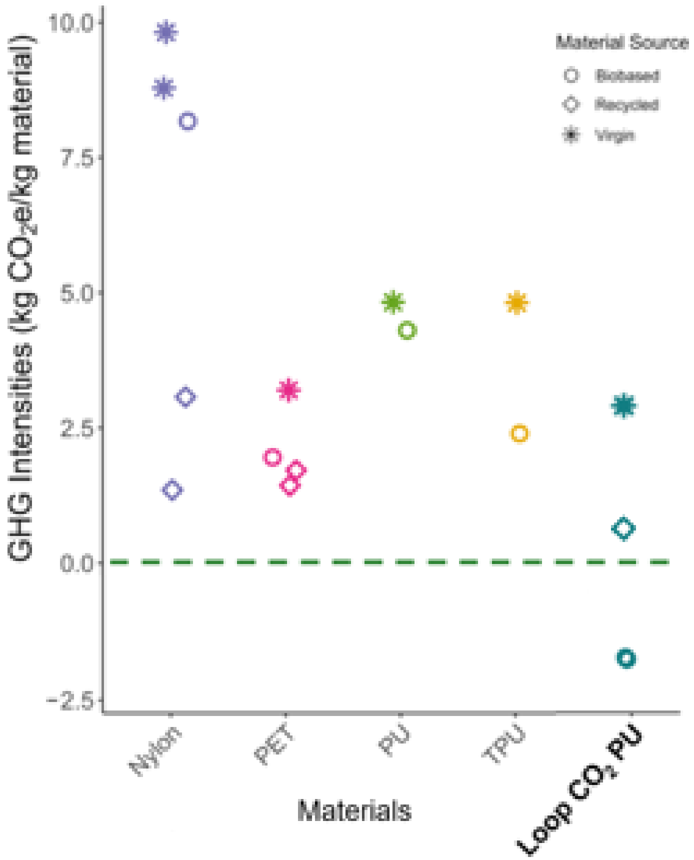
SBIR·STTR America's Seed Fund

MASS VENTURES

Objective 1 & 3: Optimize Lactone Synthesis

Objective 1 & 3: Optimize Lactone Synthesis

Life Cycle Analysis with WAP Sustainability:



	Result [kg CO2e/kg of TPU]
April 2023	200
June 2024 (excluding captured CO_2)[1]	5.0
June 2024 (including captured CO_2)	3.8

[1]Scenario modeled assuming no CO_2 capture as a conservative estimate given uncertainty around captured CO_2 source.

- **cradle-to-gate LCA has improved dramatically for our new process**
- **LCA does *not* account for potential biobased butadiene sources, which would result in potentially *negative carbon emissions***
- **sticking point: how to get CO_2 at high pressure cheaply and in an energy-efficient manner?**
- **sticking point: Pd catalyst is still a CO_2 LCA problem. can we use a heterogeneous catalyst?**

Objective 1 & 3: Optimize Lactone Synthesis

Initial lab scale 1 kg polyester production

EVP		EtVP		Poly(EtVP)	
Raw Material	**Cost**	**Raw Material**	**Cost**	**Raw Material**	**Cost**
CO_2	$5.9	trichlorosilane	$2.0	(initiator)	$0.2
Butadiene	$5.6	EVP	$41.3	(catalyst)	$0.4
$Pd(dba)_2$	$1.5	(catalyst)	$2.3	EtVP	$58.0
$P(o\text{-}OMePh)_3$	$22.5	(solvent)	$0.7		
MeCN solvent**	$0.5				
Sum	**$35.9**	Sum	$46.4	Sum	**$58.6**

1-L continuous miniplant 1 kg polyester production

Raw Material	**Cost***	**Raw Material**	**Cost***	**Raw Material**	**Cost***
CO2	$3.7	trichlorosilane	$2.0	(initiator)	$0.2
Butadiene	$2.4	EVP	$7.7	(catalyst)	$0.4
$Pd(acac)_2$ (catalyst)	$0.5	(catalyst)	$2.3	EtVP	$15.9
PPh_3 (ligand)	$0.0	(solvent**)	$0.7		
MeCN solvent**	$0.1				
Sum	**$6.7**	Sum	$12.7	Sum	**$16.6**

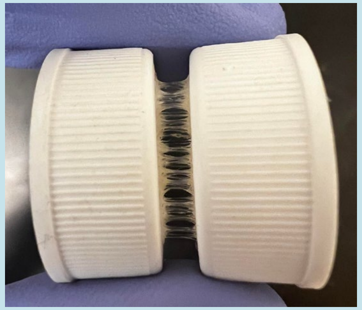
****Solvent was assumed to be recycled 20 times for both processes**

SBIR·STTR America's Seed Fund

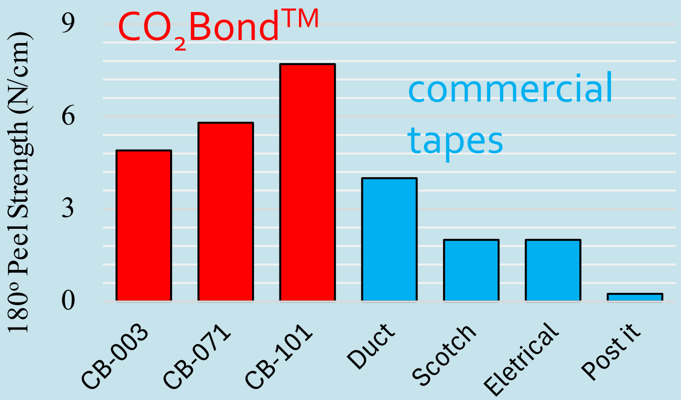
MASS VENTURES

Objective 2: Develop Applications

Pressure-Sensitive Adhesives



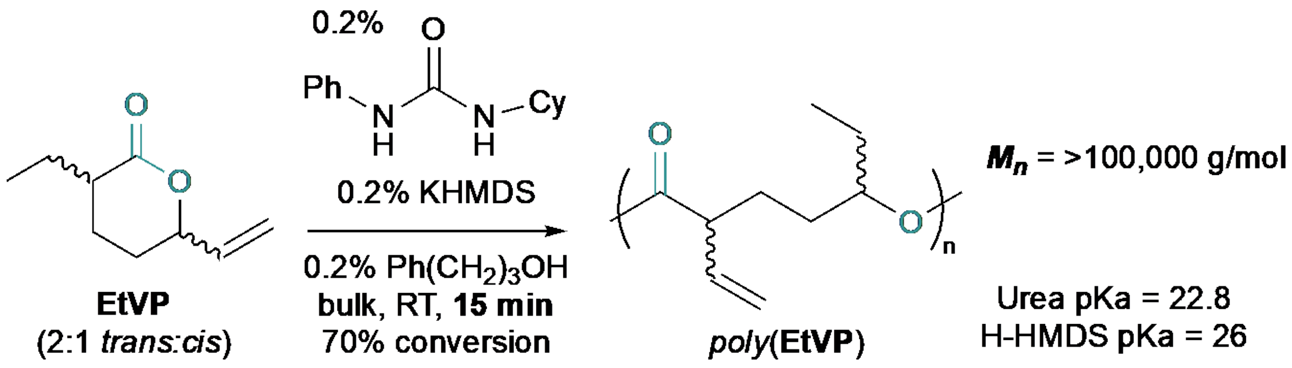
Technical Data of Exemplary Adhesives



- **key discovery: high molar mass (100 kDa) polyesters are needed for efficient adhesion**

(well above entanglement Mn of 15 kDa)

- **more efficient, long-lived urea catalysts discovered in UMN lab enabled access to high enough molar masses**



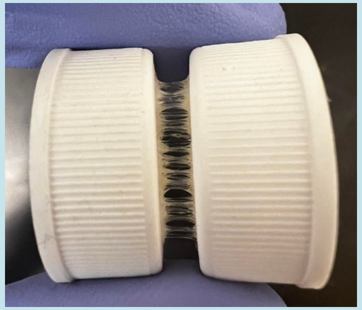
- **useful application for degradable *single use plastics***

SBIR STTR America's Seed Fund

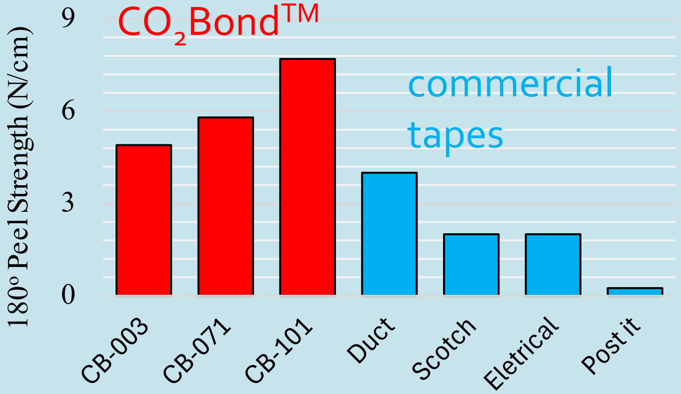
MASS VENTURES

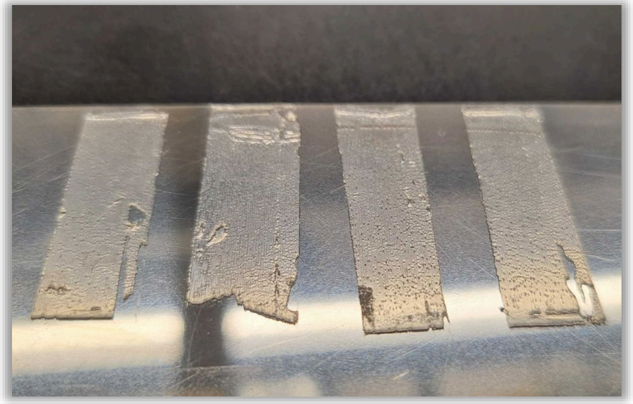
Objective 2: Develop Applications

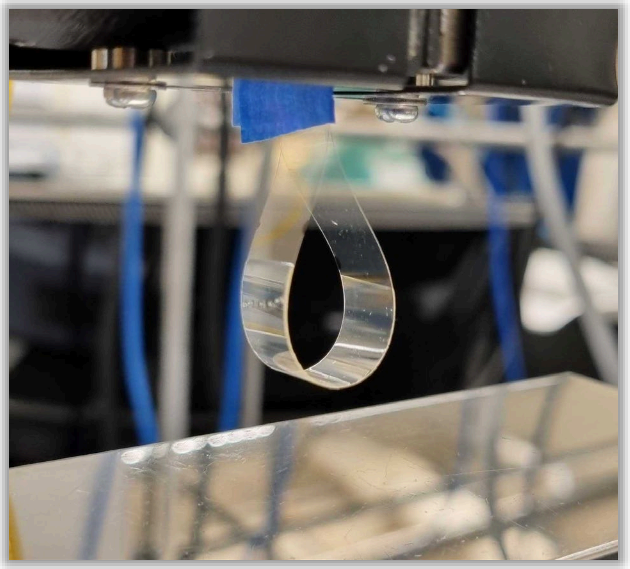
Pressure-Sensitive Adhesives

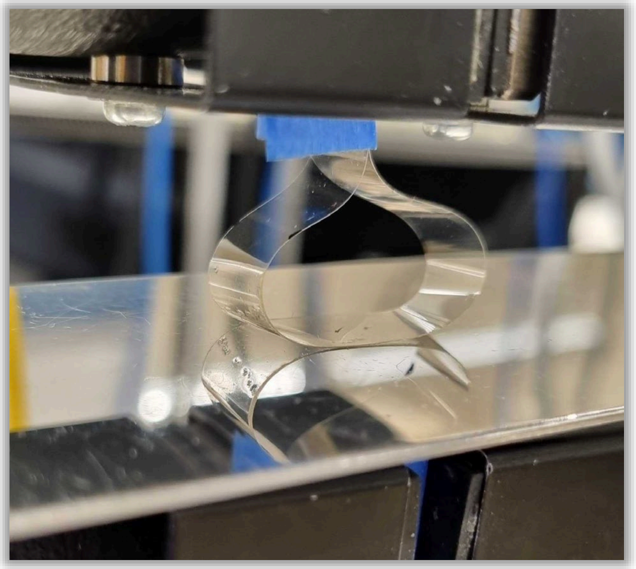


Technical Data of Exemplary Adhesives



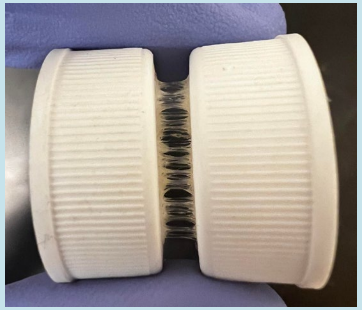




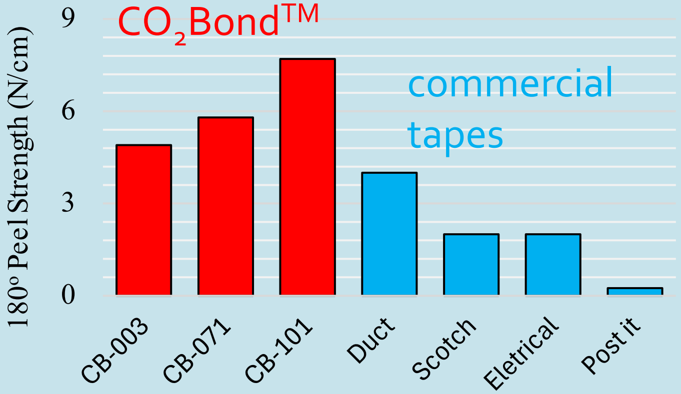


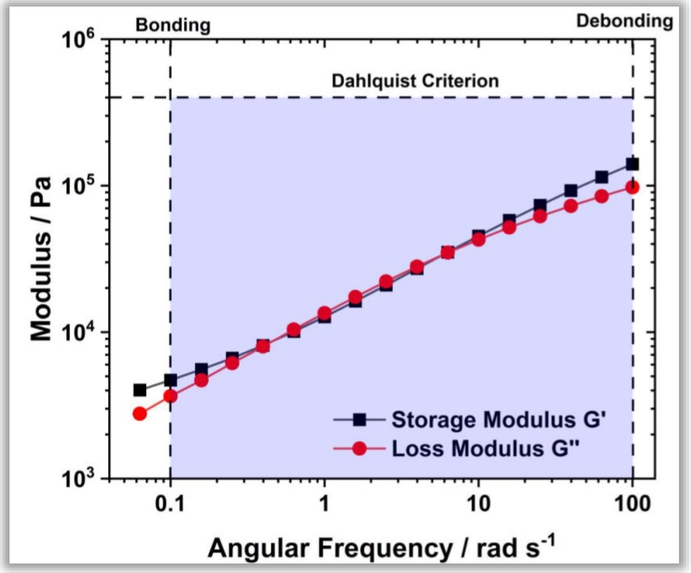
Objective 2: Develop Applications

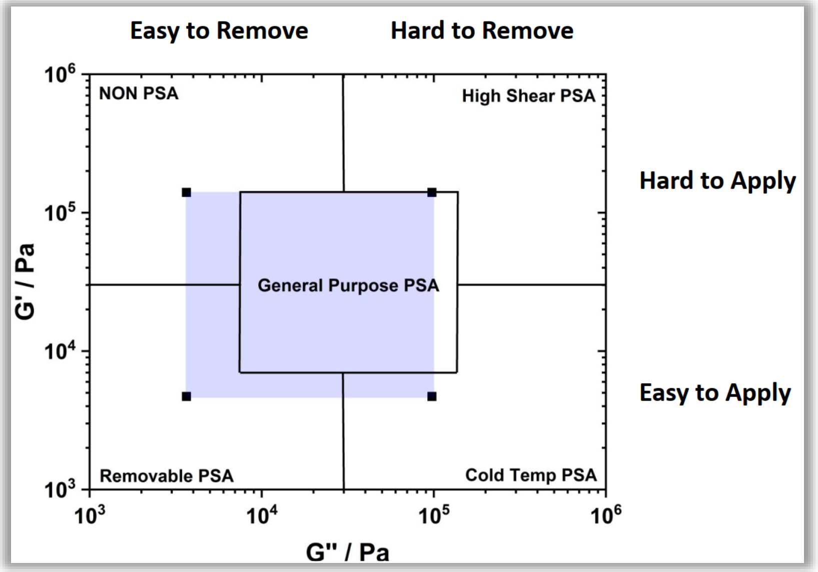
Pressure-Sensitive Adhesives



Technical Data of Exemplary Adhesives







rheology experiments indicate that CO_2Bond adhesives are great candidates for general purpose pressure-sensitive adhesives

SBIR · STTR America's Seed Fund

MASS VENTURES

Objective 2: Develop Applications

- key discovery: LoopCO2 polyols can be used as drop-in replacements for diols in TPUs and TPEs in simple 1-step processes to make elastomers

Elastomers & Chemical Recycling

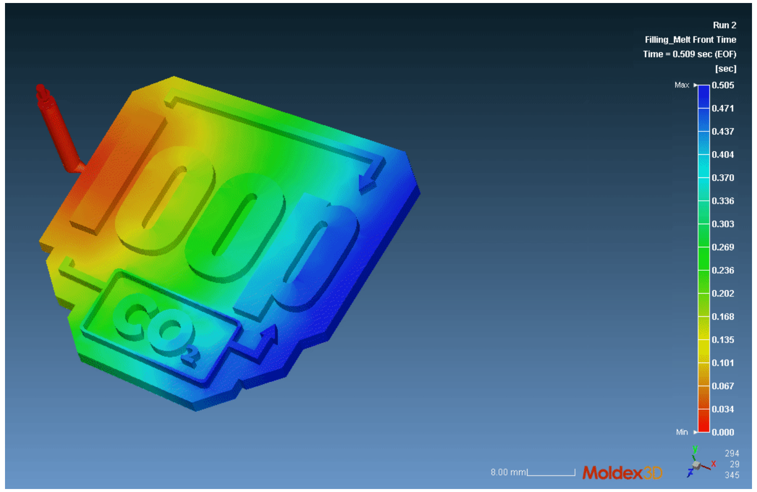
Technical Data of Exemplary Elastomers

Elastomers	Tensile Strength	Elongation	Hardness
CO2Stretch-107	10 MPa	350%	82A
CS-116	3.4 MPa	560%	54A
CS-161	11 MPa	810%	65A

T_g = -35 °C

Objective 2: Develop Applications

- **key discovery: LoopCO2 polyols can be used as drop-in replacements for diols in TPUs and TPEs in simple 1-step processes to make elastomers**



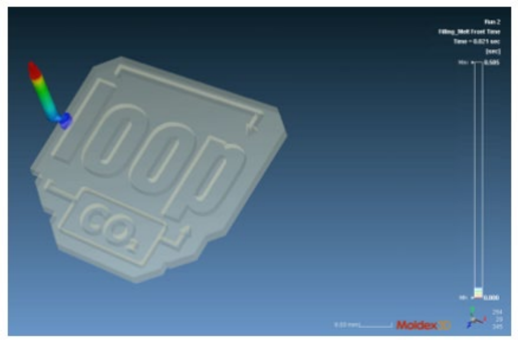
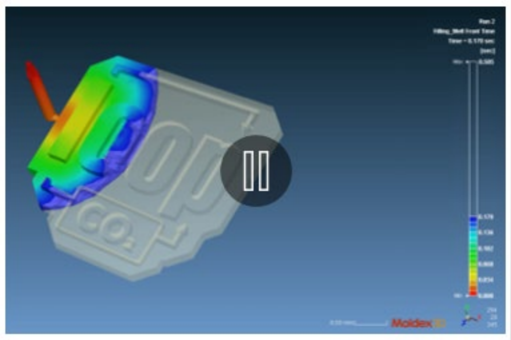
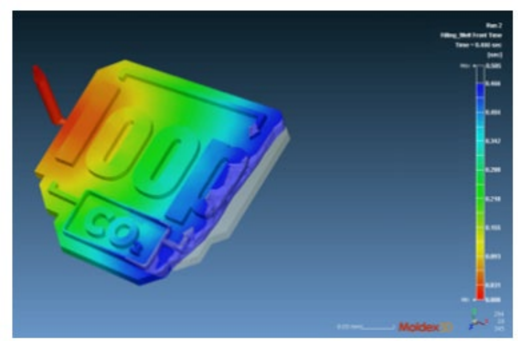
Elastomers & Chemical Recycling

Technical Data of Exemplary Elastomers

Elastomers	Tensile Strength	Elongation	Hardness
CO2Stretch-107	10 MPa	350%	82A
CS-116	3.4 MPa	560%	54A
CS-161	11 MPa	810%	65A

$T_g = -35\ ^{o}C$

CO2Stretch™ → Monomer (90+%)

Benchmark Analysis – Carbon Utilization

Loop CO2's material have more benefits over other CO2 incorporated polymers

	Materials	Key players	Biomass utilization	Chemical recyclability	Bio-degradability	Product coverage
polyesters	Polylactone	Loop CO2	Yes	Easy	Yes	Wide
polyesters	Polyethylene furanoate (PEF/FDCA)	Resource	Yes	Not easy	Not reported but possible	Limited
	Polycarbonate	Aramco Covestro Econics Twelve	No	Not exactly	No	Wide

SBIR · STTR America's Seed Fund

MASS VENTURES

Benchmark Analysis – Soft Polyesters

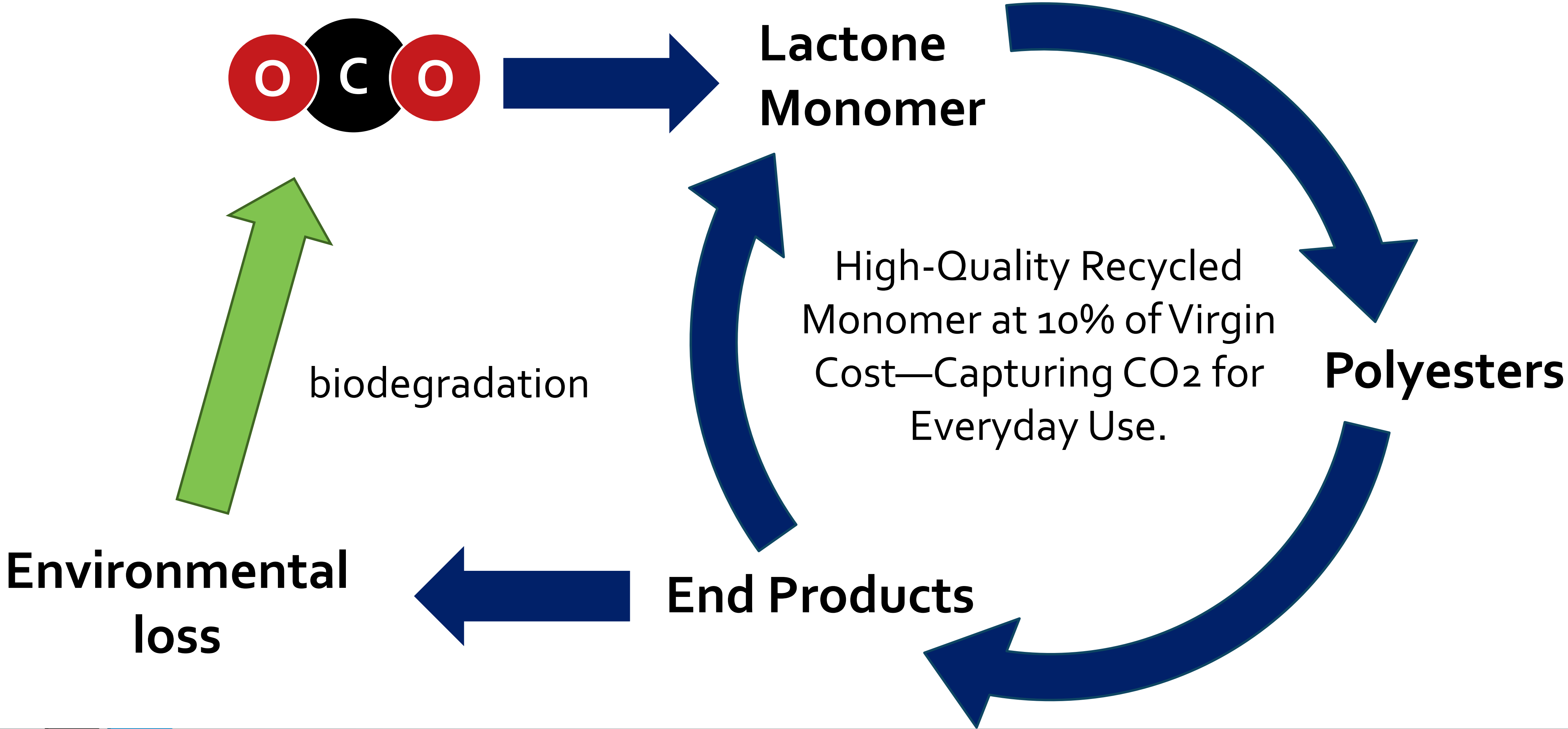
Loop CO2' materials have more benefits from the input end compared to other soft polyesters.

Materials	Key players	Carbon-negative production	Chemical recyclability	Bio-degradability	Product coverage
CO2 polyester	Loop CO2	Yes	Easy (100 °C)	Yes	Wide
Poly Caprolactone	BASF Ingevity Daicel Corbion	No	More difficult (180+ °C)	Yes	Wide
Poly adipates	BASF Emery Oleo Cargill	Not really (biobased still positive emission)	More difficult (230+ °C)	Yes	Wide

SBIR · STTR America's Seed Fund

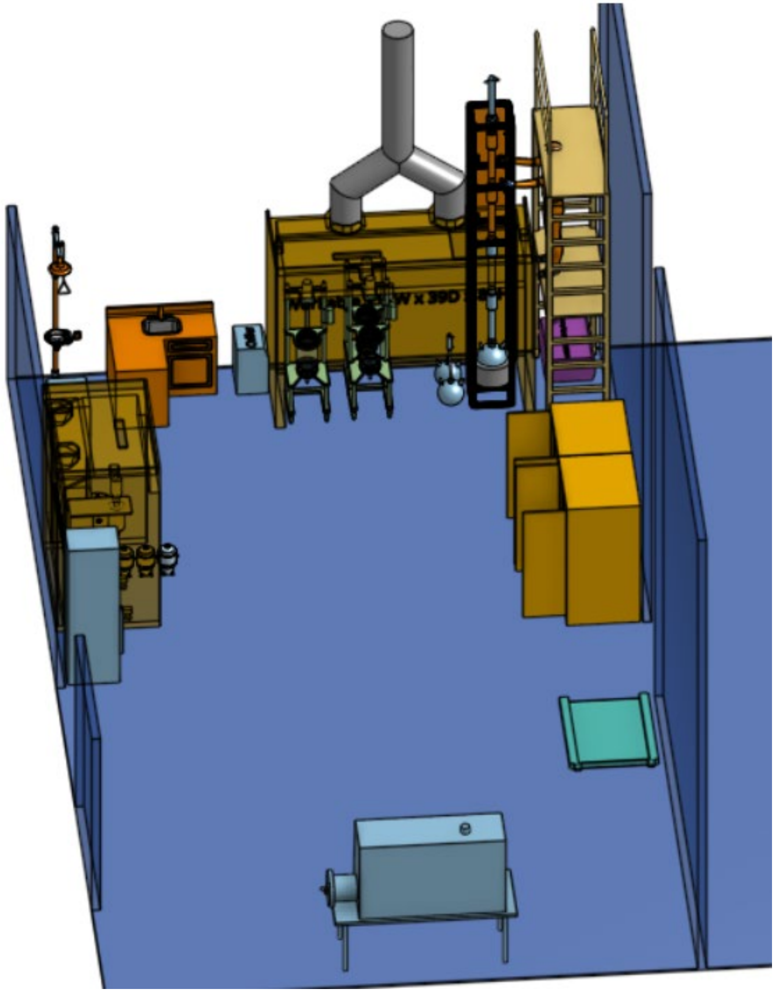
MASS VENTURES

Circular Polyester Uses



Objective 4: Pilot Plant

- 20 L pilot plant under construction in Marlborough, MA
- Uses optimized reaction and purification conditions from UMN team research
- Engineering contracted out with Hickory Run Consulting
- Contract installation and safety assessment by SPEC process engineering
- Completion date: December 2024
- Anticipated cost of CO_2-derived monomers: $1.5-$3/kg (compare to $2-$3 for petroleum-derived monomers)



Hickory Run Consulting, LLC SPEC

Objective 5: Customer/Partner Outreach

Participating in DOE Phase II Shift Program and MassChallenges Program

- **Interviewed >50 companies across the industry to identify potential needs**
- **Identified parallel commercialization strategies around monomer sales and specialty polymer sales/licensing/partnerships**
- **Monomer/polymer samples will be shared with interested companies (BASF, Evonik, Naopao, IVT, Eternal, L'Oreal, your company??) for formulation (co)development upon completion of pilot plant in Dec 2024**

Lessons Learned

- *Everyone loves the idea of CO_2 derived polyesters but needs to be cost-competitive with petroleum and have specific properties companies are looking for. There is more leeway on cost in higher-margin industries such as cosmetics, providing entrypoints*

- *Pressure-points remain in our process:*

    (1) how do we access inexpensive high-quality, high-pressure CO_2?

    (2) can we move beyond Pd, or use heterogeneous catalysts?

- *There is significant interest in both monomer and polymer production: chemical companies can use monomers as drop-in replacements; manufacturers can use polymers in new/replacement formulations*

- *University-Start Up Partnerships help with simplify and streamline complex process engineering + materials development projects*

SBIR·STTR America's Seed Fund

MASS VENTURES

Thank You!

Looping CO2 in our Circular Future

DE-SC0022839