Tailored Polymers Through Rational Monomer Development

Technology Session Review Area: Performance-Advantaged Bioproducts and Separations Consortium

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Los Alamos NATIONAL LABORATORY EST.1943

NNSA National Nuclear Security Administration

Goal Statement

Goal: Develop polymers that provide a performance advantage over current petroleum based polymers and incorporate a readily accessible degradation pathway

- *Performance advantages include thermal stability, processability, cost, and primarily biodegradability*
- *Valorize by-products of biofuel production, e.g. glycerol, acetoin*
- *Develop a degradation route in order to avoid long-term environmental accumulation problems*

Outcome: Multiple new bio-derived polymers using the highly versatile acetal monomer platform

- *Identify petroleum based competitors where these polymers can offer a performance advantage*
- *Adaptable functionality to address multiple applications and polymer synthesis pathways*
- *Bio-derived materials with improved environmental impact at end-of-life*

Relevance: Advance bioeconomy by providing performance advantaged materials

- *Eliminates the need to charge a "Green Premium" through economical pathways*
- *Production of materials with no long-term environmental impact*
- *Byproduct valorization reduces production costs of bio-renewable products*

Quad Chart Overview

Timeline

- Start Date: October 2018
- End Date: September 2020
- Percent Complete: 25 %

	Total Costs Pre FY17	FY17 Costs	FY18 Costs	Total Planned Funding (FY19-Project End Date)
DOE funded	--	--	$0k	$550k

Partners:

BETO Projects: Inverse Biopolymer Design through Machine Learning and Molecular Simulation, Performance Advantaged Bioproducts from Catalytic Fast Pyrolysis, Analysis in support of novel bio-based products and functional replacements

Nat'l labs, universities, companies: National Renewable Energy Lab (NREL)

Barriers addressed

- **Ct-J Identification and Evaluation of Potential Co-products**
  - Using bioderived building blocks to synthesis novel monomers
- **Ct-K Developing methods for co-product production**
  - Developing pathways to novel polymeric materials using simple bio-derived molecules.

Objective

Synthesis of performance advantaged polymers from small, readily available bio-derived molecules to valorize byproducts of biofuel production.

End of Project Goal

Synthesize, characterize and test > 1 new bio-derived polymer that offers improved thermal and physical properties over petrochemical polymers with the additional ability to degrade readily to the monomer precursors under certain conditions. Perform initial TEA on these materials in order to present a cost and performance based value-proposition for further work or commercialization.

Project Overview

History: *Dioxolane synthesis for fuel applications inspired potential chemical applications*

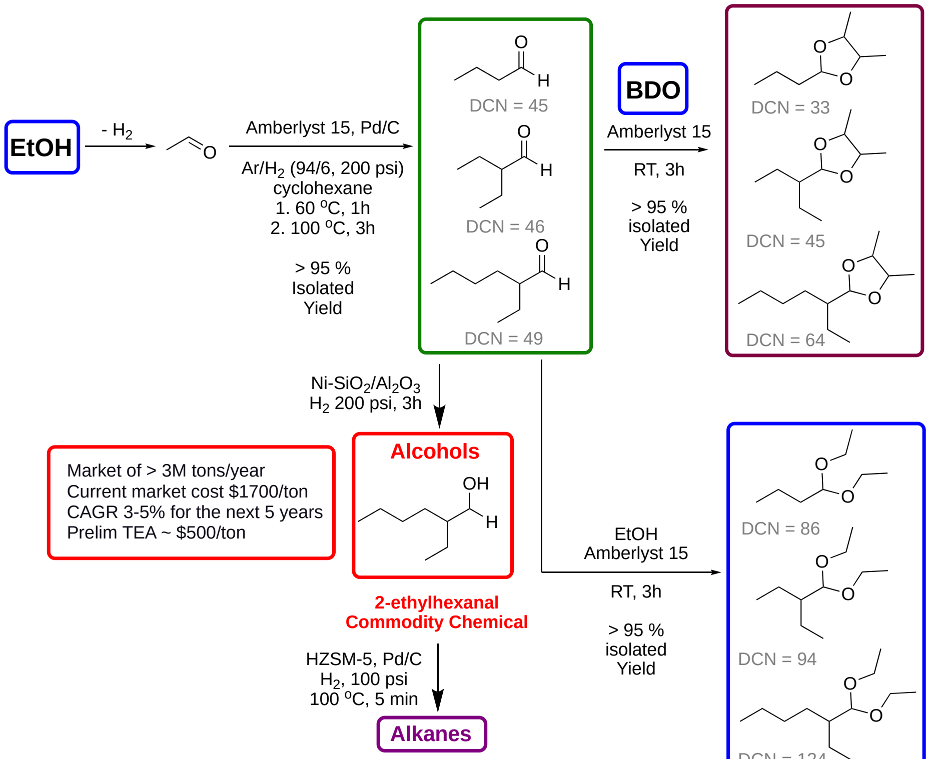
- Focus: Use simple bio-derived building blocks to construct tunable monomers through defunctionalized/derivatized functional groups
- Leverage catalysis expertise developed within the BETO portfolio
- Expands work developed on acetalization for fuels use[1,2].

Context: *Develop polymers which can degrade to benign starting materials*

- Develop polymers with improved performance and no long-term environmental accumulation problems
- Use the performance advantages to avoid a "Green Premium"

Project Goals:

- Develop a range of monomers comprised of benign building blocks that can be selectively defunctionalized/derivatized
- Produce polymers and test for performance advantaged properties
- Identify stimuli that can decompose polymers to monomers and the original building blocks



[1]Moore *et al*, Green Chem., **2017**, 19, 169
[2]Staples *et al*, Sustainable Energy Fuels, **2018**, 2, 2742.

Management Approach

- Team Structure
  - Andrew Sutton (PI)
  - Cameron Moore (Co-PI)
  - Chris Roland (PD)
  - Gregg Beckham (NREL)
    - Material characterization and performance
  - Mike Crowley (NREL)
    - Machine learning for improved polymer development

- Consortium Interfacing
  - Monthly conference call with PABP and BETO technology manager
  - Discussions with other PABP projects as interests converge

- Industry Engagement
  - Customer discovery interviews underway (Q2 Milestone)

Selected Project Milestones

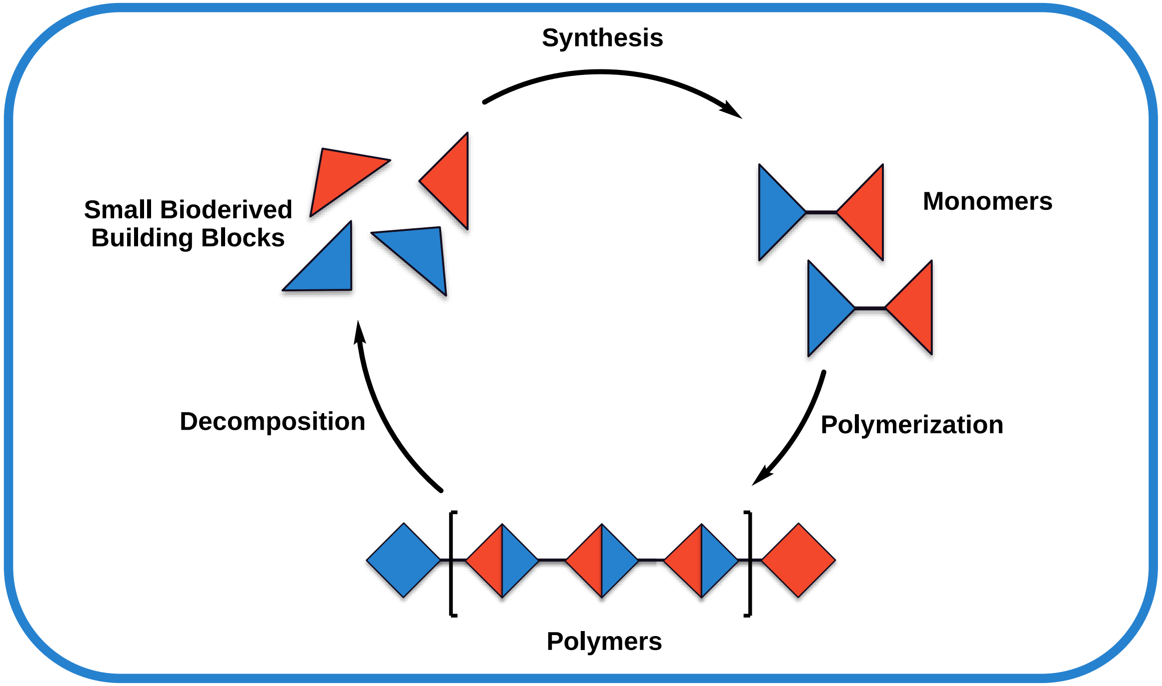
Q3 FY19 : Synthesize and characterize *at least* 3 monomers from bioderived building blocks. Measure physical properties and hydrolytic stability.

Q4 FY19 : Perform polymerization on *at least* 5 monomers and perform initial characterization/testing of these materials.

End of Project : Synthesize, characterize and test > 1 new bio-derived polymer that offers improved thermal and physical properties over petrochemical polymers with the additional ability to degrade readily to the monomer precursors under certain conditions.

Technical Approach

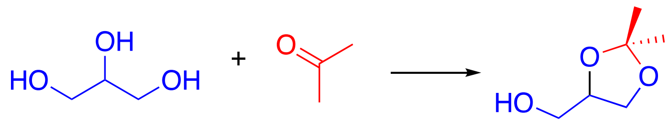
Hypothesis: Can we construct polymers from environmentally benign building blocks that can be degraded by a stimulus to give the original, benign starting materials?



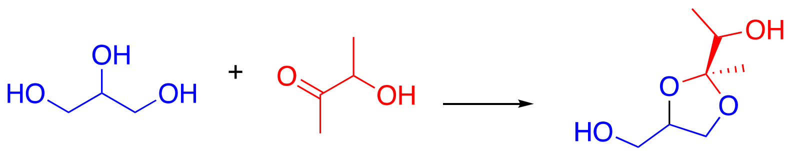
This gives the opportunity to develop monomers that can provide a pathway for safe plastic degradation/recycle upon reaching end-of-life to avoid plastic accumulation

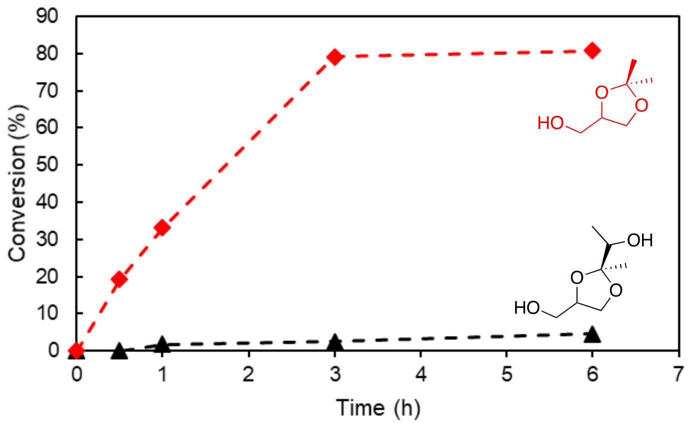
Technical Approach

Glycerol and acetone known to give solketal which is prone to hydrolysis



Would subtle modification increase thermal stability and increase synthetic utility?



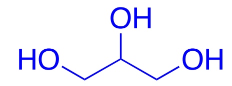
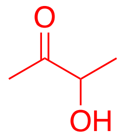
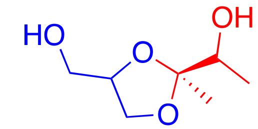
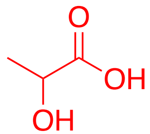
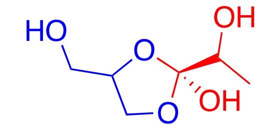
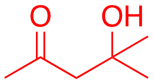
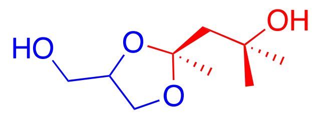
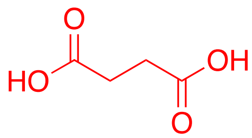
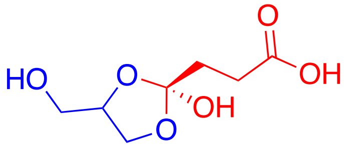
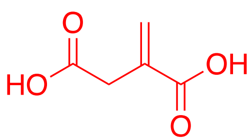
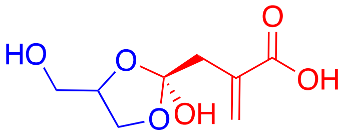


Decomposition of dioxolanes at 80 °C.

Demonstrates that subtle structural and therefore electronic changes in the molecule can change the physical properties. Does this provide an opportunity to tune monomers and influence polymer performance?

Technical Approach

- Acetal/Ketal functionality can be incorporated into polymer backbone using monomers made from bio-derived small molecules
- 2 million metric tons/year of glycerol produced as a byproduct of biodiesel production
- Large effect of small structural changes on monomer properties has been previously demonstrated
- Incorporation of functional groups allows for extensive derivatization or defunctionalization and alternative polymerization approaches

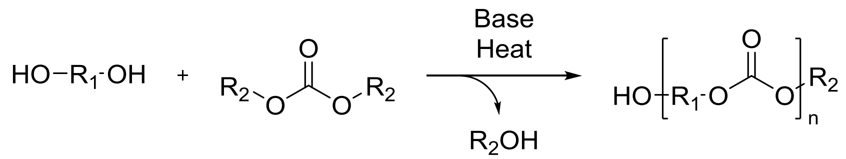
Bio-derived Linker	Toxicity*	Chemical Structure	Resulting Responsive Monomer
Glycerol	Not hazarous Not California Prop. 65		———
Acetoin	Not a known carcinogen. Food flavoring		
Lactic acid	Not listed in CWA as toxic, hazardous or as a pollutant		
Diacetone alcohol	Not persistent, bioaccumulative and toxic (PBT)		
Succinic acid	Aerobic biodegradability 28d 96.55%		
Itaconic acid	Not a known carcinogen		

*Data from MSDS

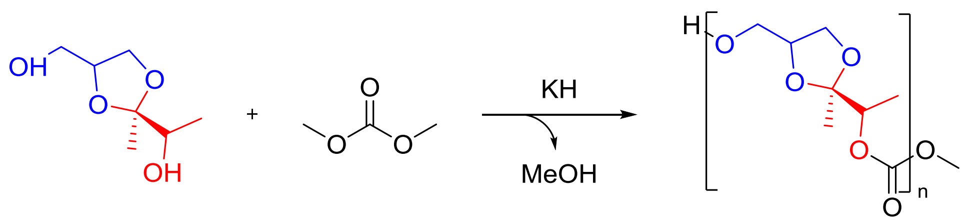
Technical Approach

- Potential polycarbonate applications:
  - Polycarbonates are commonly used for their combination of impact strength, optical clarity, heat resistance, favorable processability and in lightweight applications such as vehicle composites
  - 5100 Kt/year global polycarbonate production capacity in 2016
  - Global market valued at $13,000,000,000 in 2016, expected to grow to $17,000,000,000 by 2020

- Polycarbonates are commonly synthesized via base-catalyzed reaction between diols and carbonates



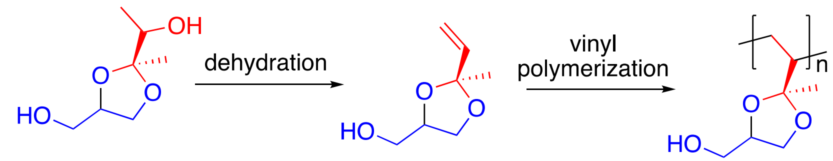
- By using bio-derived pH responsive diols, stimuli response can be incorporated into polymer backbone



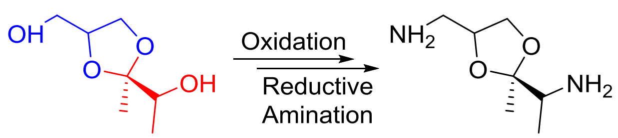
Plastics Insights, *Polycarbonate Production, Price and Market Demand*

Technical Approach

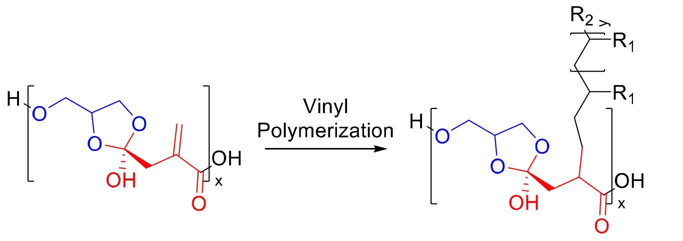
Highly versatile monomers can be functionalized to be suitable for conventional alkyne polymerization



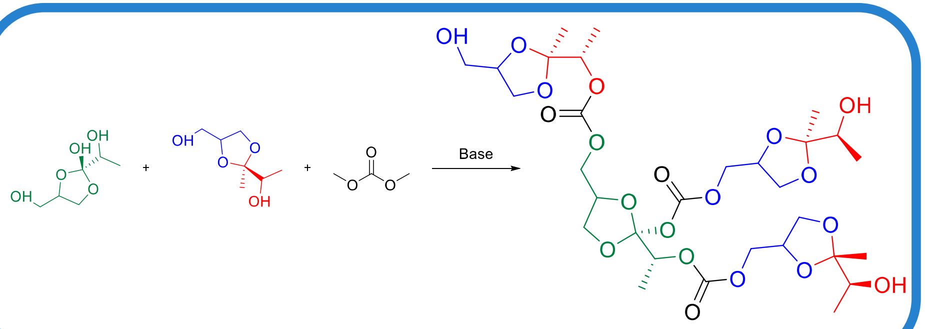
Functional groups can be derivatized through reactions such as aminations to increase chain-chain H-bonding



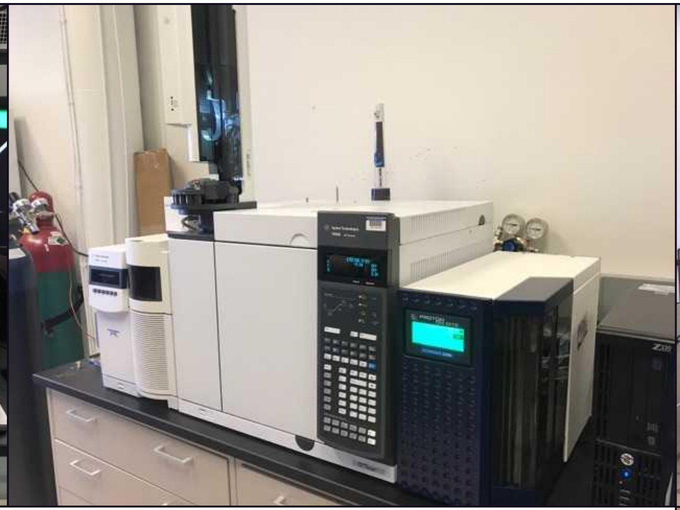
Combination of condensation and vinyl polymerization can be combined to make graft copolymers



Using tri or multifunctional monomers in blend will introduce cross-linking, improving physical properties



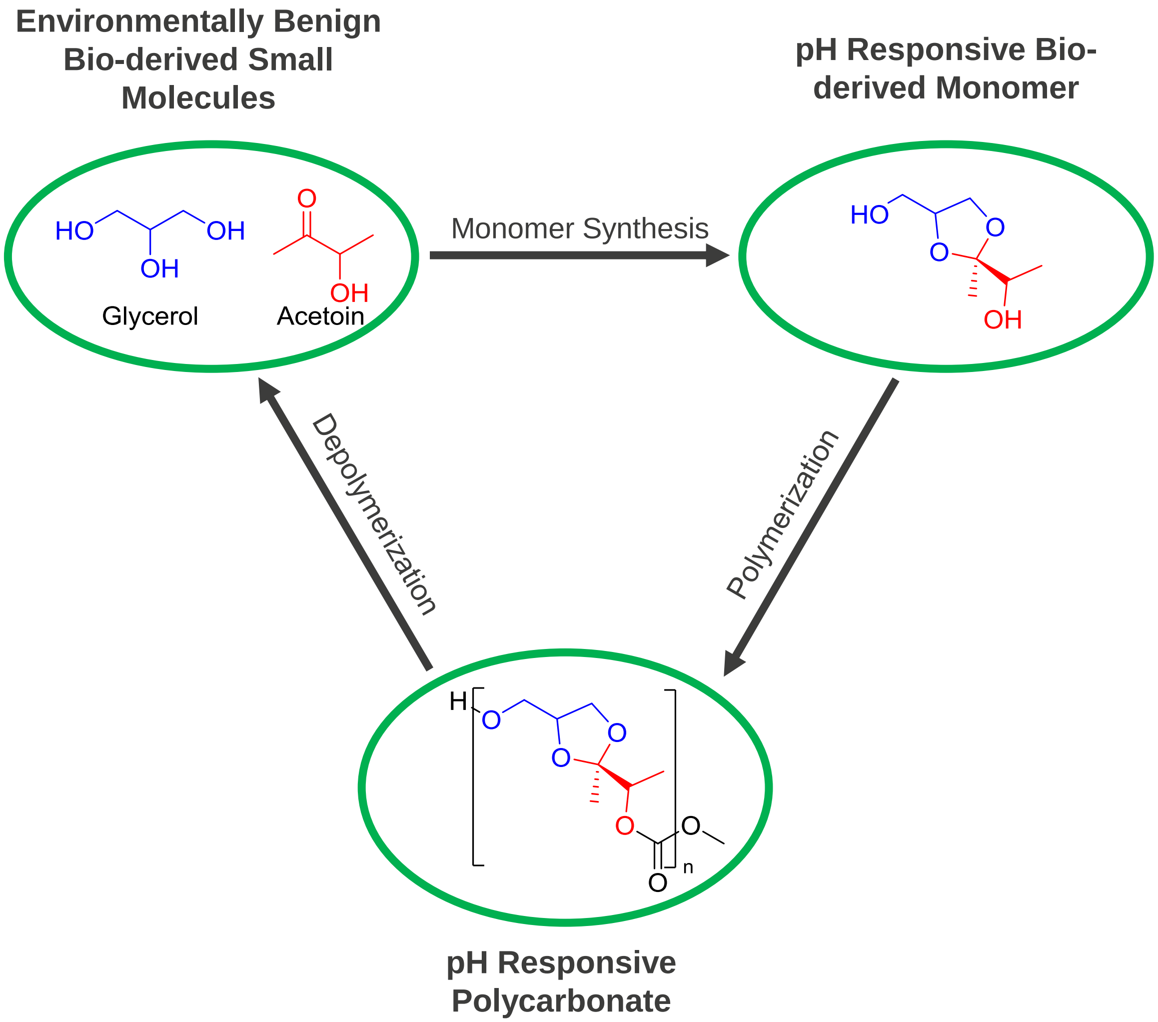
Laboratory Capabilities



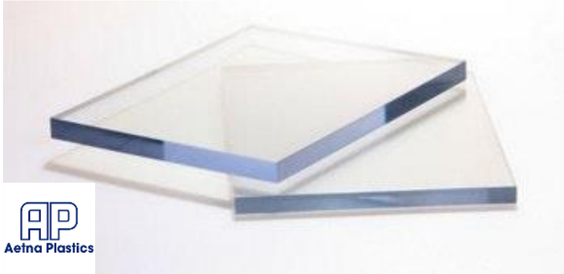
- Lab equipped with DSC, GC-MS/FID/PolyArc, NMR, TGA, HPLC, and GPC
  - All polymer and small molecule characterization can be done in-house
- New Infinity II GPC equipped with triple detection – viscometer, RI and Light Scattering
  - Particle size, intermolecular interactions and polymer topology
- Material properties will be measured in collaboration with NREL (Beckham)

Technical Accomplishments

- Aggregation of physical and material properties of commercial polycarbonates
- Synthesis of pH responsive monomer from bio-derived small molecules
- Biorenewable polymers from bio-derived monomers
- Depolymerization of biorenewable polymers
- Bio-derived Monomer design optimization



Baseline Performance Property Report



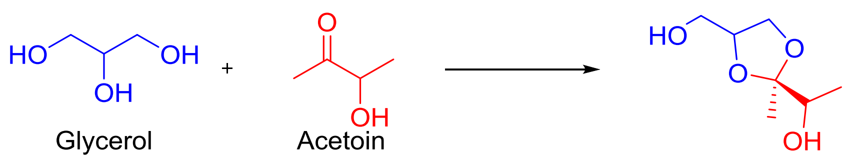
- **Goal:** Establish baseline set of material properties bioproducts must meet in order to compete with petroleum based materials
- Properties pulled from Technical Data sheets for 25+ commercial polycarbonates

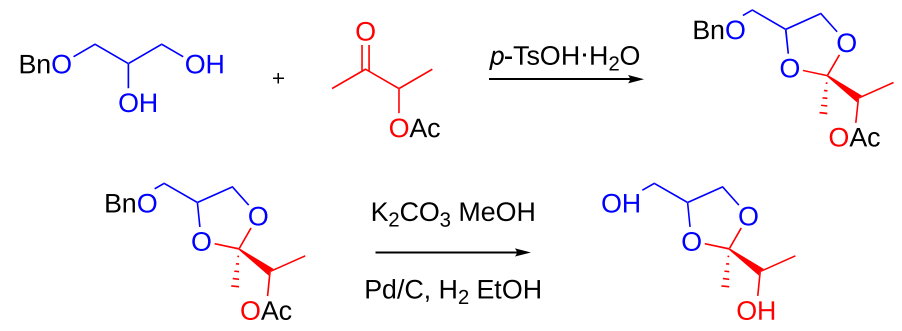
Commercial Aliphatic Polycarbonates	Commercial Aromatic Polycarbonates
T_g range -10°C - 40°C	T_g range 110°C - 230°C
Tensile Strength 300 – 600 PSI	Tensile Strength 8500 – 10500 PSI

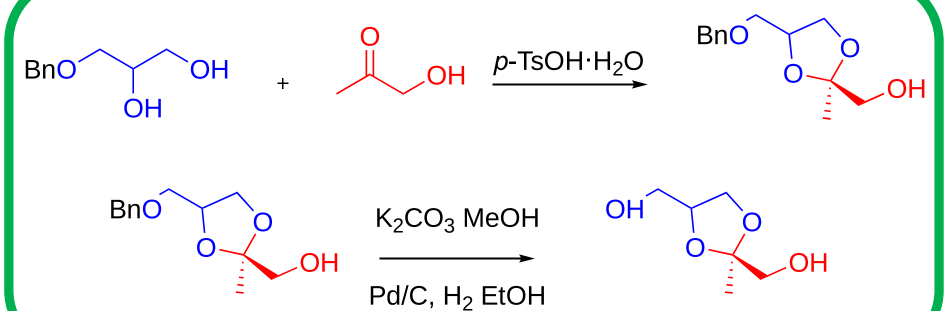
- **Lessons Learned:** Aliphatic polycarbonates more niche uses, smaller market share and inferior mechanical properties, while aromatic polycarbonates possess more robust mechanical and thermal properties, and are a larger share of commercial polycarbonate market

Bio-derived Monomer Synthesis

Model Reaction

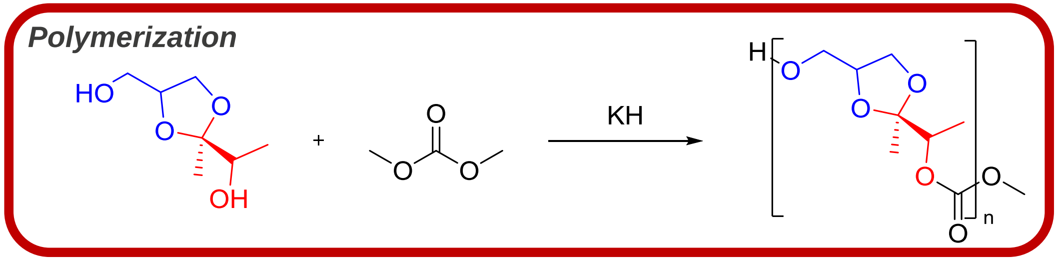




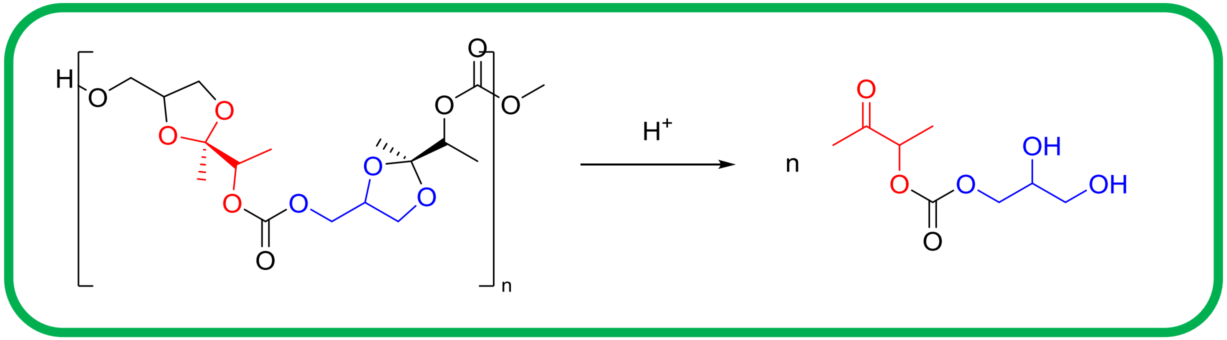


- Standard acetalization yield is currently low
  - Direct synthetic method is being refined
- Model monomer synthesis can be achieved using protected starting materials
- Monomer isolated in high yield (~ 90 %) and high purity as mixture of several isomers.
- Two monomers synthesized and characterized
- Solketal model monomer compound gives mixed primary/secondary alcohols
- Gycerol with hydroxyacetone gives dual primary monomer

Polymerization/Degradation



- Intentionally limited *n* (3:1 monomer to carbonate ratio) to derive a small oligomer for degradation studies (Average Mn ~ 5200, D = 1.75)
- Initial physical properties, including glass transition temperature are similar/superior to commercial aliphatic carbonates – should improve when *n* is not constrained



- **Preliminary Results:** Depolymerization appears successful to carbonate linked unit
  - *10 mg of poly(solketal carbonate) in 2mL of aqueous hydrochloric acid (0.5 – 12M), solubility increases with acidity*
  - *GPC indicates one species and no polymer remaining*
  - *Structure confirmed by GC-MS and NMR*

Relevance and Impact to BETO

Goal: Develop polymers that provide a performance advantage over current petroleum based polymers and incorporate a readily accessible degradation pathway

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

- A polymer with improved properties vs. a direct replacement has the potential for rapid market entry
- Co-products can enable the production of biofuels and therefore stimulate the bio-economy due to higher selling price
- Utilization of small commonly produced by-products and bio-derived molecules will increase overall carbon yield of biomass processes.
- ***Support of BETO milestone: By 2025 produce bioproducts at needed scales (20-100kg) for product testing to support off-take agreements and end-user/market acceptance***
  - **Increase Yield from Catalytic Processes.** Identifying catalyst and process conditions to increase overall reaction yield, minimize carbon loss and decrease the formation of undesirable intermediates (Ct-F).
  - **Identify and Evaluate Potential Bioproducts.** Conversion processes need to integrate bioproduct production with that of drop-in fuels. Link intermediates from specific processes with potential products. Novel molecules also require high-throughput screening to characterize and optimize them for properties that are advantageous to the molecules already used in industrial processes (Ct-J).
  - **Develop Methods for Bioproduct Production.** Properties present in molecules tested at the lab and bench scale must be understood fundamentally to enable a transfer to larger scales (Ct-K).

Relevance and Impact to Advance State of Technology

Goal: Develop polymers that provide a performance advantage over current petroleum based polymers and incorporate a readily accessible degradation pathway

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

- Using versatile monomers where functional groups can be readily altered will help guide rational design of monomers based on structure-function relationships and guided my machine learning and molecular modelling
- Production of bioproducts is essential to enable biofuel production and therefore the bioeconomy

Technology transfer activities

- Customer discovery interviews underway based on previous Energy I-Corp participation
- Results will be published in peer reviewed journals
- LANL invention disclosures have been filed

Future Work

- Expand monomer scope – incorporation of different bio-derived linkers to tune physical properties e.g. cross-linking, H-bonding
- Optimize polymer synthetic conditions for increased yield and pH response/hydrolytic stability
- Increase polymer yields and fully characterize the physical and material properties
- Incorporate milder stimuli for polymer decomposition
- Explore alternative polymerization approaches
- Work closely with Inverse Polymer Design to develop iterative design cycles
  - Demonstrate at least one cycle of iteration with predictive modelling to improve monomer/polymer properties (Milestone Q4 FY19)
  - Feedback from NREL will direct research towards ideal monomer properties
- Full materials characterization on most promising polymers (collaboration with NREL)

Summary

Overview

– Develop polymers that can readily degrade to benign molecules while providing a performance advantage over current petroleum based polymers

Approach

– Use current expertise in acetal formation to synthesize monomers that can be converted to the parent building blocks and capitalize on the abundant functional groups to allow for structural and electronic optimization in collaboration with computational approaches

Technical accomplishments

– Increased stability of monomers
– Multiple monomers have been synthesized and characterized
– Polymerization and degradation of the polymers has been performed

Relevance

– Provides a polymer with a designed degradation route in order to avoid long-term environmental accumulation problems
– Give pathway for lesser used bioproducts (i.e. glycerol) to be reintroduced to the bioeconomy and increases global carbon efficiency
– By making a better product we can accelerate commercialization

Future work

– Increase polymer yields and fully characterize the physical and material properties
– Develop milder stimuli for polymer decomposition
– Expand substrate scope to introduce additional functionality
– Explore alternative polymerization approaches
– Work closely with Inverse Polymer Design to develop iterative design cycles

Acknowledgments

BETO

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Performance Advantaged Bioproducts via Selective Biological and Catalytic Conversion

Mary Biddy

Analysis in Support of Novel Bio-based Products and Functional Replacements

Mike Crowley

Inverse Biopolymer Design Through Machine Learning and Molecular Simulation

Mark Nimlos

Performance Advantaged Bioproducts from Catalytic Fast Pyrolysis

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

BIOENERGY TECHNOLOGIES OFFICE

Polycarbonate Physical Property Data

Physical Properties by repeat unit

Polymer	Trade Name	Chemical Formula	Molecular Weight Range	Density	RI	Tg	Tm	Thermal Conductivity (J/molK)	Entanglement Molecular Weight	Technical Data Sheet
Poly(ethylene carbonate)	QPAC 25	$(C_3H_4O_3)_n$	50k-200k	1.42	1.47	0-10 C	NR	NR	NR	http://empowermaterials.com/wp-content/uploads/2014/11/QPAC-25-Technical-Data-Sheet.pdf
Poly(propylene carbonate)	QPAC 40	$(C_4H_6O_3)_n$	100k-300k	1.26	1.463	15-40C	NR	NR	NR	http://empowermaterials.com/wp-content/uploads/2014/11/QPAC-40-Technical-Data-Sheet.pdf
Polyco(proplyene cyclohexene carbonate)	QPAC 100	$(C_{11}H_{16}O_6)_n$	150k-200k	1.04	NR	90-100C	NR	NR	NR	http://empowermaterials.com/wp-content/uploads/2014/11/QPAC-100-Technical-Data-Sheet.pdf
Poly(Cyclohexene carbonate)	QPAC 130	$(C_7H_{10}O_3)_n$	150k-200k	1.1	NR	120-130C	NR	NR	NR	http://empowermaterials.com/wp-content/uploads/2014/11/QPAC-130-Technical-Data-Sheet.pdf
Poly(butylene carbonate)	QPAC 60	$(C_5H_8O_3)_n$	NR	NR	NR	0-20C	NR	NR	NR	http://empowermaterials.com/wp-content/uploads/2017/11/QPAC-60-Safety-Data-Sheet.pdf
Poly(pentene carbonate)		$(C_6H_{10}O_3)_n$	8k-50k	NR	NR	-4C	NR	NR	NR	https://onlinelibrary.wiley.com/doi/10.1002/app.12355
Poly(Hexene Carboante		$(C_7H_{12}O_3)_n$	10k-50k	NR	NR	-10C	NR	NR	NR	https://onlinelibrary.wiley.com/doi/10.1002/app.12355
Poly(Bisphenol A Carbonate)	Lexan/Makrolon	$(C_{16}H_{15}O_3)_n$	NR	1.2	1.53-1.59	147-174C	NR	305	1700-4800	https://polymerdatabase.com/polymers/polybisphenolacarbonate.html
Poly(Bisphenol B Carbonate)	Same	$(C_{17}H_{17}O_3)_n$	NR	1.18	1.58	134-149C	NR	NR (Calc 321-337)	NR (Calc 2700-2800)	https://polymerdatabase.com/polymers/polybisphenolbcarbonate.html
Poly(Bisphenol F Carbonate)	Same	$(C_{14}H_{11}O_3)_n$	NR	1.24	NR (Calc 1.49-1.64)	120-147C	NR	NR (Calc 249-267)	NR (Calc 2350-2450)	https://polymerdatabase.com/polymers/polybisphenolfcarbonate.html
Poly(2,6,3',5'-tetrachloro bisphenol A Carbonate)	Same	$(C_{16}H_{11}O_3Cl_4)_n$	NR	NR (Calc 0.89-0.95)	1.59-1.61	220-230C	NR	NR (Calc 360-390)	NR (Calc 2500-5700)	https://polymerdatabase.com/polymers/Poly2635-tetrachlorobisphenolAcarbonate.html
Poly(tetramethyl bisphenol A carbonate)	Same	$(C_{20}H_{23}O_3)_n$	NR	1.08	NR (Calc 1.49-1.53)	194C	NR	NR (Calc 389.6-420.7)	3230-3620	https://polymerdatabase.com/polymers/polytetramethylbisphenolacarbonate.html
Poly(4,4'-thiodephenylene carbonate)	Same	$(C_{13}H_9O_3S)_n$	NR	1.36	NR (Calc 1.63-1.69)	110-115C	NR	NR (Calc 255-262)	NR (Calc 2500-2750)	https://polymerdatabase.com/polymers/poly44-thiodiphenylenecarbonate.html

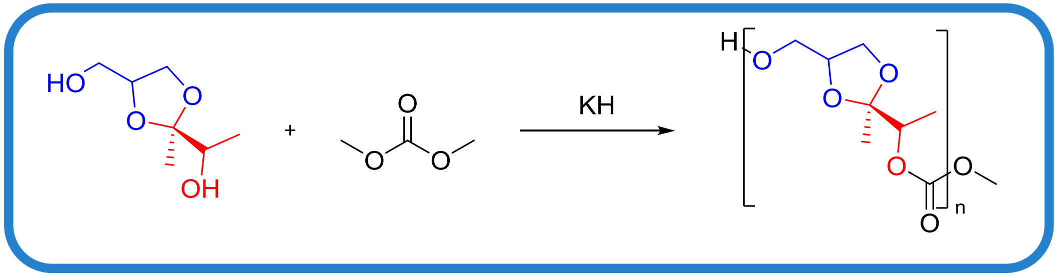
Polycarbonate Physical Property Data

Physical Properties by Trade Name

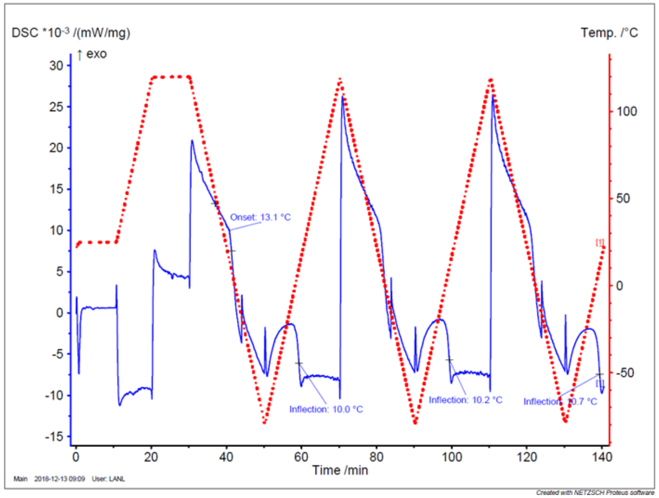
Company	Resin	Product #	Density	Tensile Strength (PSI)	Glass Transition	RI	Thermal Conductivity (BTUin/hrft^2F)
Lubrizol	Carbothane TPU Aliphatic	PC-3575A	1.15	600	-29	NR	NR
		PC-3585A	1.15	425	-27	NR	NR
		PC-3595A	1.15	400	-25	NR	NR
		PC-3555D	1.15	325	-25	NR	NR
		PC-3572D	1.15	325	NR	NR	NR
	Carbothane TPU Aromatic	AC-4075A	1.19	400	-23	NR	NR
		AC-4085A	1.2	400	-24	NR	NR
		AC-4095A	1.21	370	-10	NR	NR
		AC-4055D	1.22	300	NR	NR	NR
Aetna	Makrolon	GP	1.2	9500	NR	1.586	1.35
		GP-V	1.2	9500	NR	1.586	1.35
		AR	1.2	9500	NR	1.586	1.35
		MG	1.2	9500	NR	1.586	1.35
		FI	1.2	9500	NR	NR	NR
SABIC	LEXAN	123X	1.2	61625	NR	NR	NR
		4251R	1.2	58000	NR	NR	NR
		4501	1.2	47125	NR	NR	NR
		943X	1.2	47125	NR	NR	NR
		ADX1016R	1.2	58000	NR	NR	NR
Empower Materials	QPAC	25	1.42	NR	0-10C	1.47	NR
		40	1.26	NR	15-40C	1.26	NR
		100	1.04	NR	90-100C	NR	NR
		130	1.1	NR	120-130C	NR	NR
Plaskolite (Covestro)	Tuffak	GP	1.2	9500	NR	1.586	1.35
		M5	1.2	9500	NR	NR	NR
		LD	1.2	9500	NR	NR	1.35
DSM Engineering	Xantar	17	1.01	8700	NR	NR	1.67
		C CF 107	1.17	8700	NR	NR	NR
		G2F 23 UR	1.25	9430	NR	NR	NR

Biorenewable Polymers from bio-derived Monomers

- Polycarbonates are used for medical plastics, heat resistance, transparent materials, etc.
- **Performance Advantage:** Maintain physical properties and selectively depolymerize
- **Bio-Based monomer:** Solketal derived from Glycerol and Acetoin
- **Hypothesis:** Intentionally limited *n* (3:1 monomer to carbonate ratio) in order to derive a small discrete oligomer for degradation studies.



Polymer	T_g (°C)
Poly(ethylene carbonate)	0-10
Poly(propylene carbonate)	15-40
Poly(butylene carbonate)	0-20
Poly(pentene carbonate)	-4
Poly(hexene carbonate)	-10
Poly(solketal carbonate)	10



Outcome: Initial physical properties, including glass transition temperature are similar/superior to commercial aliphatic carbonates – should improve when *n* is not constrained