

Performance Advantaged β -ketone containing polymers – Benefits in Manufacturing, Performance, and End-of-Life

Nicholas A. Rorrer, National Renewable Energy Laboratory

Acknowledgements

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Nicholas A. Rorrer



Davinia Salvachua
Fermentation Lead



Chris Johnson
Metabolic
Engineering Lead



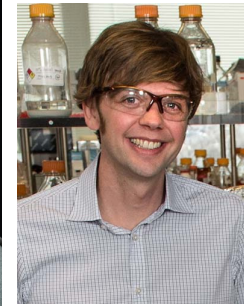
Brandon Knott
MD Simulations



Brenna Black
Analytic
Development



Michelle Reed
Project Manager



Gregg Beckham
Mentor/PI

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VEHICLE TECHNOLOGIES OFFICE



Sandra Notonier



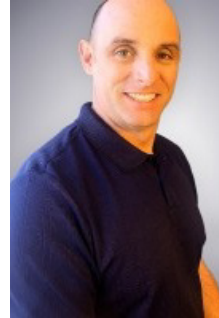
Avantika Singh
TEA Analysis



Scott Nicholson
MFI Analysis



Erik Rognerud
Research
Technician



Joel Miscall
Research
Technician



Caroline Hoyt
Former NREL
Experimentalist

Plus
Many
More!



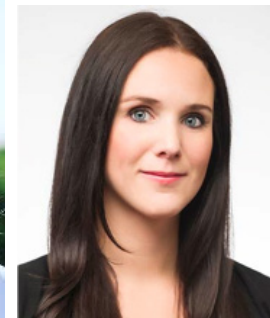
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ADVANCED MANUFACTURING OFFICE



Bob Allen



Kat Knauer
BOTTLE CTO



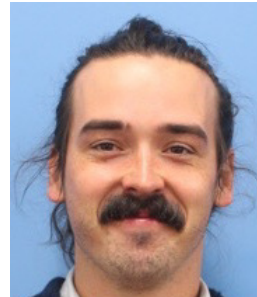
Robynne Murray
Sr. Researcher



Robin Cywar
Postdoc



Michael McGraw
Postdoc



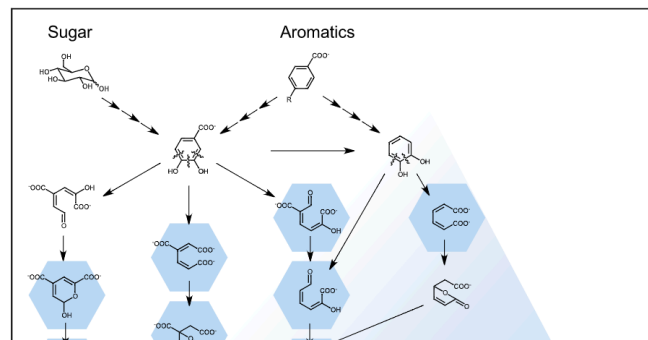
Sam Dahlhauser
Postdoc



Joule

Article

Innovative Chemicals and Materials from Bacterial Aromatic Catabolic Pathways



Christopher W. Johnson, Davinia Salvachúa, Nicholas A. Rorrer, ..., Yannick J. E. Broeze, Adam M. Guss, Gregg T. Beckham

gregg.beckham@nrel.gov

HIGHLIGHTS

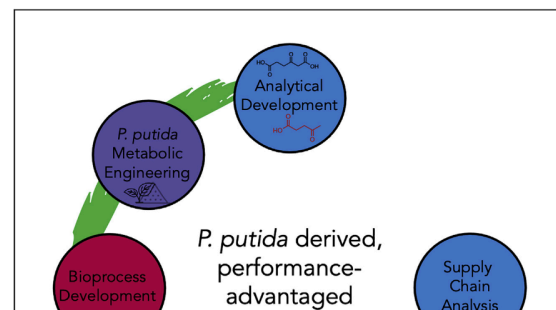
Pseudomonas putida was engineered to produce intermediates of aromatic catabolism

Cell Reports
Physical Science

CellPress
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Article

Production of β -keto adipic acid from glucose in *Pseudomonas putida* KT2440 for use in performance-advantaged nylons



Nicholas A. Rorrer, Sandra F. Notonier, Brandon C. Knott, ..., Davinia Salvachúa, Michael F. Crowley, Gregg T. Beckham

gregg.beckham@nrel.gov

Highlights

Pseudomonas putida is engineered to produce β -keto adipic acid (β KA) from glucose

β KA-nylon exhibits enhanced

PLASTICS

REVIEWS

Check for updates

Bio-based polymers with performance-advantaged properties

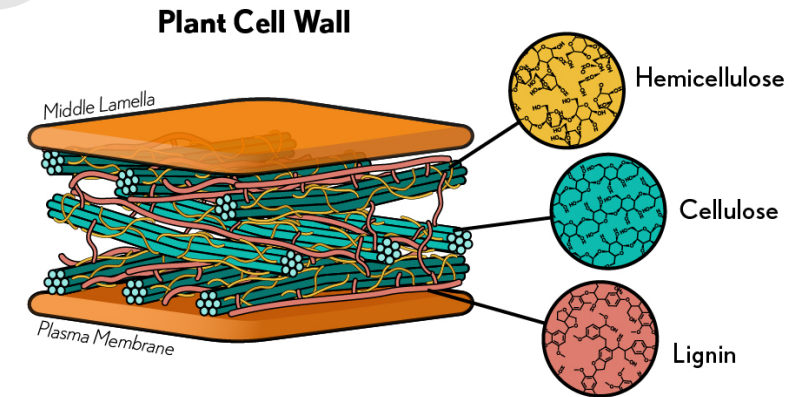
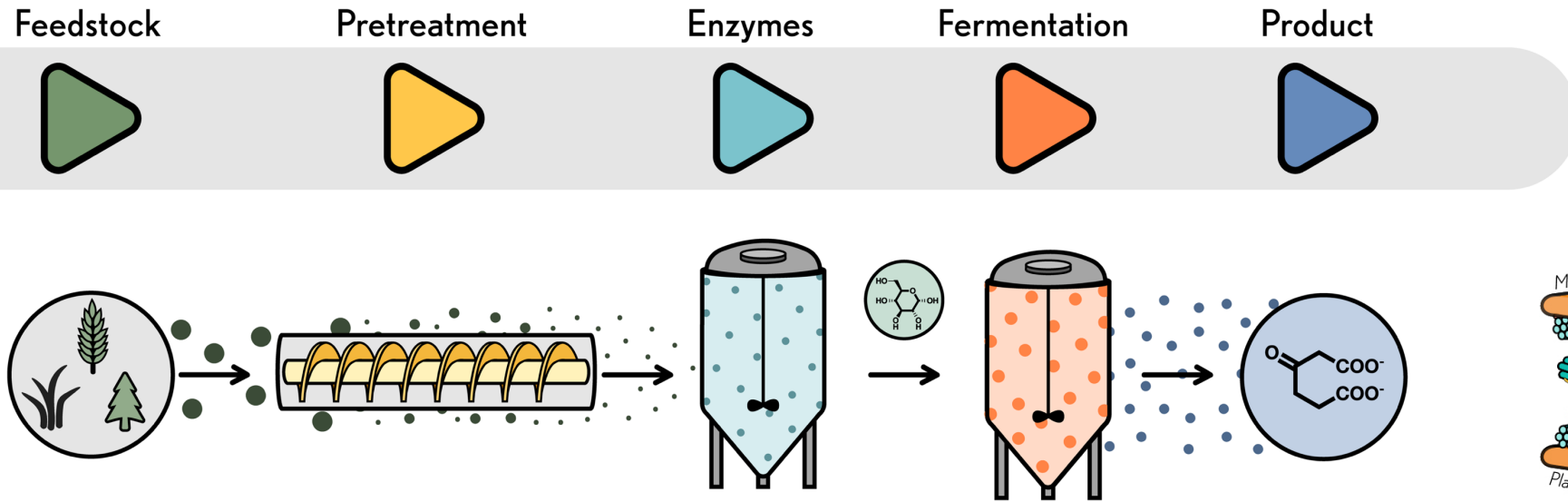
Robin M. Cywar^{1,2}, Nicholas A. Rorrer^{1,2}, Caroline B. Hoyt^{1,2}, Gregg T. Beckham^{1,2} and Eugene Y.-X. Chen^{1,2}

Abstract | Bio-based compounds with unique chemical functionality can be obtained through selective transformations of plant and other non-fossil, biogenic feedstocks for the development of new polymers to displace those produced from fossil carbon feedstocks. Although substantial efforts have been invested to produce bio-based polymers that are chemically identical to and directly replace those from petroleum, a long-pursued goal is to synthesize new, sustainable, bio-based polymers that either functionally replace or exhibit performance advantages relative to incumbent polymers. Owing to anthropogenic climate change and the environmental consequences of global plastics pollution, the need to realize a bio-based materials economy at scale is critical. To that end, in this Review we describe the concept of performance-advantaged, bio-based polymers (PBPs), highlighting examples wherein superior performance is facilitated by the inherent chemical functionality of bio-based feedstocks. We focus on PBPs with C–O and C–N inter-unit chemical bonds, as these are often readily accessible from bio-based feedstocks, which are heteroatom-rich relative to petroleum-derived feedstocks. Finally, we outline guiding principles and challenges to aid progress in the development of PBPs.

Most of Today's Information Will Be Taken From Three Publications Plus Some Patent Data

Today: What do we target to make from biomass? What is needed to make new biobased monomers? Can biobased monomers offer multiple benefits?

NREL's Approach to New Polymers



Images courtesy of Rita Clare, Formerly NREL

NREL Takes a Holistic Approach to Biomass Conversion

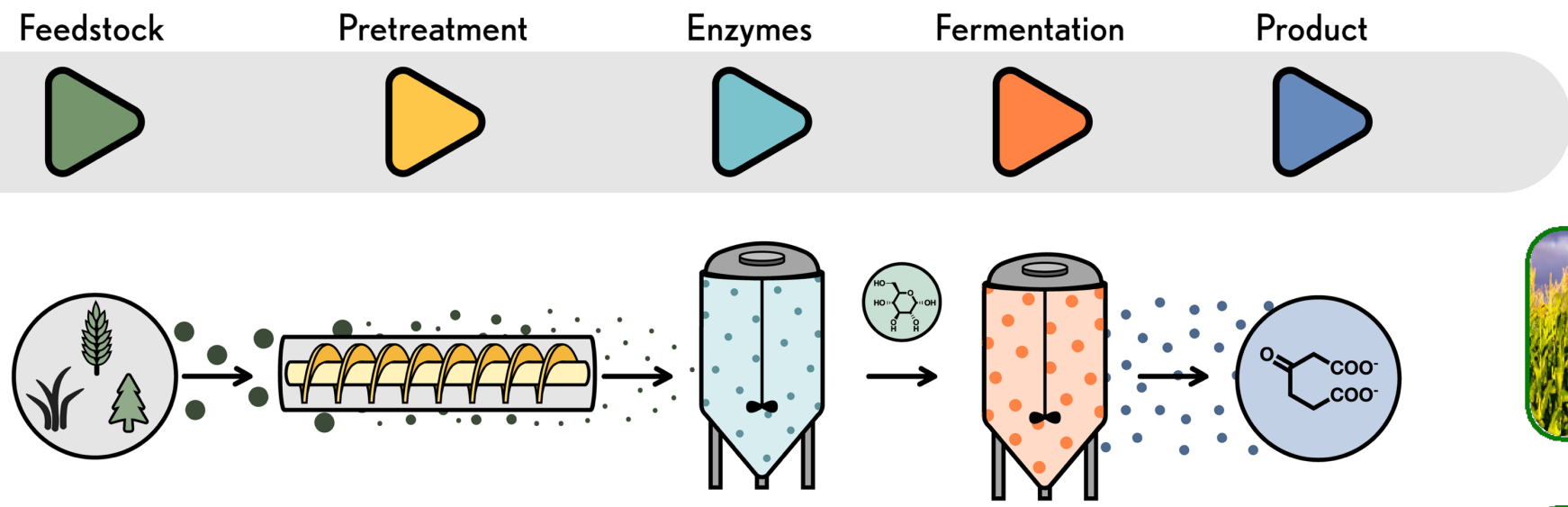
Our work attempts to enable the biorefinery by utilizing the entirety of biomass

- Recent work has also included the conversion of 'waste' plastics (e.g. PET) into the same monomers

Early work focused on direct replacements (e.g. Adipic and Terephthalic acid) however, as our work evolved we started to target "Performance Advantaged Bioproducts" (PABPs)

- We classify performance advantages in three areas: **Manufacturing, Performance, End-of-Life**

NREL's Approach to New Polymers





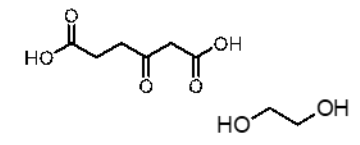
Lignocellulosic Biomass

PET

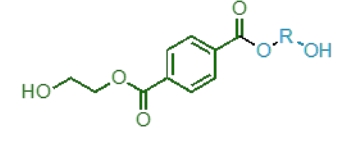


No Biodegradable Moieties

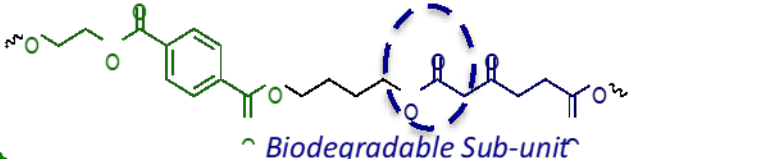
Polymer Precursors



Glycolysis Product



Biodegradable PET Alternative



~ Biodegradable Sub-unit

Poly(butylene β-ketoadipate) [PBKAT]

NREL Takes a Holistic Approach to Biomass Conversion

We classify performance advantages in three areas: **Manufacturing, Performance, End-of-Life**

Eventually, we will talk about how certain biobased building blocks can enable biodegradation and more facile chemical recycling; however, we will first discuss how to make these monomers

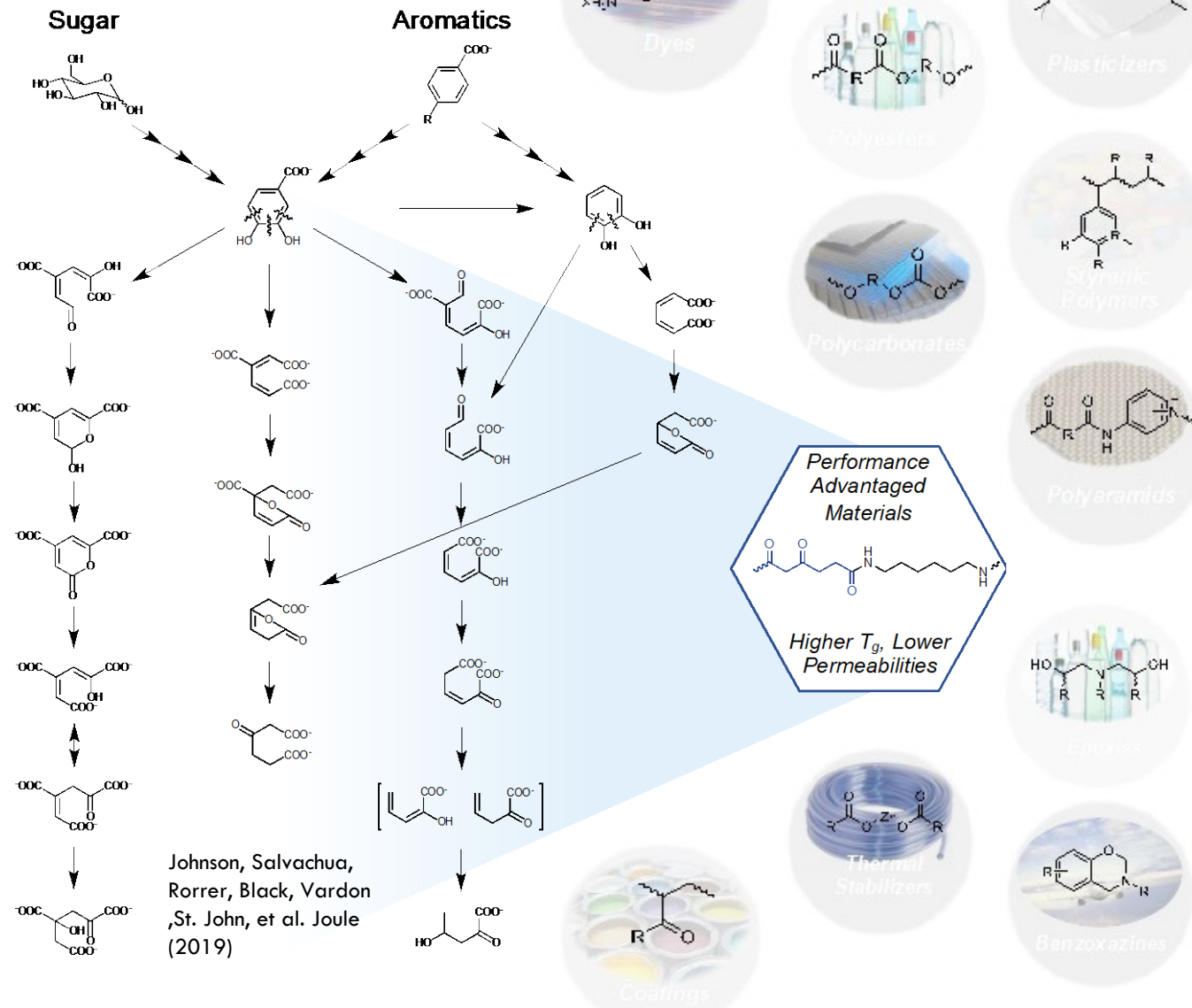
A Large Design Space

Chemical, biological, and hybrid transformation offer plenty of unique monomers

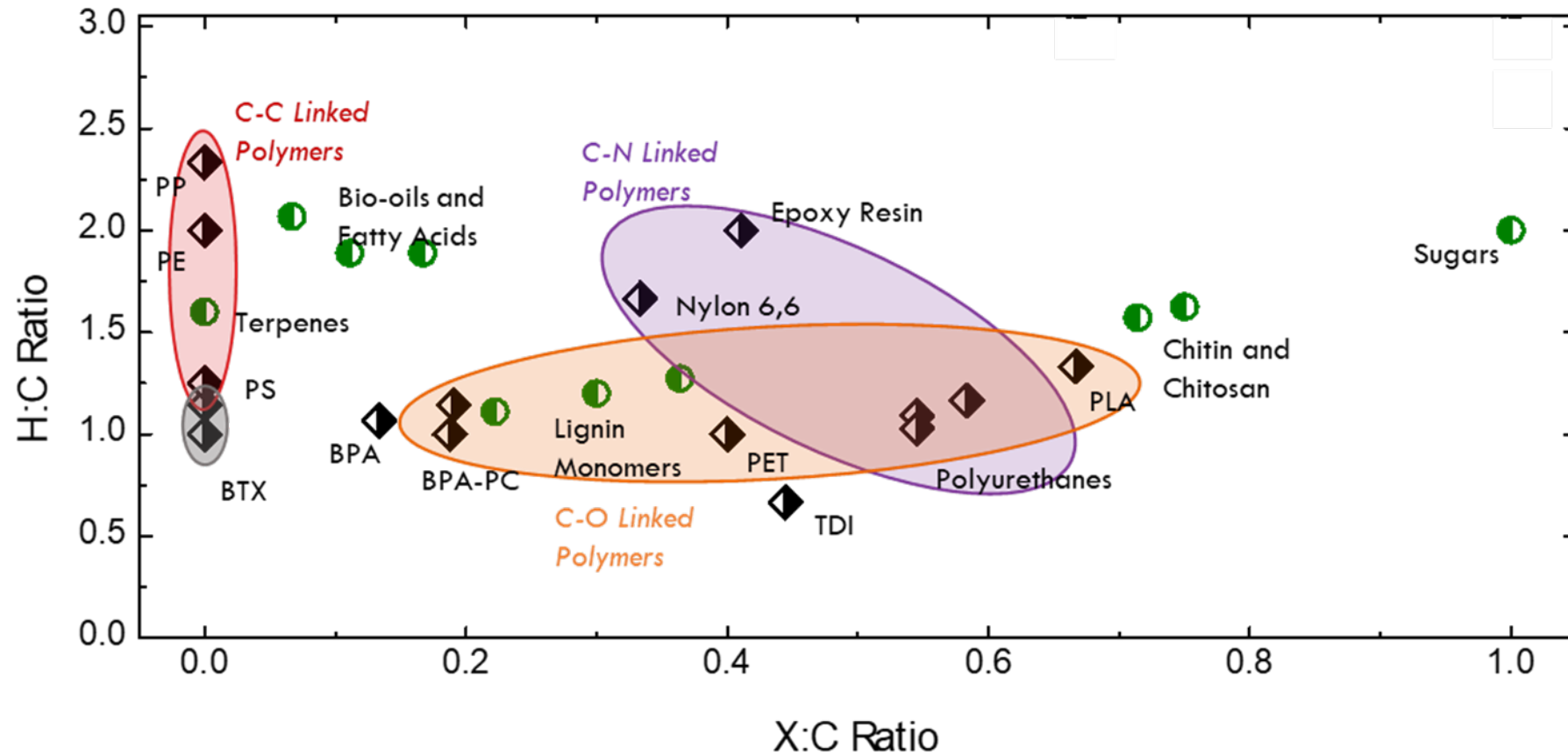
The transformation of biomass provides access to a wide variety of functionality such as:

- Carboxylic Acids, including Diacids
- Anhydrides
- Alcohols, including diols and polyols
- Amines, including diamines and multifunctional amines
- Epoxies
- Styrenic Monomers
- Olefinic or Unsaturated Structures

These chemicals provide access to a wide variety of material classes and narrowing the chemical design space is a constant challenge



Maintaining Biomass' Functionality to Target Engineering Plastics



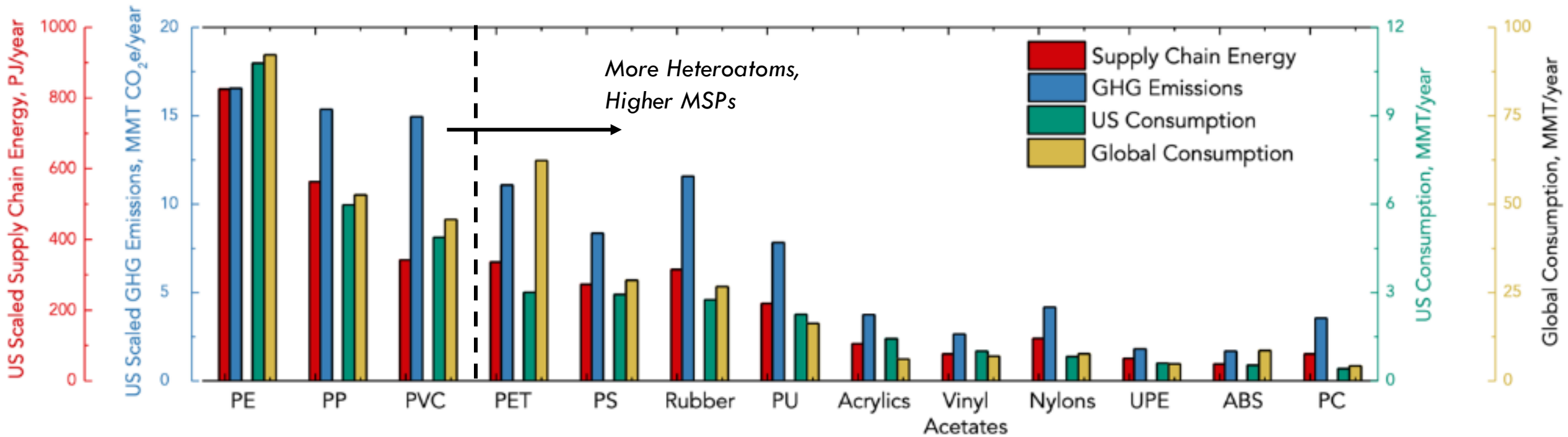
Van Krevelen diagram showing chemical distances of feedstocks to polymers (X is a heteroatom, typically oxygen or nitrogen)

Maintaining Biomass' Functionality

Adding or removing functionality, especially heteroatom functionality, from chemicals (biobased or petrochemical) requires energy and emits GHG

- Thus, the heteroatom functionality of biomass makes it ideal for PABPs, notably performance polymers

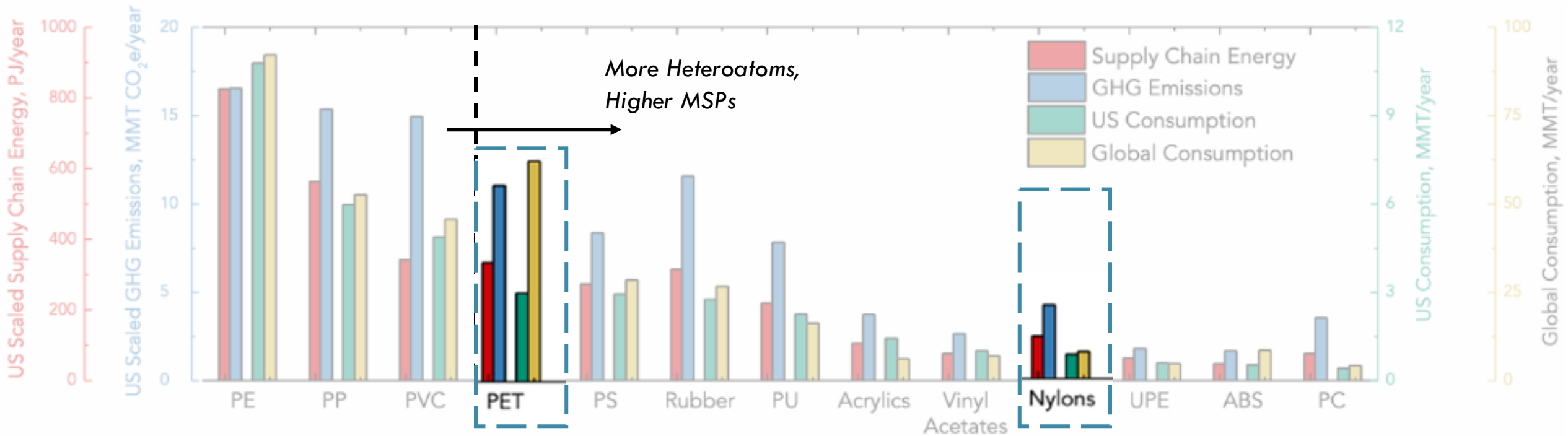
Maintaining Biomass' Functionality to Target Engineering Plastics



From Nicholson, Rorrer, Joule 2021

Heteroatom Containing Polymers Are Formulated For Specific Applications

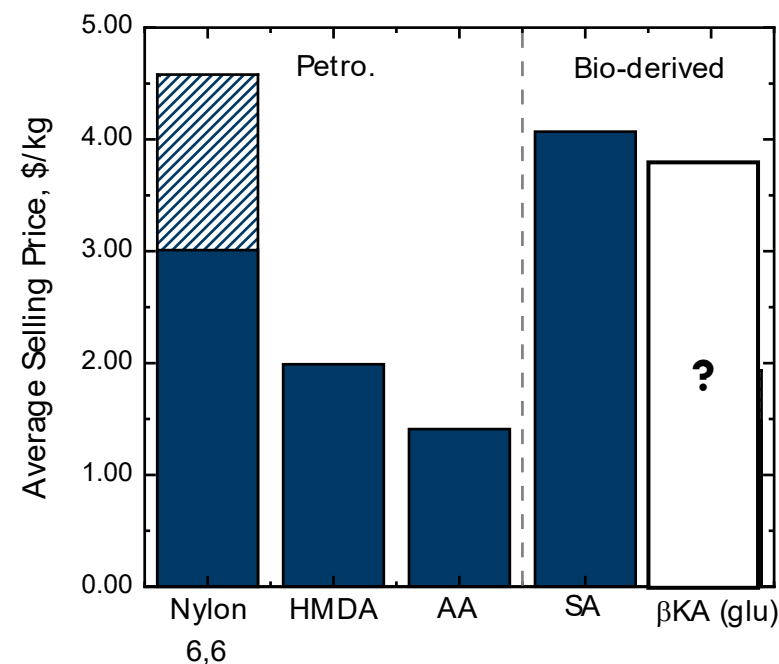
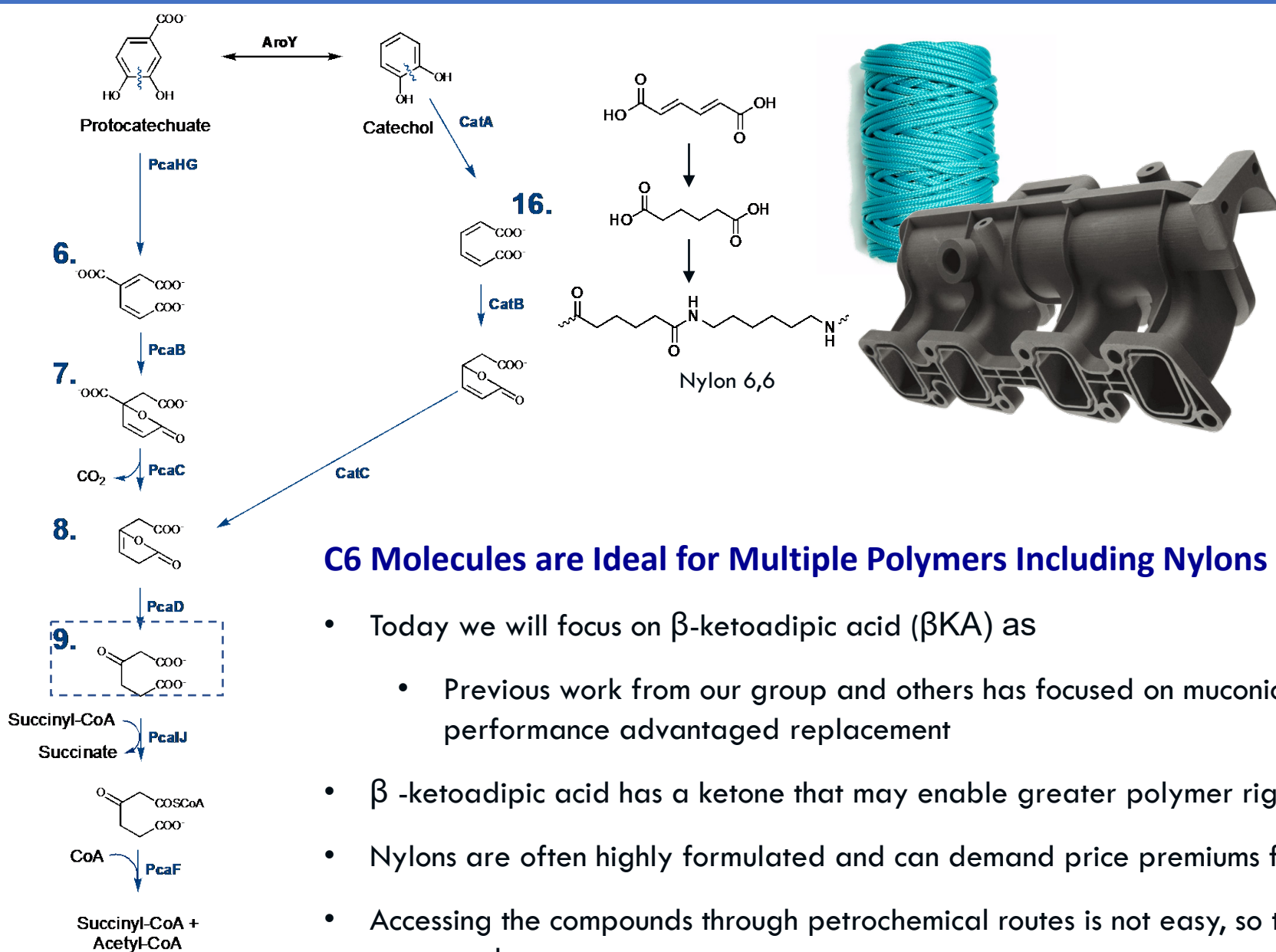
Maintaining Biomass' Functionality to Target Engineering Plastics



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Heteroatom Containing Polymers Are Formulated For Specific Applications

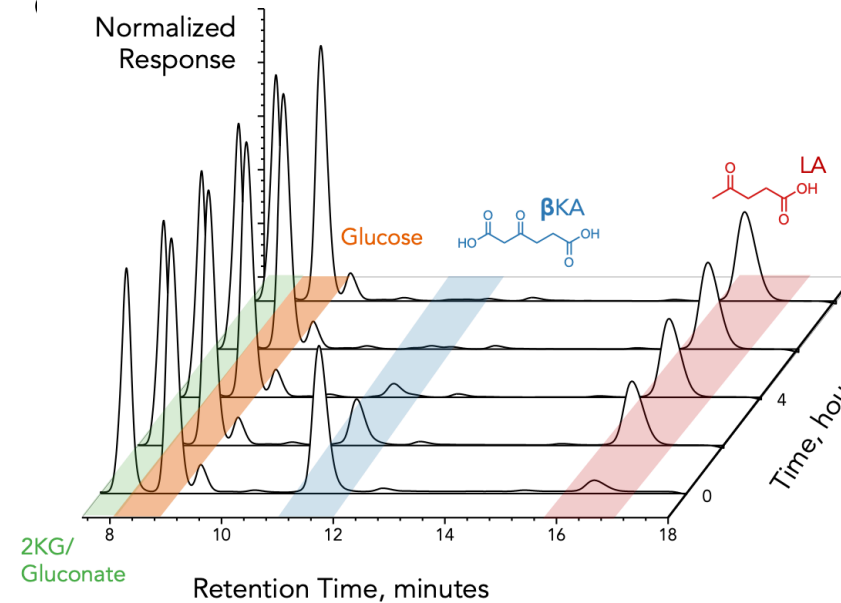
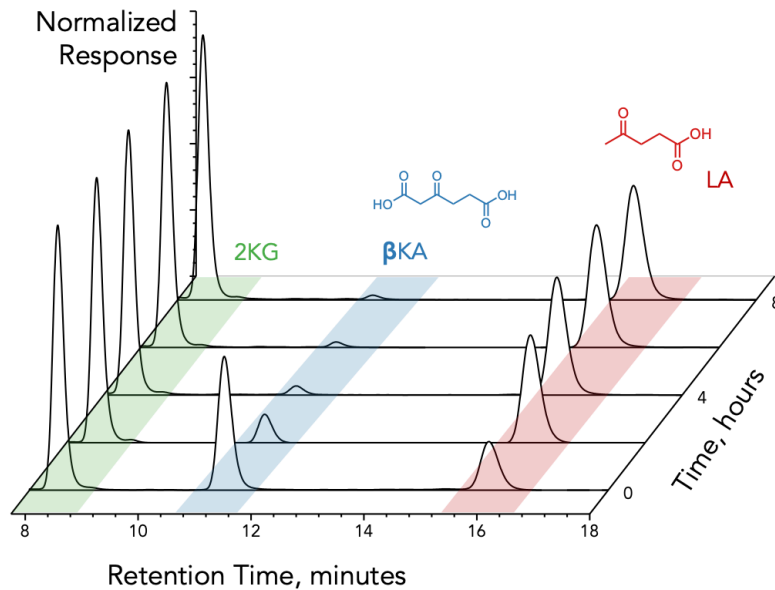
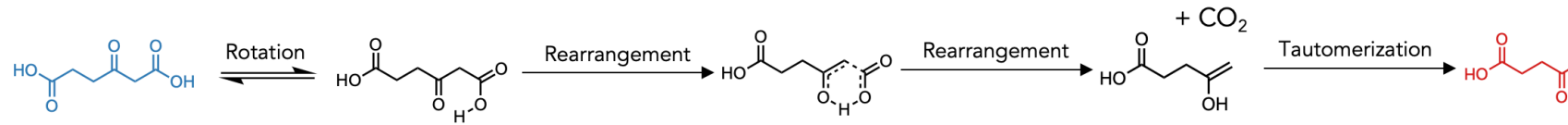
C6 Dicarboxylic Acids are Natural Polymer Targets



C6 Molecules are Ideal for Multiple Polymers Including Nylons

- Today we will focus on β -ketoadipic acid (β KA) as
 - Previous work from our group and others has focused on muconic acid and its diene structure as a direct and performance advantaged replacement
- β -ketoadipic acid has a ketone that may enable greater polymer rigidity
- Nylons are often highly formulated and can demand price premiums for performance
- Accessing the compounds through petrochemical routes is not easy, so thus we must develop strategies to produce these compounds.

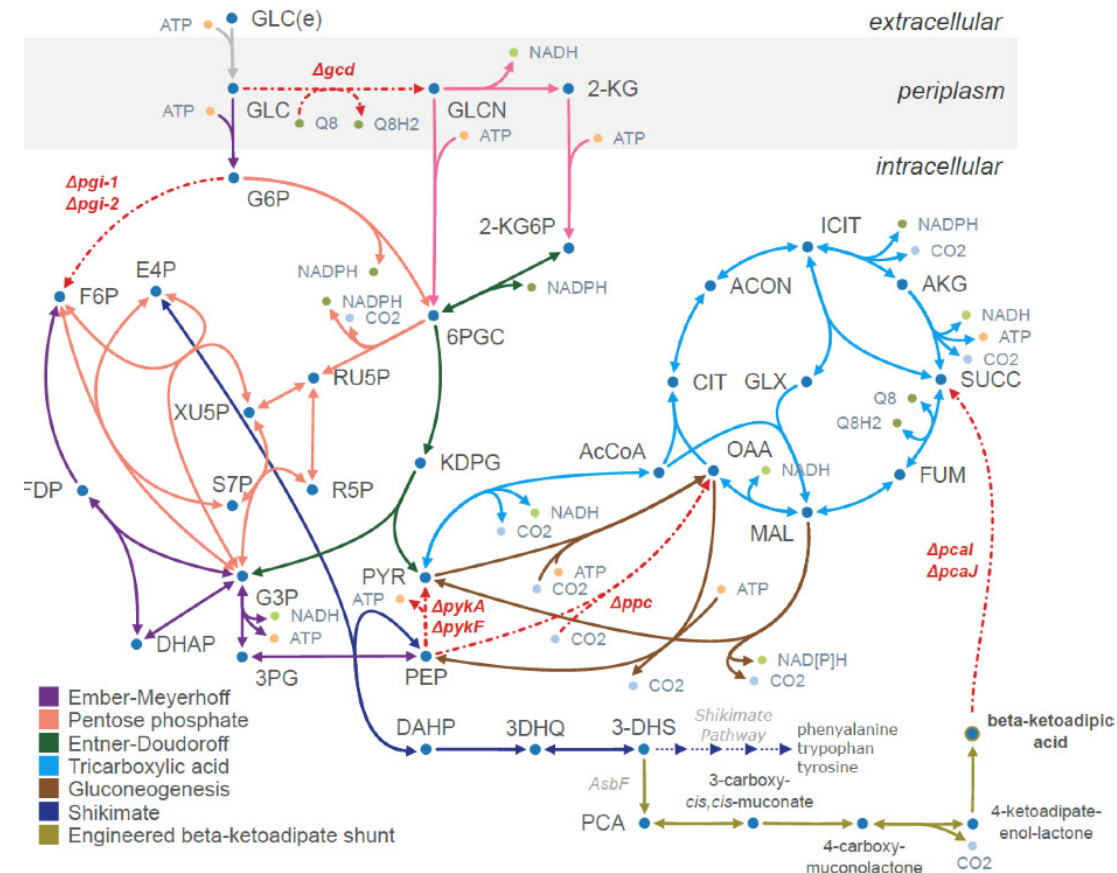
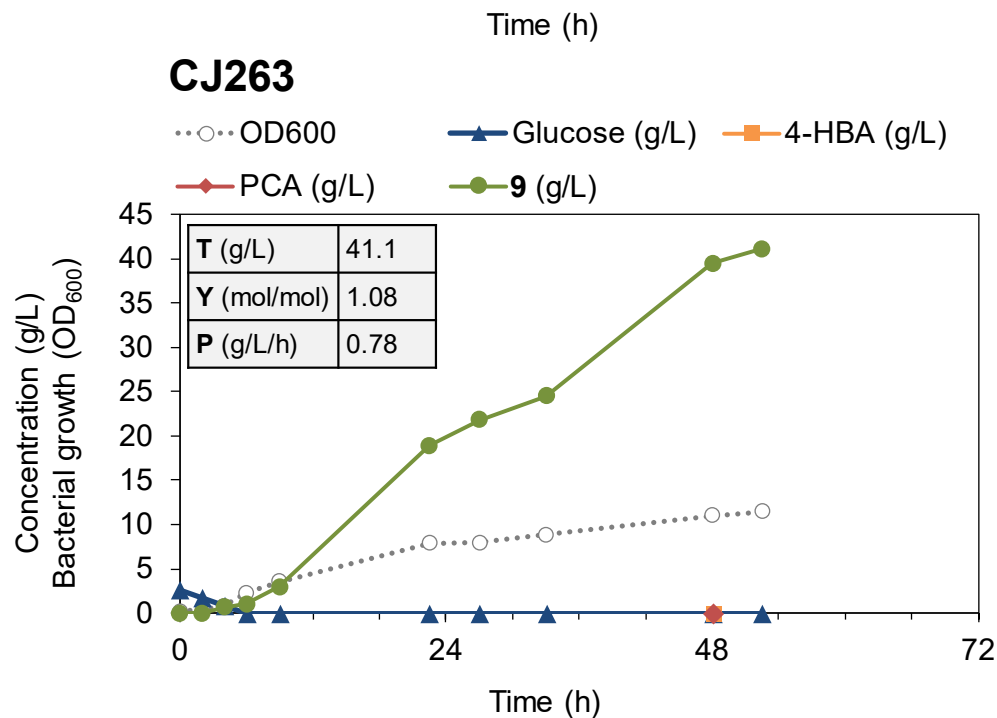
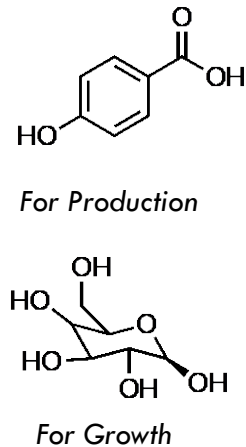
Analytical Development for β KA



β KA Quantification is Not Straightforward

- β KA can decarboxylate abiotically to levulinic acid
 - This will require care in polymerizations and separations
- In order to enable quantification, we forced β KA to levulinic acid and ensured that it did not overlap with other metabolites

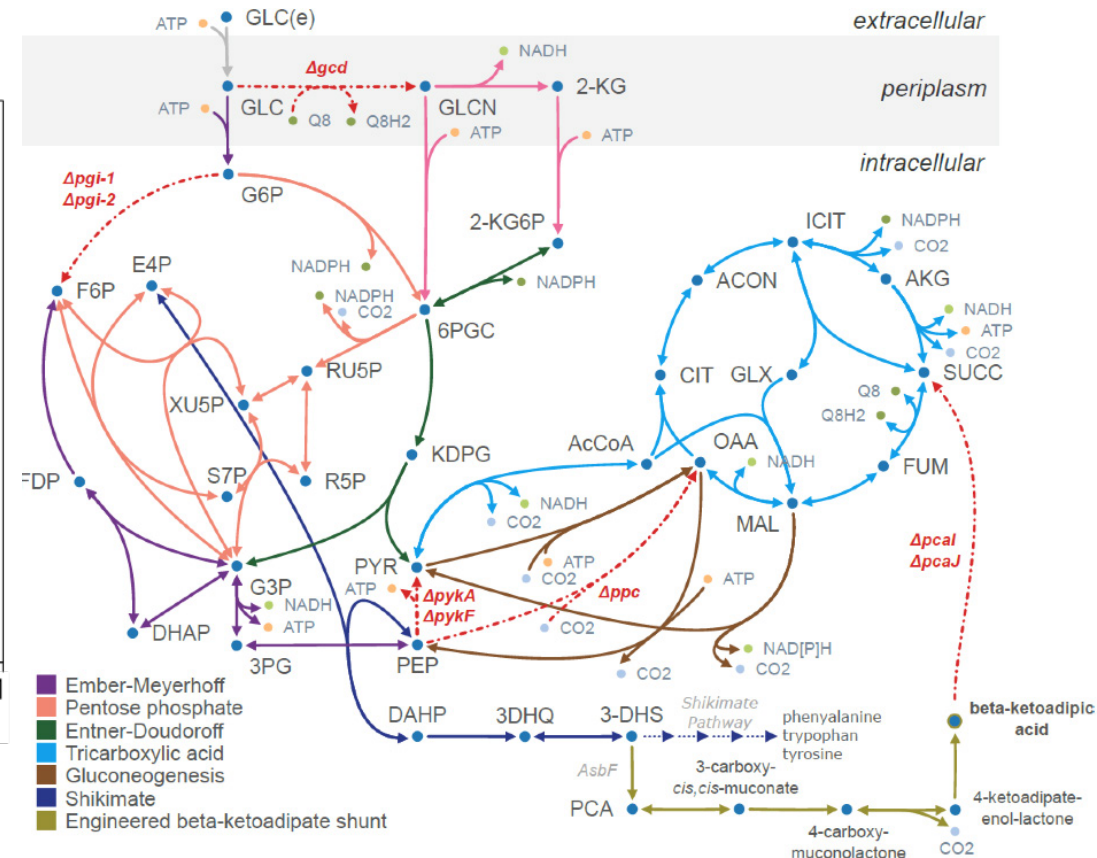
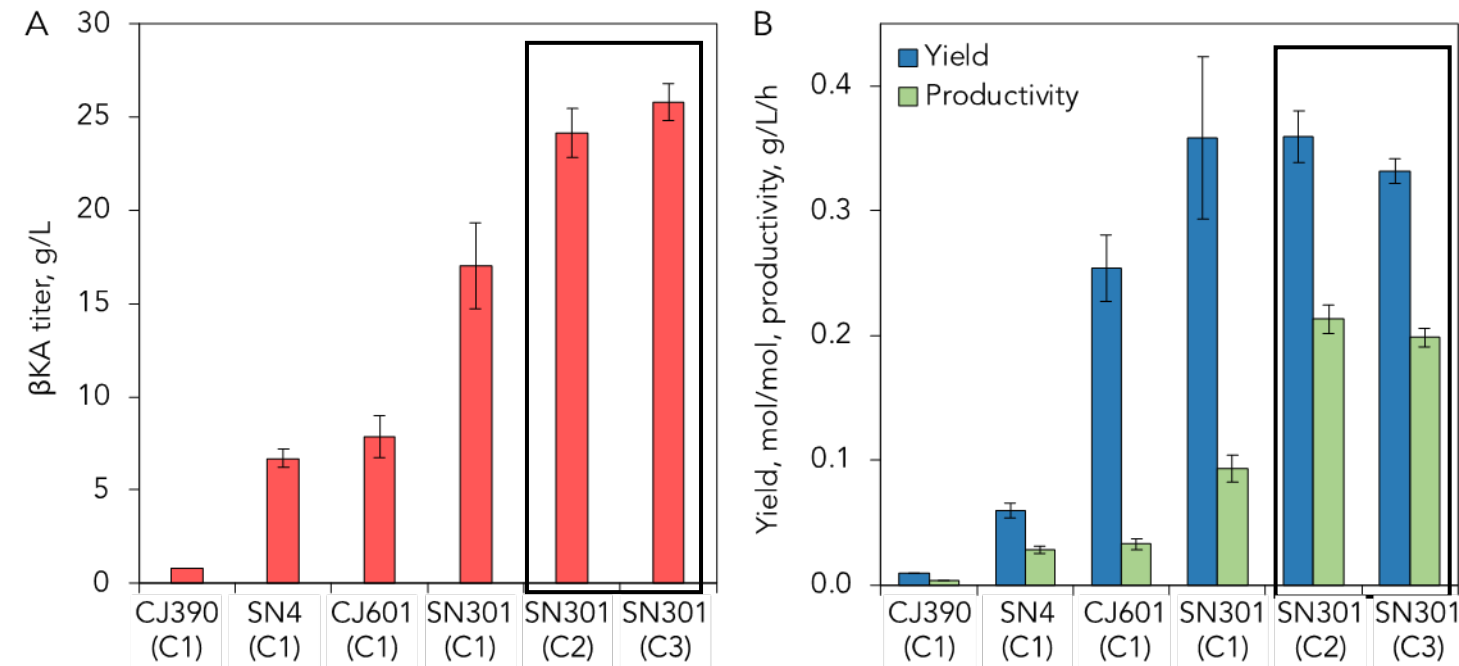
β KA Production from Aromatic Compounds



β KA Was Initially Demonstrated from Aromatic Compounds

- Strains were initially engineered to produce β KA in *Johnson et al.* in which high yields, titers, and moderate productivities were achieved
- However, there are advantages to demonstrating molecule production from sugars (e.g. single carbon source, higher TRL, etc.)

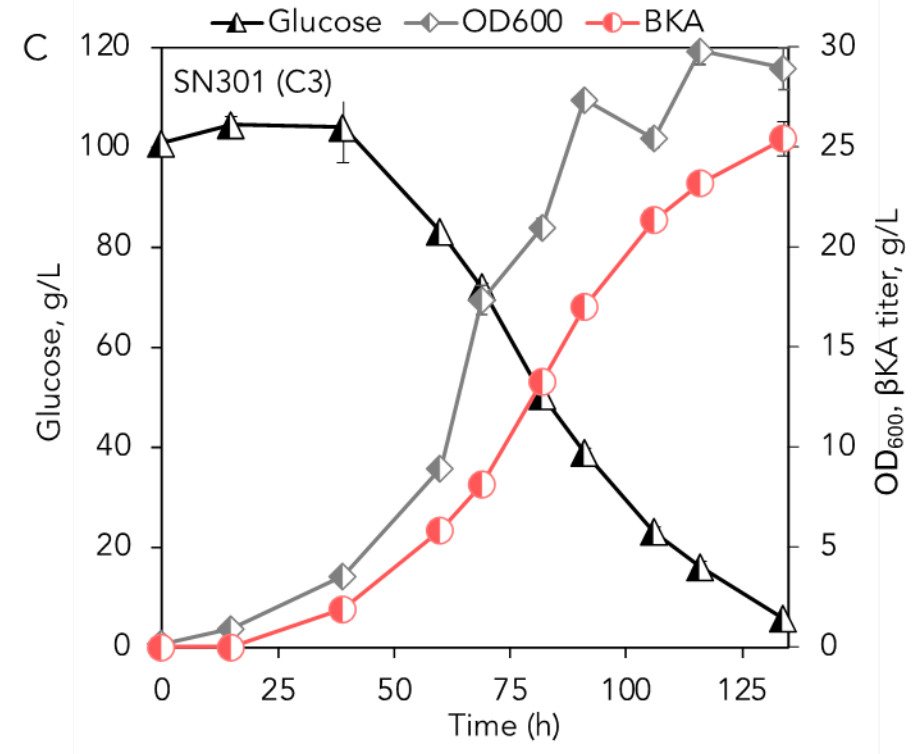
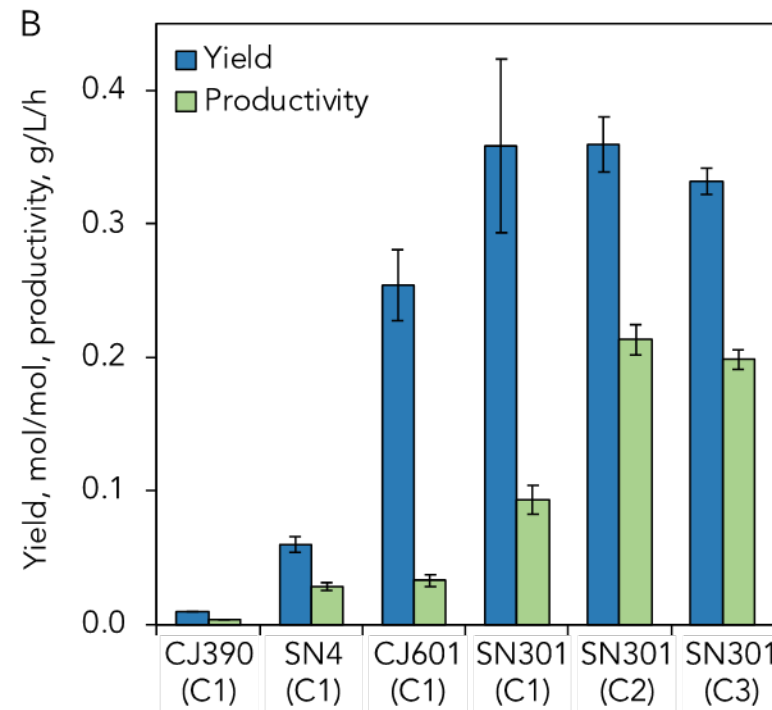
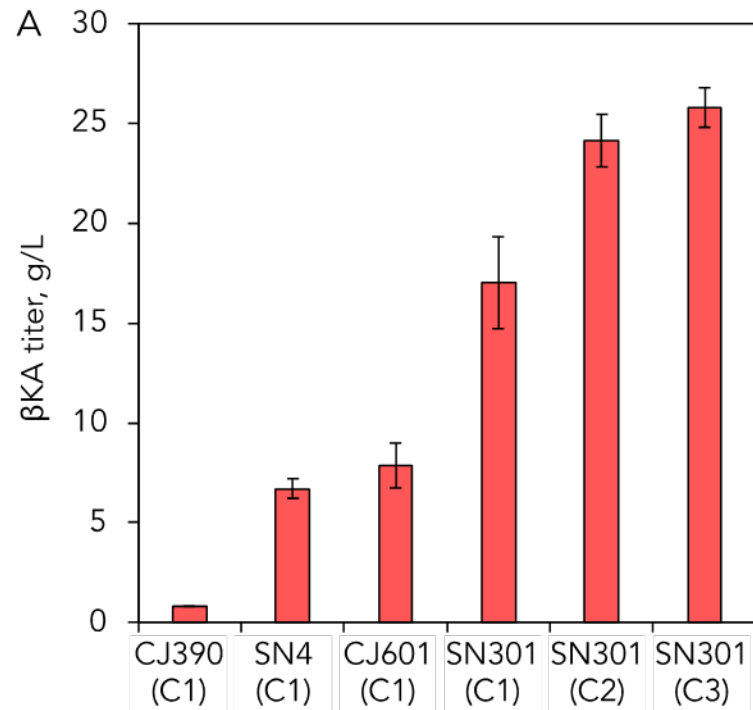
βKA Production from Glucose



βKA Metabolic Engineering Required Multiple Evolutions

- Initially, *AsbF* was introduced to convert 3-dehydoshikamate into protocatechuate to enable conversion into βKA (CJ390). Further engineering applied previous learnings from muconic acid production to increase production (SN4)
- Two other strains, SN4 and CJ601, accumulate metabolic intermediates (e.g. 2-ketogluconate) and *HexR*, a transcriptional repressor, was deleted to yield our final strain SN301

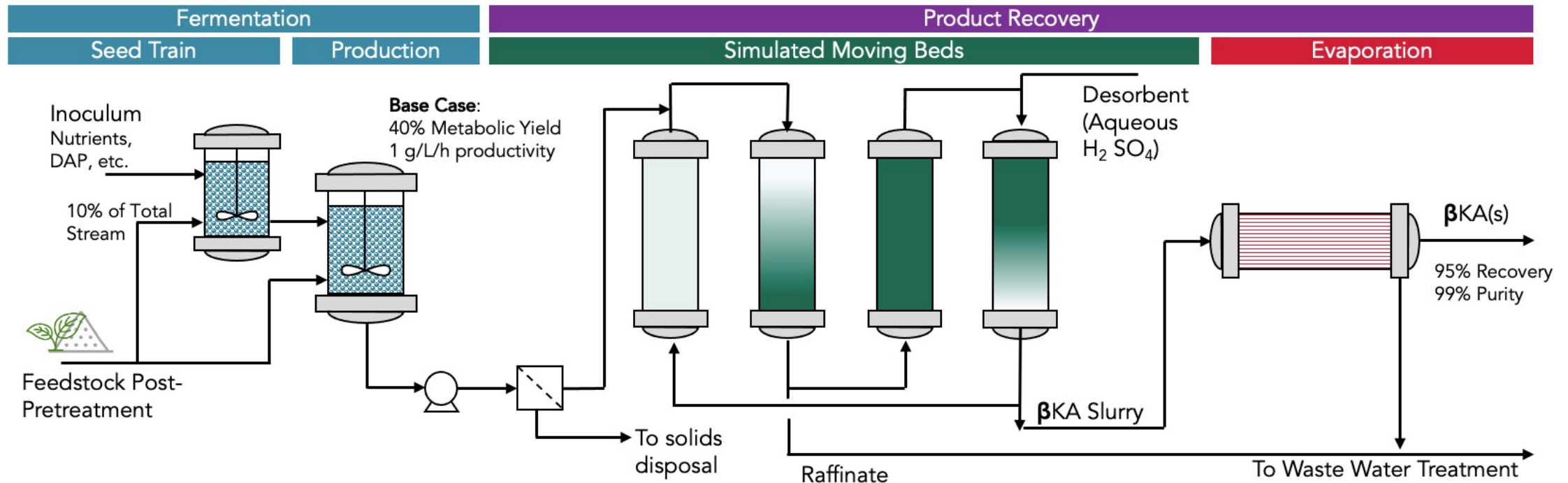
β KA Production from Glucose



Bioreactor Feed Strategy Can Also Yield Improvements in Titer

- Multiple feed strategies were implemented to resemble industry relevant strategies
 - C1 – Fed Batch, 1L Volume, C2 – Fed Batch, 1.5L Volume, C3 – Batch with Non-washed cells
- Optimum conditions resulted in a 26 g/L titer, 0.21 g/L/h productivity, a 36% yield, and near complete glucose consumption

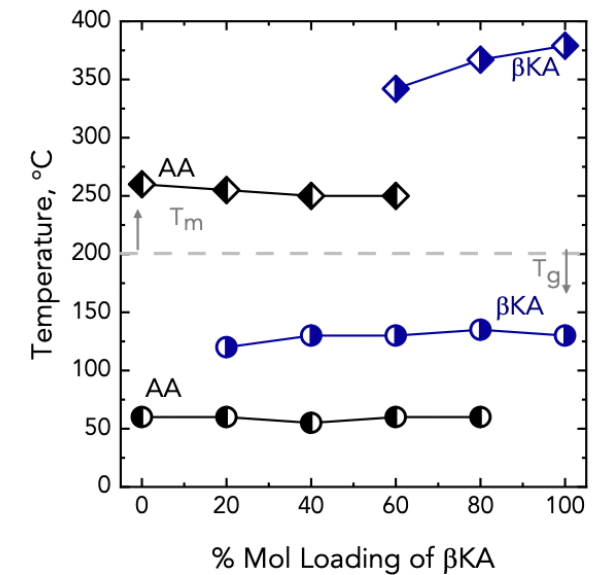
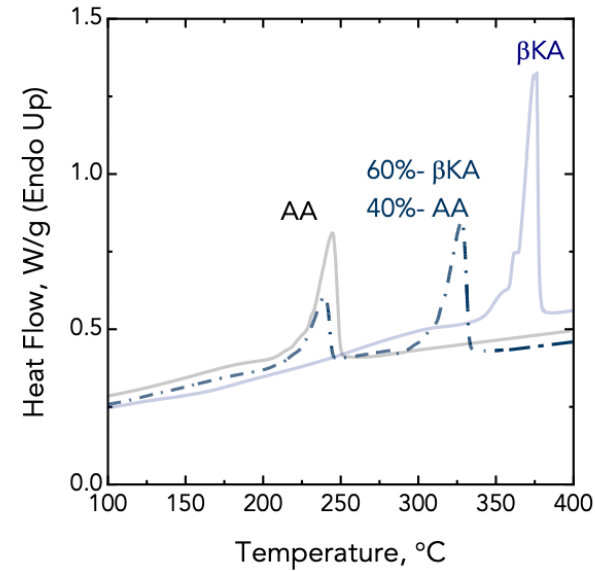
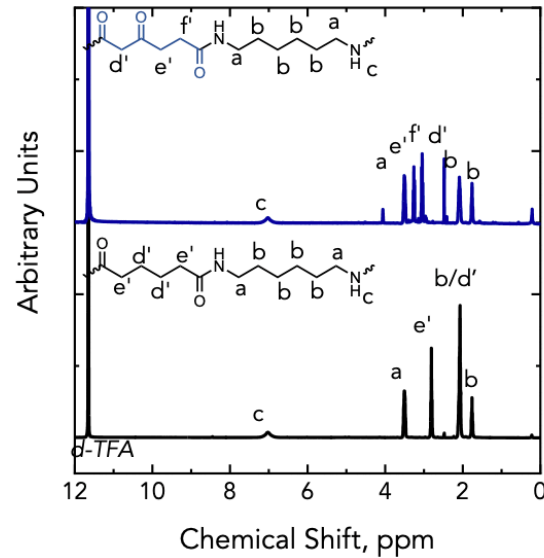
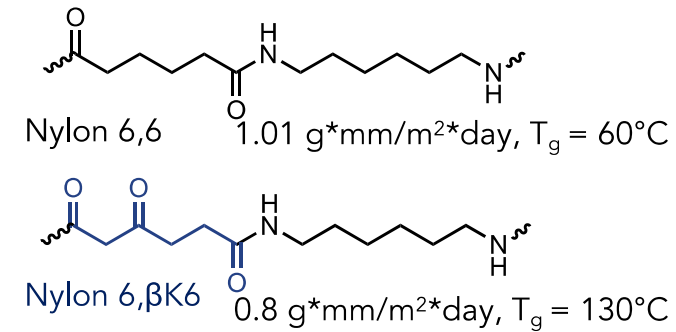
Scale up and Separation of β KA



β KA was recovered from fermentations for all subsequent polymer work

- On a lab scale this was accomplished by acidification, liquid-liquid extraction, and rotovap
- This process will be modeled later in this presentations where the implemented separation method is simulated moving beds

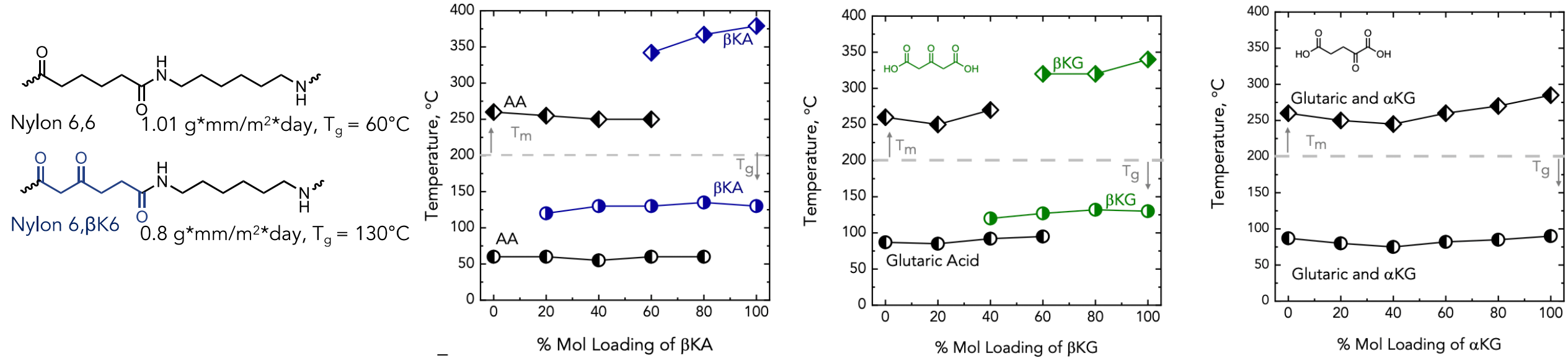
Performance-advantaged nylons enabled by β -keto diacids



C6 dicarboxylic acids with β -ketone enable enhanced nylon performance

- Nylon 6,6, analogues were synthesized by multiple methods including an industry relevant salt polymerization, the use of acyl chlorides, and other couplings to avoid decarboxylation
- NMR indicates no imine formation while DSC reveals blocky behavior in co-polymers
- The use of β KA reduced water permeability by 20% while simultaneously increasing the T_g by 216% in the homopolymer

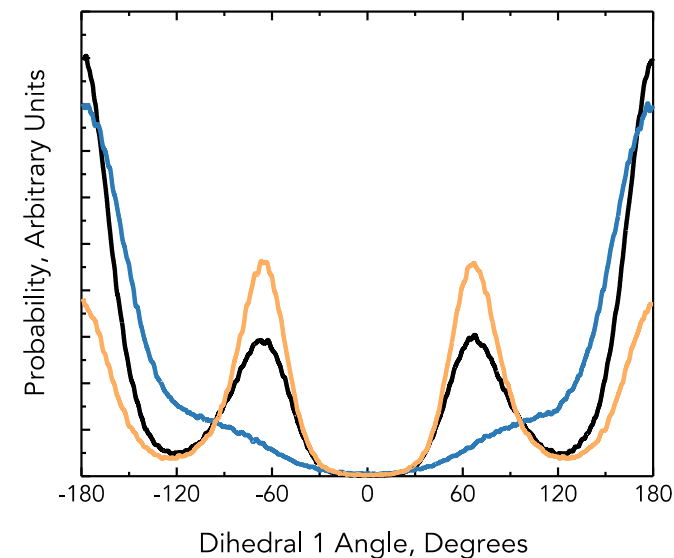
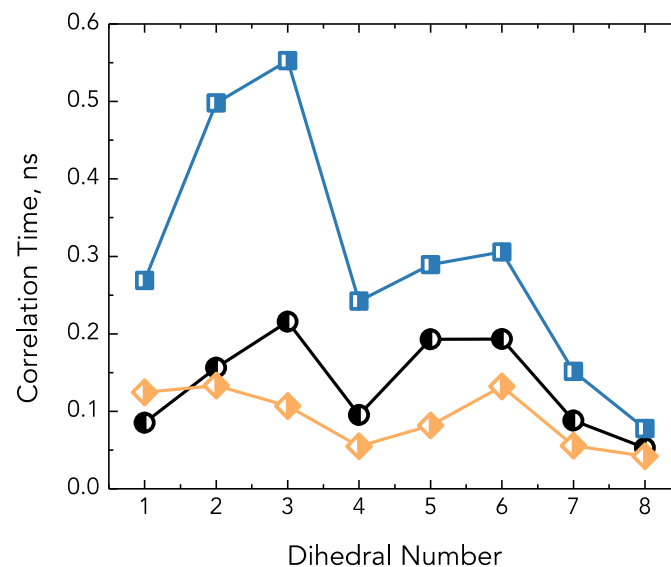
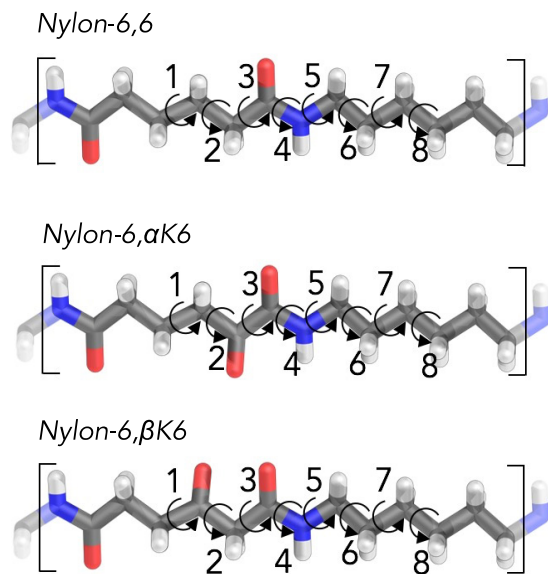
Performance-advantaged nylons enabled by β -keto diacids



The β -ketone enables enhanced nylon performance over α -ketones

- We expanded our diacid suite to include other keto diacids to be used in polymerization
- β -ketoglutaric acid demonstrates similar thermal trends to β KA while α -ketoglutaric acid does not exhibit the same trends
- These results indicate that the β -ketone may induce further backbone rigidity

Performance-advantaged nylons enabled by β -keto diacids

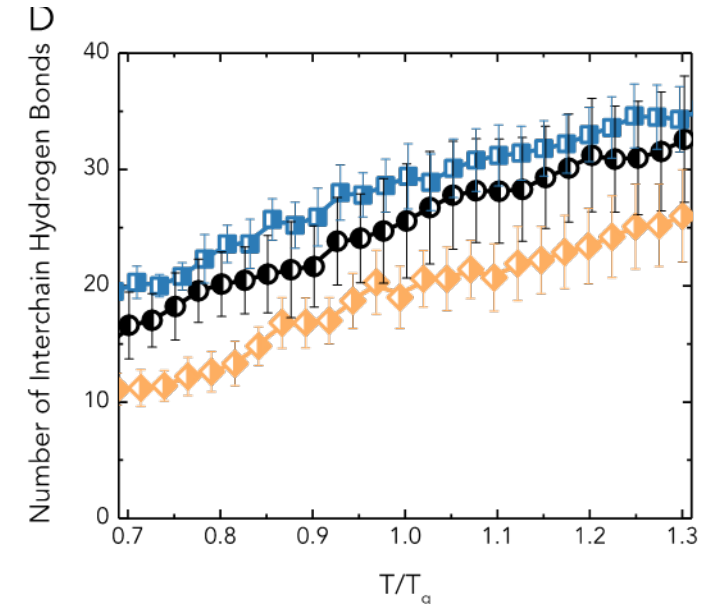
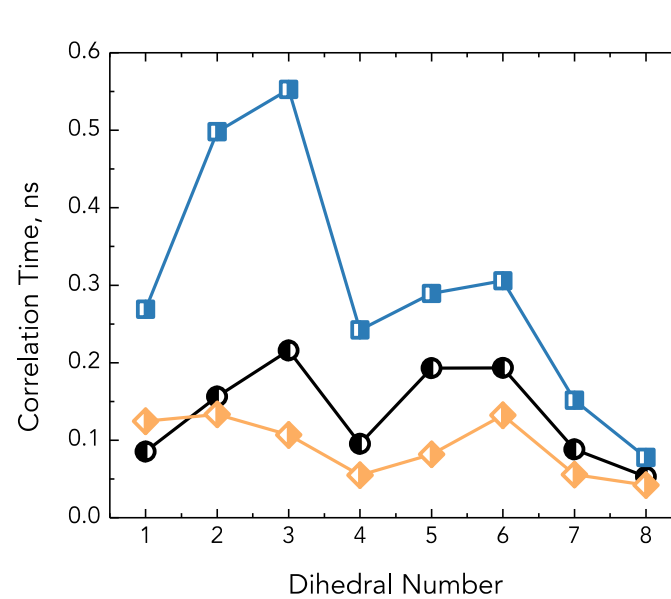
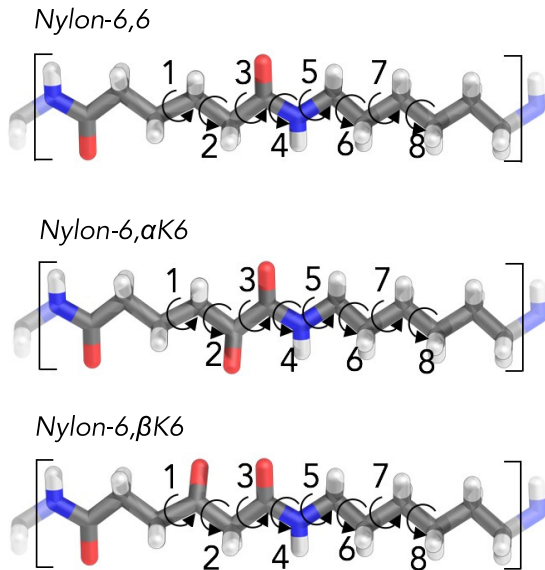


—●— Nylon-6,6 —◇— Nylon-6, α K6 —■— Nylon-6, β K6

C6 dicarboxylic acids with β -ketones enforce backbone rigidity

- Nylon 6,6, forcefields were generated to ensure that the nylon crystal structure could be replicated
- To understand backbone rigidity, we examined the dihedrals along the polymer backbone centered on the amide bond
- The β -ketone results in longer correlations times and fewer configurations that the polymer backbone can exist in, confirming enhanced rigidity

Performance-advantaged nylons enabled by β -keto diacids

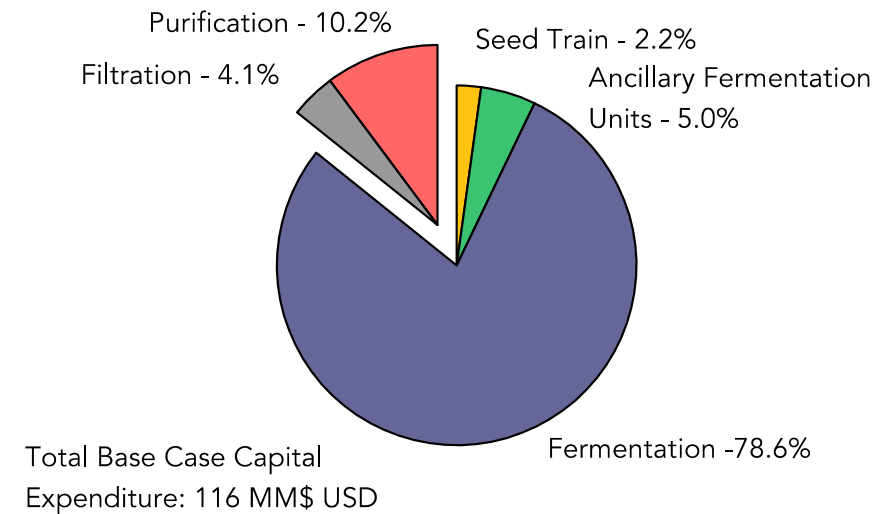
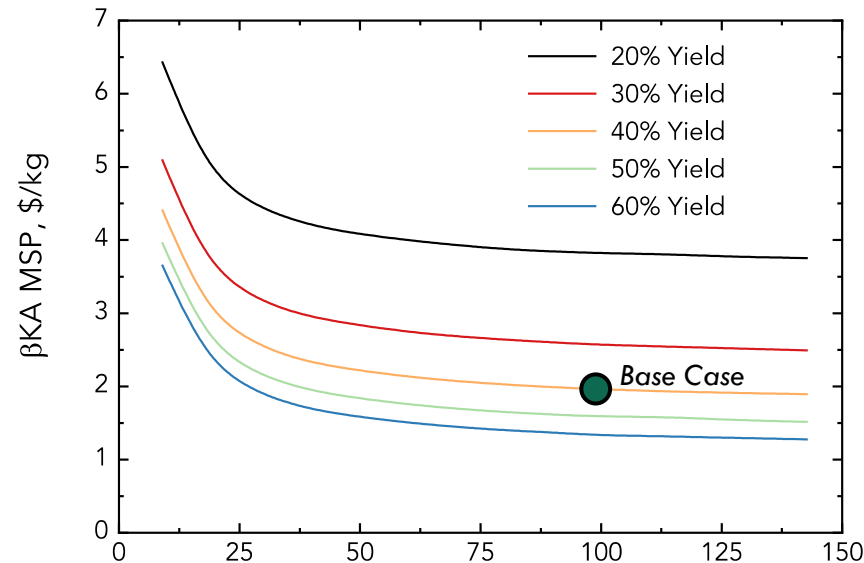
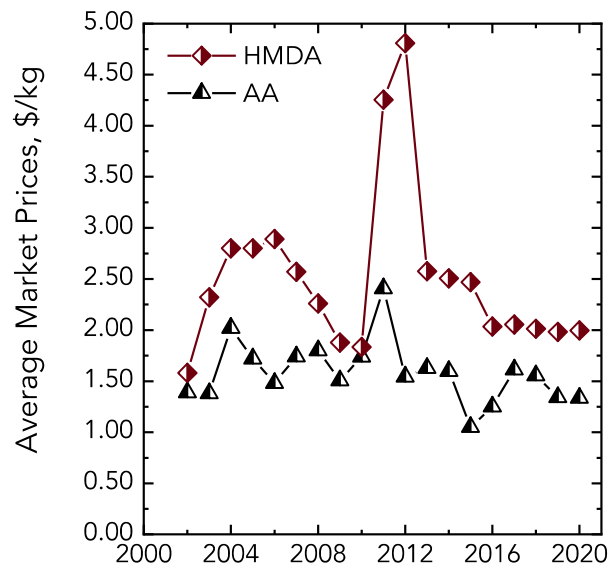


—●— Nylon-6,6 —◇— Nylon-6, α K6 —□— Nylon-6, β K6

C6 dicarboxylic acids with β -ketones enable enhanced nylon performance

- The enhanced rigidity explains the enhanced T_g , but does not *fully* explain the lower permeability
- Thus, we examined the intermolecular interactions between the polymers, namely hydrogen bonding
 - The β -ketone does possess enhanced interactions across a wide thermal range while the α -ketone may interfere with hydrogen bonding

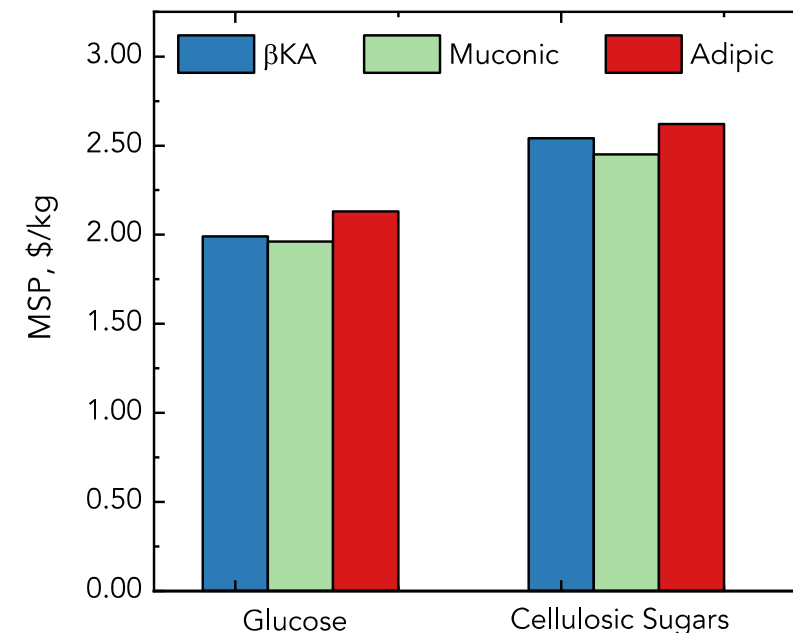
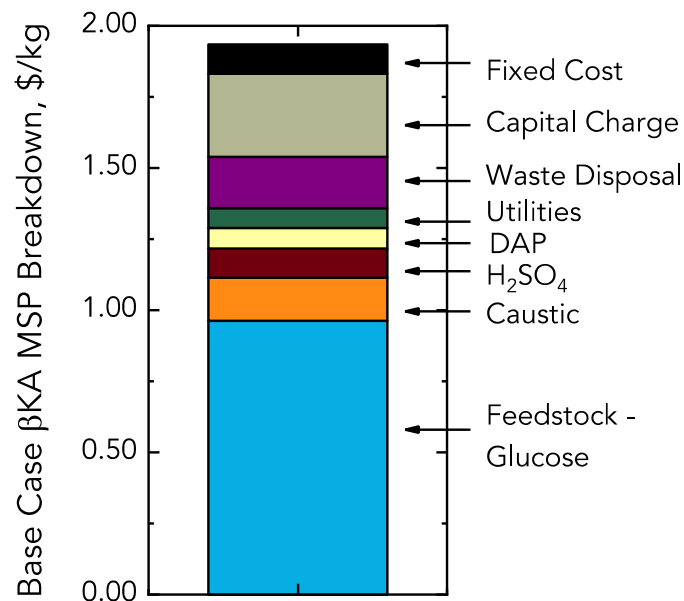
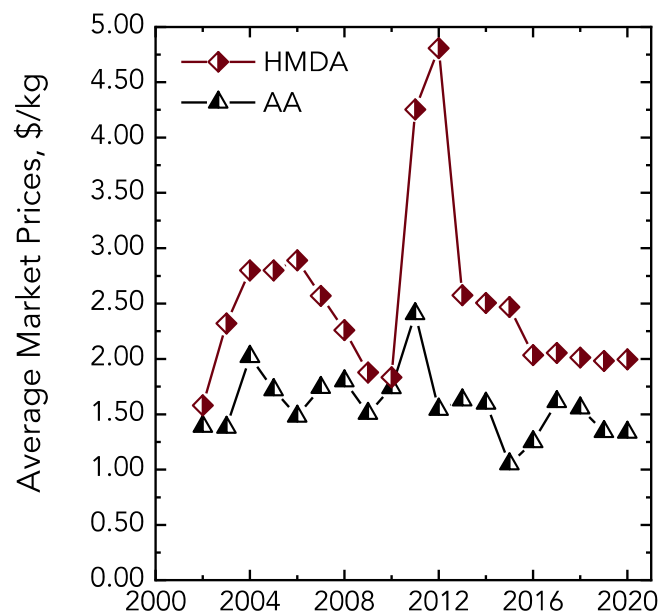
Production of β KA – Base Case



β KA analysis is affected by titer, yield, feedstock and production plant size

- β KA production has baselined relative to adipic acid production
- Most analysis was compared to a base case, which also corresponds to a titer of 1 g/L/h
- Capital expenditures are driven by fermentations which is the result of the size of the fermenters needed

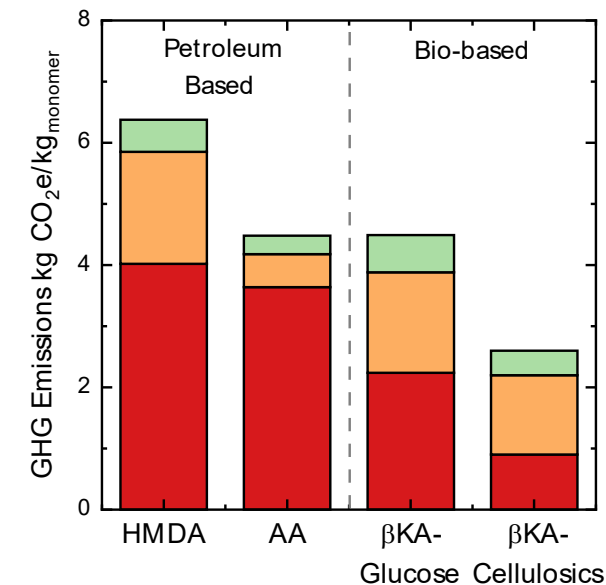
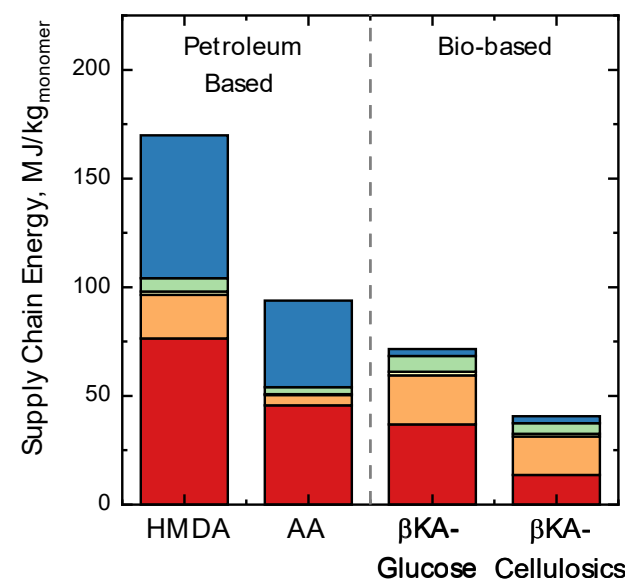
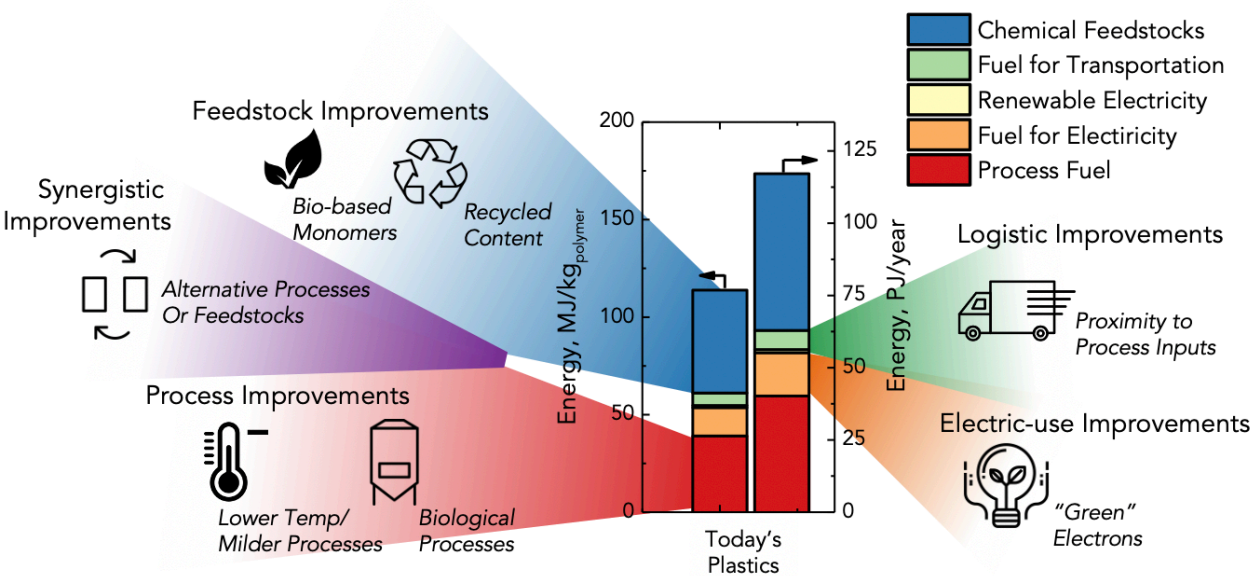
Production of β KA – Minimum Selling Price



β KA costs more than adipic acid and more from cellulosic sugars

- Feedstock is the largest contributor to cost
- The use of acid and base contribute to multiple other factors
- Different diacids from biological conversion have similar MSPs despite processing alternative separation strategies

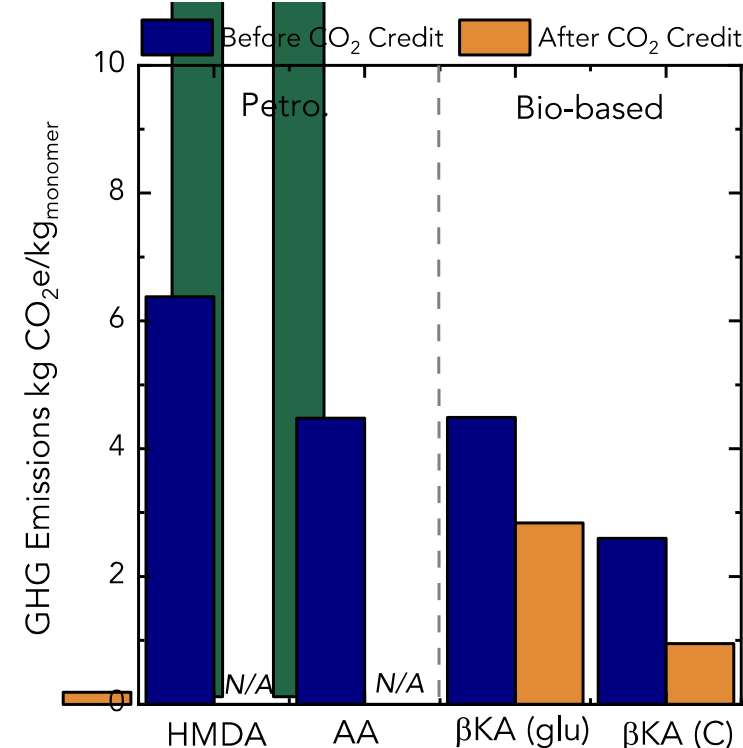
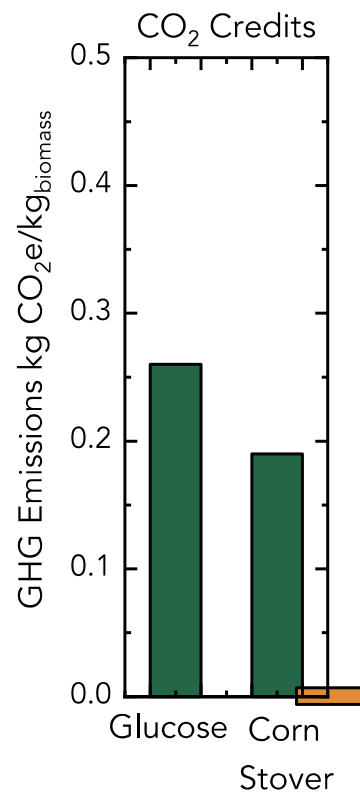
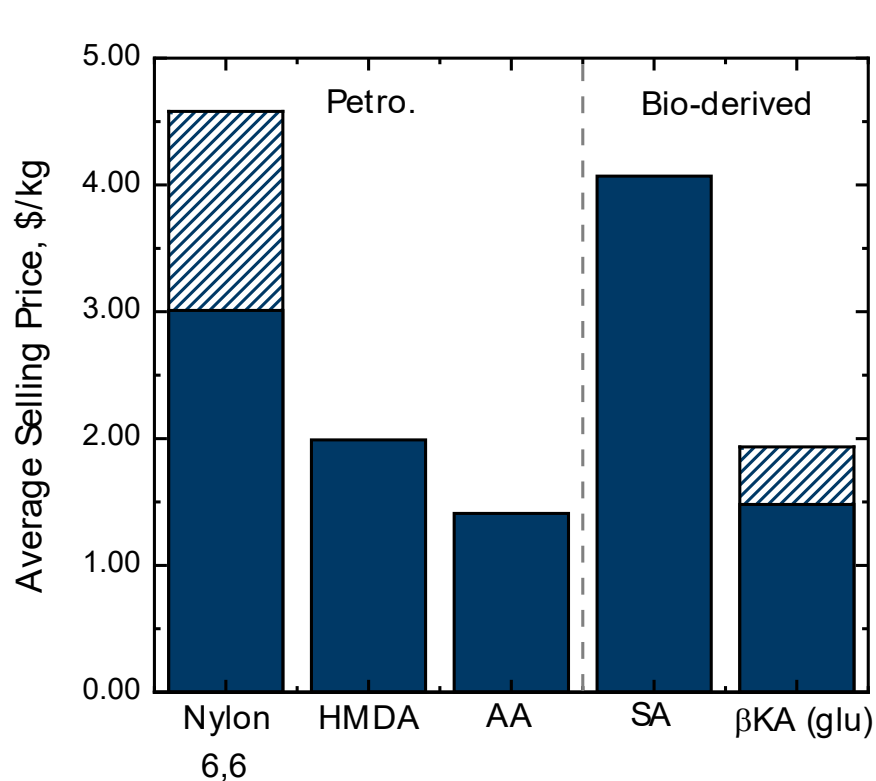
Performance-advantaged nylons – advantages in manufacturing



The use of βKA can reduce supply chain energies and GHG emissions

- Supply chain energies and GHG emissions depend on feedstock: in all cases, they are lower for bio-based monomers
- Trends are similar for the produced polymers
- Significant potential to target N-containing monomers in future work (HMDA)

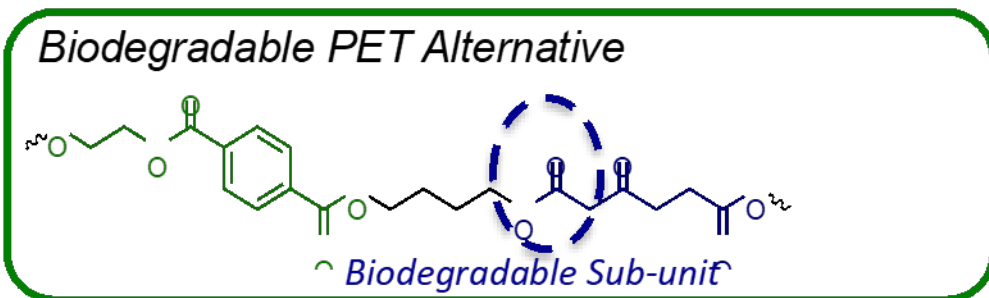
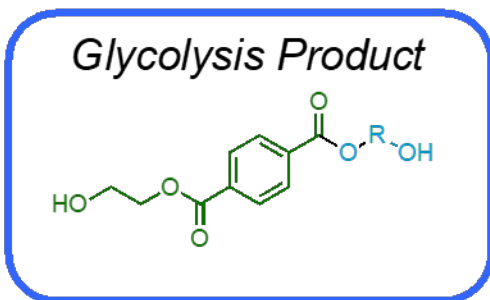
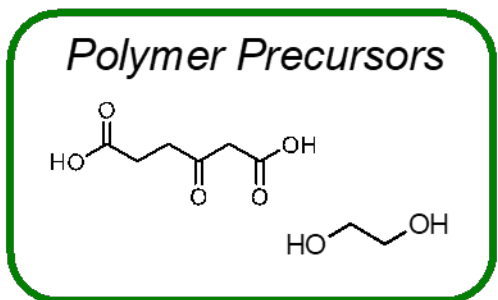
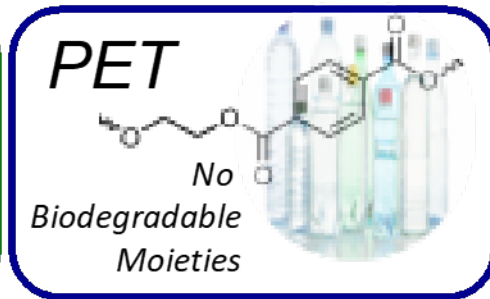
Engineering plastics – An ideal first market



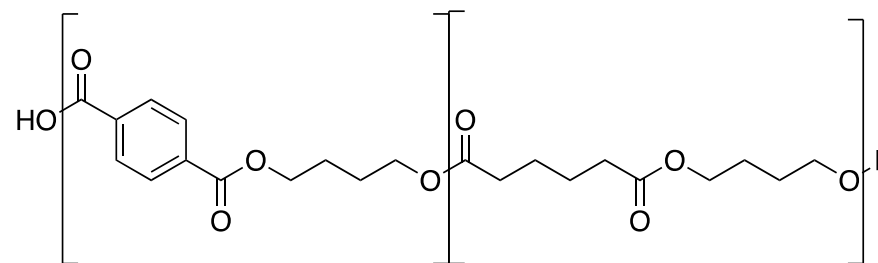
Extend analysis reveals further benefits

- Nylons are often heavily formulated and can demand a price premium
- β KA could sell for less than sebacic acid currently demands on the market. Sebacic acid has already experienced market penetration in nylon-6,10
- When CO₂ credits for biomass cultivation are accounted for there is a great GHG reduction potential

On-Going Efforts - Leveraging the β -Ketone in Polyesters



Poly(butylene β -keto adipate) [PBKAT]

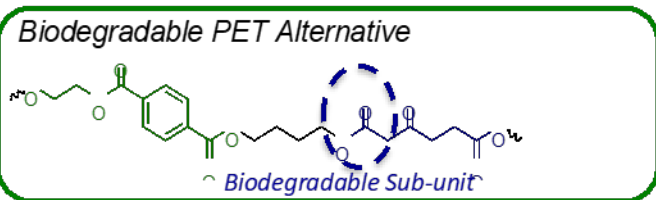
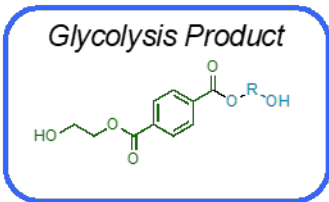
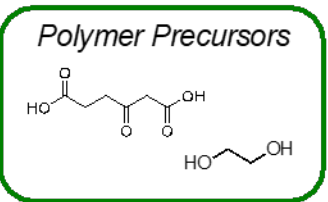
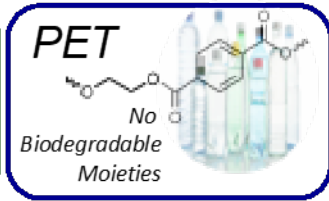


PBAT 'Biodegradable Polyethylene Replacement'
 $T_g - 40^\circ\text{C}$

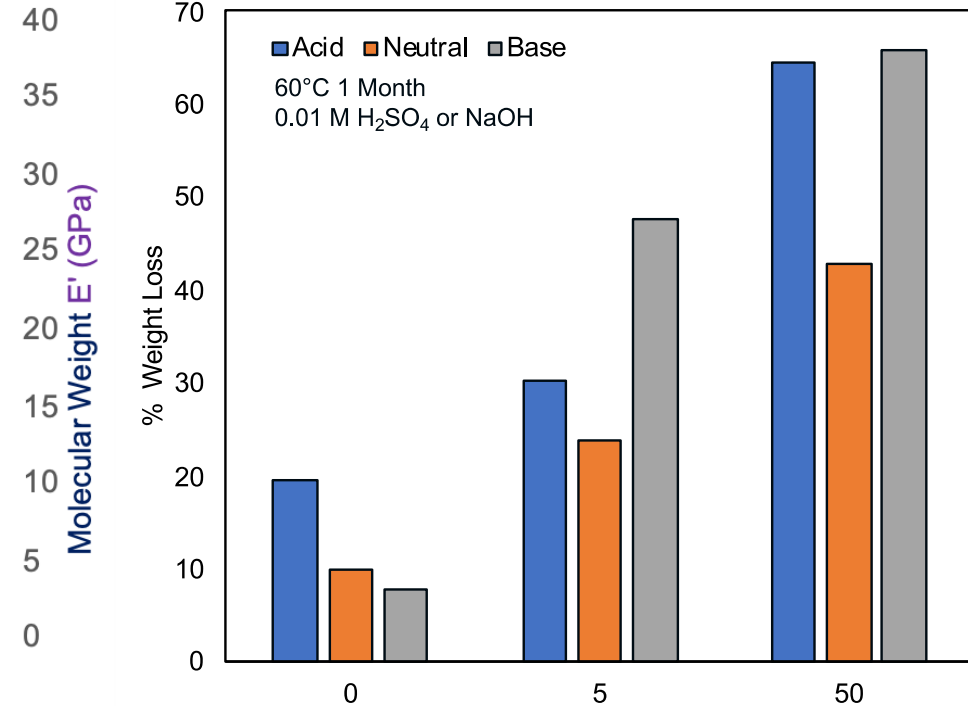
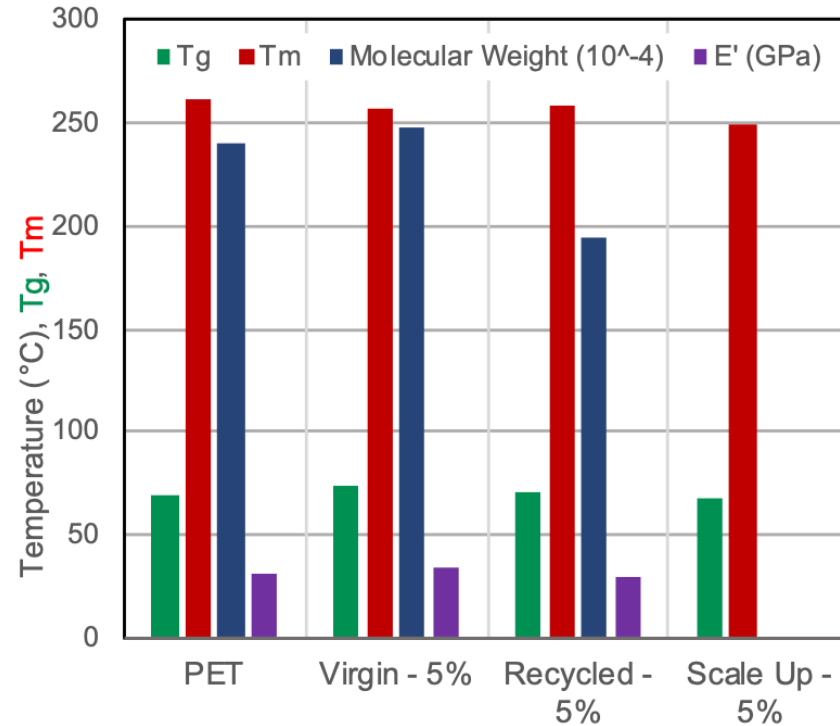
β -Ketones Can Maintain Polyester Properties, Yet Enable Degradation

- When Adipic Acid is placed into PET, the polymer is extremely plasticized.
- Designing polymers for degradability is a balancing act between performance and degradation
- When β KA is put in place of adipic acid in PET, it can maintain properties while enabling facile degradation
- Can we further leverage chemically recycled PET to decarbonize the manufacture of this new polymer in the second plus life?

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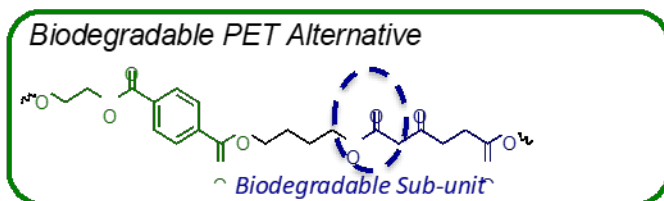
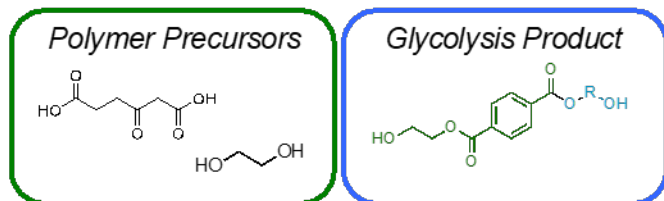
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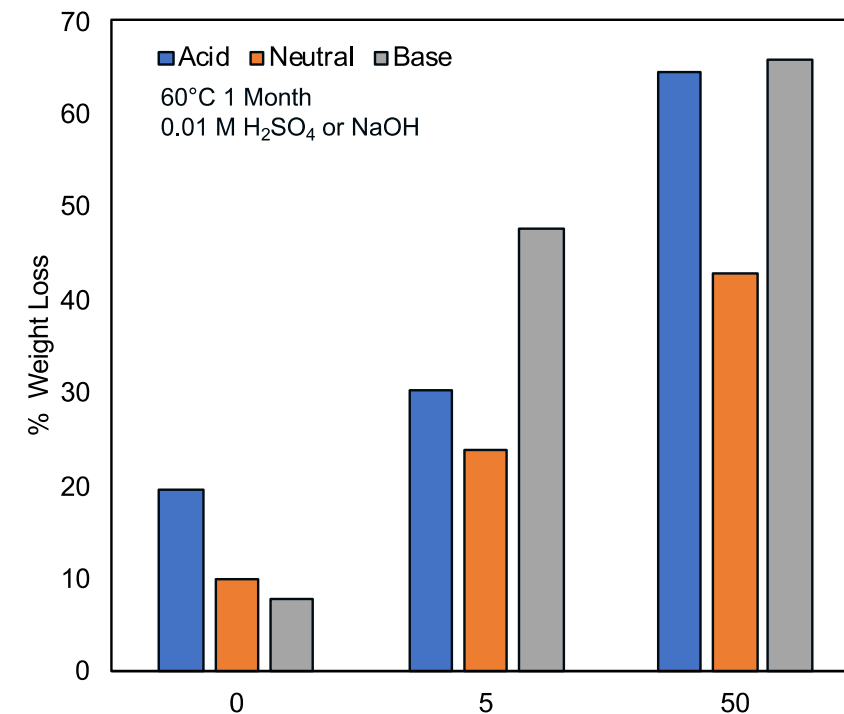
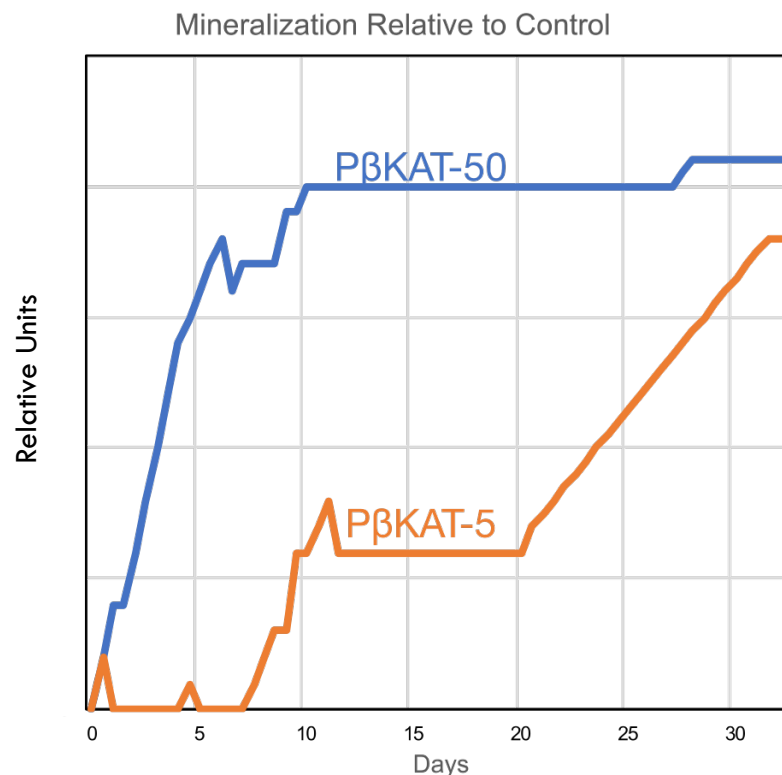
β -Ketones Can Maintain Polyester Properties, Yet Enable Degradation

- Akin to the behavior we saw in nylons, β KA can raise the glass transition temperature relative to adipic acid. This in turn maintains the thermomechanical properties of PET up to a 50% β KA replacement
- The presence of β KA can enable faster acid and base degradation (relevant to chemical recycling) of the polymer overall due to its aliphatic nature

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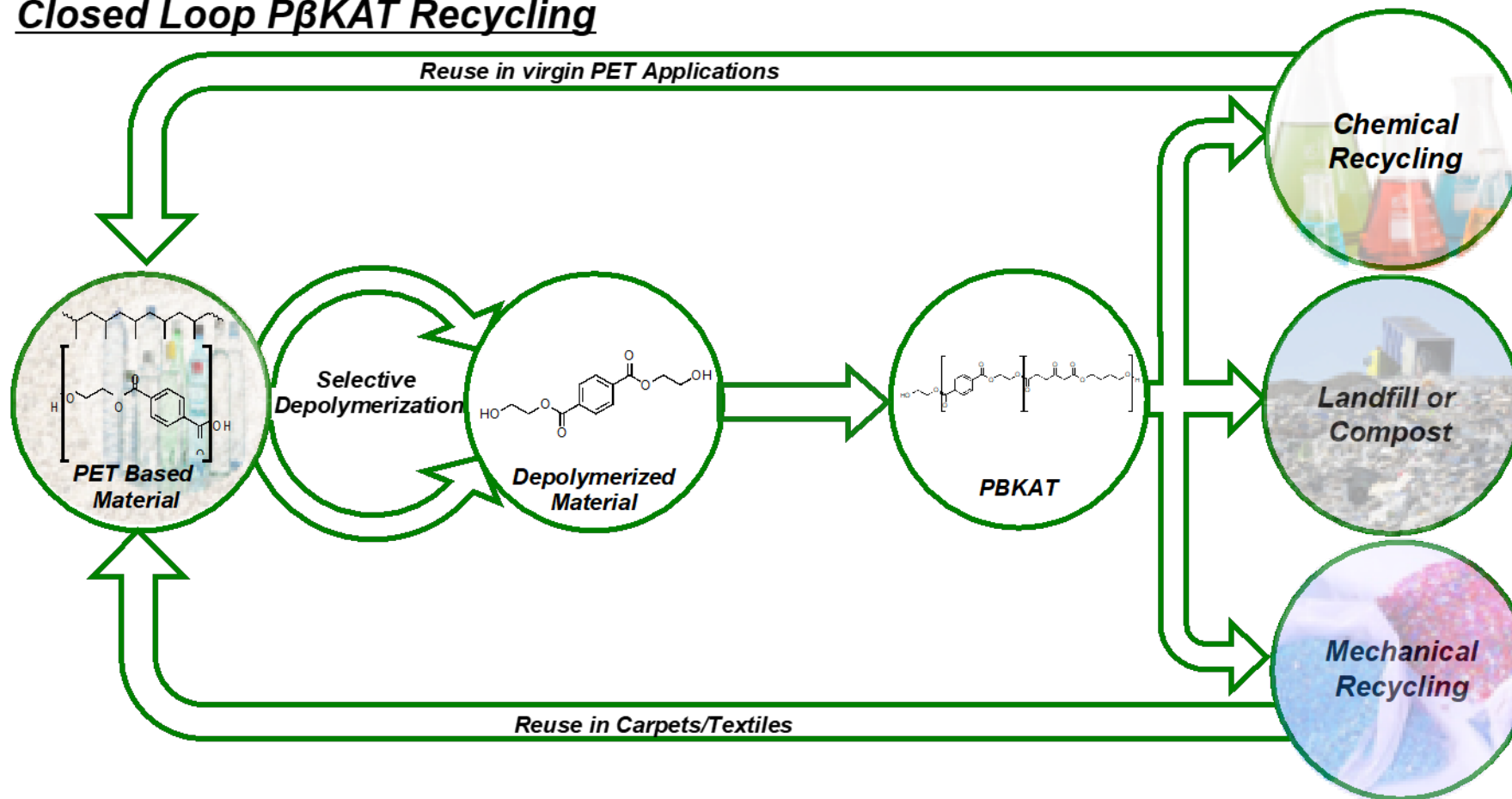


β -Ketones Can Maintain Polyester Properties, Yet Enable Degradation

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- The presence of β KA can enable faster acid and base degradation (relevant to chemical recycling) of the polymer overall due to its aliphatic nature
- **Initial Data** indicates that biodegradation can also occur in ambient conditions and is once again relative to the amount of β KA

On-Going - Leveraging the β -Ketone in Polyesters

Closed Loop P β KAT Recycling



PET Replacements MUST Not Ruin Existing Infrastructure

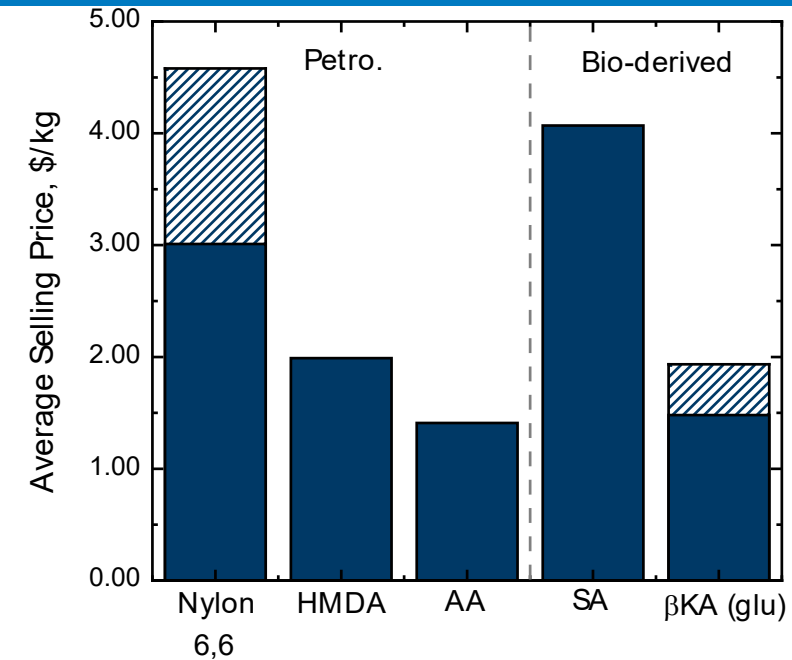
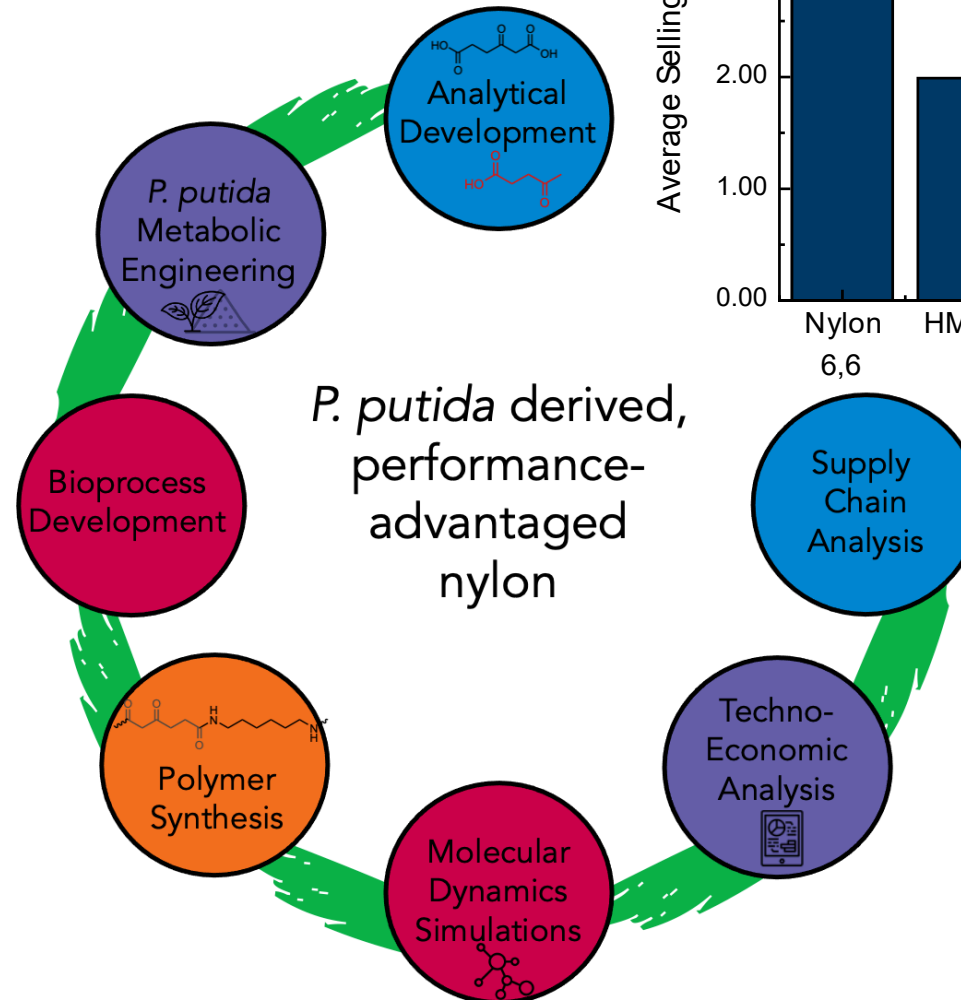
An ideal PET replacement needs to not be designed to be thrown away, but to work with existing infrastructure meaning it must be suitable to mechanical recycling

- Thus, not only does the thermomechanical performance have to be on par, but so does its recycling performance

Conclusions – Leveraging New Platform Chemicals

β ka can enable robust properties for engineering plastics

- An integrated approach to performance advantaged materials elucidates key challenges in new platform chemicals
- β -ketones provide rigidity across multiple backbone carbons and further interactions across polymer chains
- β -ketone diacids may be used in other applications to enhance T_g relative to adipic acid (e.g. PBAT)
- Designing new plastics must balance not only performance properties but
- Engineering Plastics are an ideal market for performance advantaged bioproducts from both economic and emissions perspectives



Thank You!

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