Developing Renewable Bioplastics from Bio-Derived Monomers

Preeti Jain[1], Charles Fields IV[2], Pranabesh Sahu[3], Kirk Snavely[1], Hyun Jin Lee[1], Raul Lobo[2], Tim Dawsey[3], Ram Gupta[3], and Bala Subramaniam[1,4*]

(1) Center for Environmentally Beneficial Catalysis (CEBC), University of Kansas, Lawrence, KS, (2) Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, (3) National Institute for Materials Advancement (NIMA), Pittsburg State University, Pittsburg, KS, (4) Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS

Introduction

- New eco-friendly materials and technologies are urgently needed to prepare and recycle/upcycle the plastics through the value chain enabling a circular economy. This research emphasizes sustainable ways to turn non-food biomass into recyclable polymers. The focus of this work is to make bio-derived **4,4'-Biphenyldicarboxylate (BPDC)** based co-polyesters and aramid resins with improved heat resistance, strength, mechanical, and gas barrier properties.
- The goal of this work is to develop a process for making **4,4'-Biphenyldicarboxylic acid (BPDA)** from **4,4'-Dimethylbiphenyl (DMBP)**, produced by University of Delaware (UD) researchers (project collaborators) from C5 sugar-derived 2-methyl furan and esterify the **BPDA** to polymer grade **BPDC** for supply to Pittsburg State University (PSU) researchers (project collaborators) to make new polyesters.

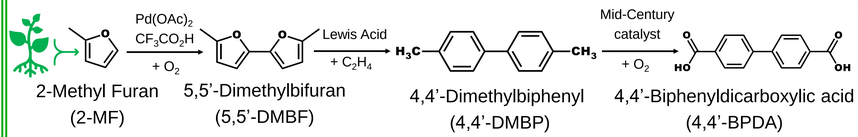
Approach

- The DMBP molecule, synthesized from bio-derived 2-methyl furan, has two *p*-methyl groups like *p*-Xylene (*p*X), the precursor for terephthalic acid (TPA) monomer used to make polyethylene terephthalate (PET). Therefore, it should be possible to produce the **4,4'-Biphenyldicarboxylic acid (BPDA)** from **4,4'-Dimethylbiphenyl (DMBP)** by the Mid-Century (MC) process chemistry used to make TPA.
- The BPDA is esterified with methanol and H_2SO_4 in a Zr Parr reactor (corrosion resistance with H_2SO_4) operated in batch mode to make polymer grade BPDC (m.p. – 217 °C) suitable to produce co-polyesters.

Research Overview

Synthesis of DMBP monomer
[Cho, Hong Je, Raul F. Lobo et al. *ACS Sus Chem & Eng 9, (2021): 3316*]

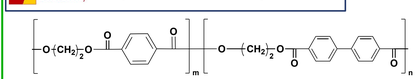
KU Synthesis of BPDA



KU Synthesis of BPDC polymer precursor

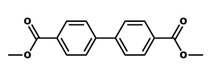
CH_3OH , H_2SO_4

Pittsburg State University Synthesis of Polyesters



Modified Polyethylene Terephthalate

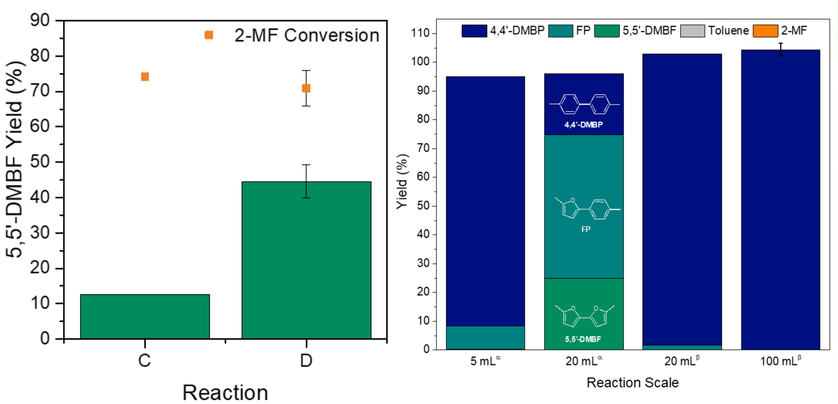
$Ti(OBu)_4$



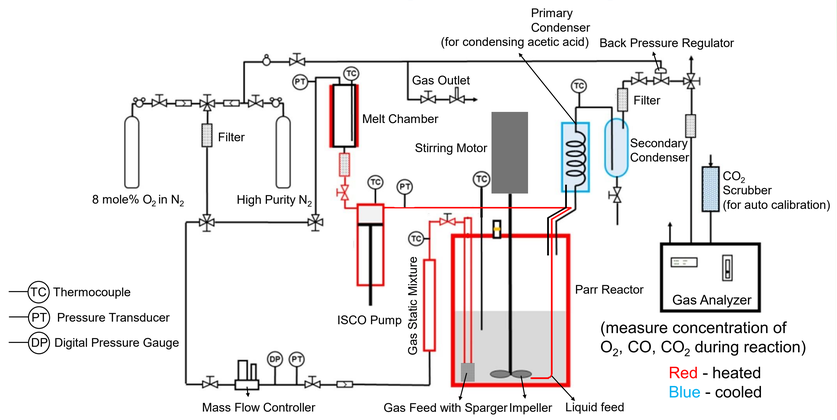
4,4'-Biphenyldicarboxylate
(4,4'-BPDC)

Synthesis of Bio-based DMBP

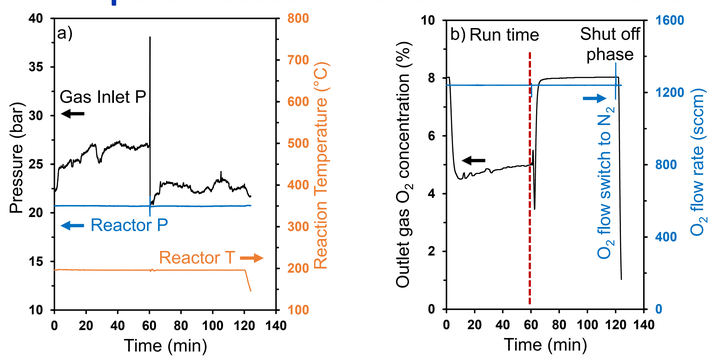
Oxidative Homocoupling of 2-MF **Diels-Alder and Dehydration of 5,5'-DMBF**



DMBP Oxidation by Mid-Century Process

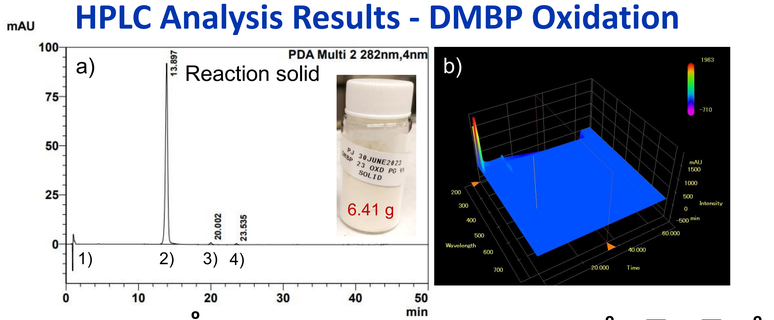


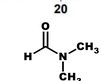
Temporal Reactor Data for DMBP Oxidation

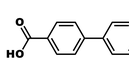


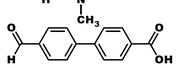
Reaction Conditions: Catalyst amount : Co = 0.354 mmol, Mn = 0.379 mmol, Br = 0.435 mmol, DMBP = 0.48 mmol/min, Aq. AcOH (95%) = 0.384 mol, 8 mole % O_2 in N_2 flow rate = 1200 sccm

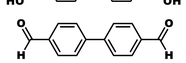
HPLC Analysis Results - DMBP Oxidation



1) DMF 

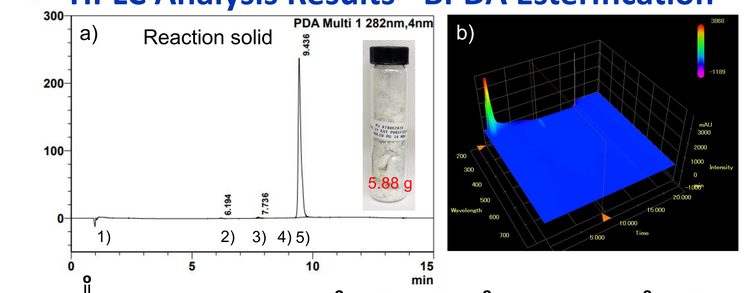
2) BPDA/di-acid 

3) Ald-acid 

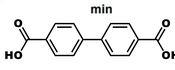
4) Ald-ald 

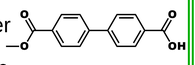
DMBP Conversion (%)	BPDA Yield (%)	BPDA Purity (%)
100	91.2	98.7

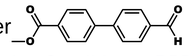
HPLC Analysis Results - BPDA Esterification

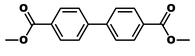


1) DMF 

2) BPDA/Di-acid 

3) Acid-ester 

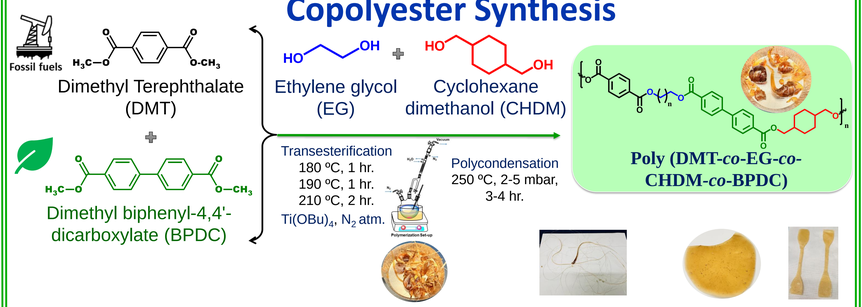
4) Formyl ester 

5) Di-ester 

Reaction Conditions: BPDA = 0.023 mol, Methanol = 3.63 mol (>100x excess), Conc. H_2SO_4 = 0.0147 mol, T = 120 °C, *t* = 6 h, Stirrer speed: 500 rpm with Zr baffle

BPDA Conversion (%)	BPDC Yield (%)	BPDC Purity (%)
99.6	92.4	99.4

Copolyester Synthesis



Summary

- Bio-derived DMBP was successfully synthesized from 2-methyl furan by UD researchers with 100% yield towards DMBP.
- High purity (98.7%) BPDA produced by continuously co-feeding DMBP in the melt phase into the reactor operated at process conditions similar to the Mid-Century (MC) process for terephthalic production suggests that BPDA can be produced industrially via the MC process.
- Polymer-grade BPDC (99.4% purity) produced by BPDA esterification successfully used by PSU researchers as a co-monomer with dimethyl terephthalate (DMT) to produce copolyesters.

Acknowledgements

Work is supported by the National Science Foundation under Grant No. OIA – 2119754.