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Chemical Upcycling of Polymers Roundtable Update

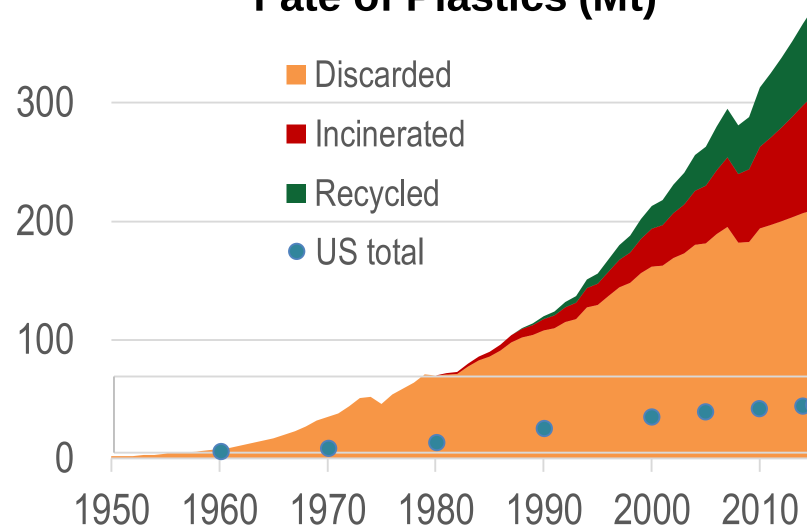
Briefing to BESAC

Phillip Britt
Oak Ridge National Laboratory
July 11, 2019

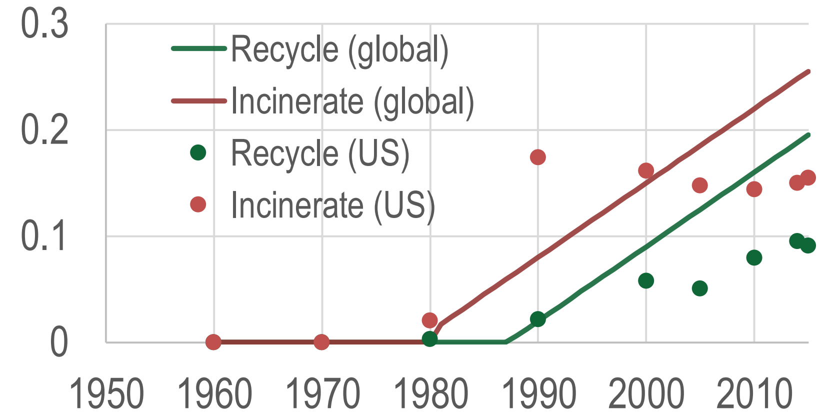
The Plastic Challenge – Reducing Accumulated Waste; Displacing Use of Energy Feedstocks

- Large and growing global production volume
  - Current production >400 Mt/year (~50 kg/human/year); US about 6-7% of global
  - Production rate increases ~6% per year
  - Cumulative production ~8000 Mt
- Majority of waste plastic is discarded
  - Current recycled: ~20% globally, ~10% US; incinerated: ~25% globally, ~15% US
  - Since 1950: <10% recycled
- Significant discharge to the environment
  - Mass of plastics in oceans > fish by 2050
- Production consumes large amounts of fossil feedstocks and energy
  - About 4% of oil produced goes to plastics; shifting from oil to natural gas
  - Recycling can reduce global energy use (the currently ~2% reduction could become ~9%)

Estimated Global Production and Fate of Plastics (Mt)



Estimated Fraction Recycled/Incinerated



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Data from Geyer et al. *Sci Adv* **3(7)**, e1700782 (2017) (http://advances.sciencemag.org/content/3/7/e1700782.full)

Plastics Wastes Represent a Largely Untapped Resource, Chemical Upcycling Presents an Opportunity to Exploit it

- Polymers are the backbone of plastic materials
  - High chemical, thermal, and mechanical stability make them great for their intended use but difficult to deconstruct and /or repackage
- Incineration and biodegradation consume a valuable feedstock and produce unwanted byproducts
  - Incineration recovers only ~ ½ of energy saved by recycling
  - Biodegradation of current plastics can take hundreds of years, motivating the need to design new polymers
- Mechanical recycling – a process of melting and extruding the material – downgrades polymers, limiting the recycle rate
- **Chemical upcycling** holds the promise of shifting the paradigm to energy-efficient production of chemicals and materials from plastic wastes instead of fossil feedstocks

87% of Plastics Are Made From 6 Polymers

Recycle Code	Polymer	Major Use	Prod	Recycle Rate (US)
1	PET	Packaging	10%	20%
2	HDPE	Packaging	16%	10%
3	PVC	Building	12%	0%
4	LDPE	Packaging	20%	5%
5	PP	Packaging	21%	1%
6	PS	Packaging & Building	8%	1%
7	Other	Various	13%	Varies

BES Roundtable on Chemical Upcycling of Polymers
April 30 - May 1, 2019 Bethesda, MD

Workshop Chair: Phillip Britt (ORNL)
Co-Chairs: Geoff Coates (Cornell Univ.)
Karen Winey (Univ. of Penn.)
SC Technical Lead: Bruce Garrett



Charge:

- Assess the fundamental challenges that would enable transformation of discarded plastics to higher value fuels, chemicals, or materials
- Identify fundamental research opportunities in chemical, materials, and biological sciences that will provide foundational knowledge leading to efficient, low-temperature conversion of discarded plastics to high-value chemicals, fuels, or materials
- Identify research opportunities for the design of new polymeric materials for efficient conversion, after end of life, to high-value chemicals or materials

Organization of Chemical Upcycling of Polymers

Attendance: Participants (23) from Universities (14), National Laboratories (6) and Industry (3) and Observers (29)

Panel 1: Design chemical mechanisms to deconstruct polymers and create targeted molecular intermediates as building blocks for new products

– Aaron Sadow, Iowa State University

Panel 2: Design of integrated processes that target the creation of desired end-products from waste polymers

– Susannah Scott, University of California Santa Barbara

Panel 3: Design of new polymeric materials that are easily separated and upcycled

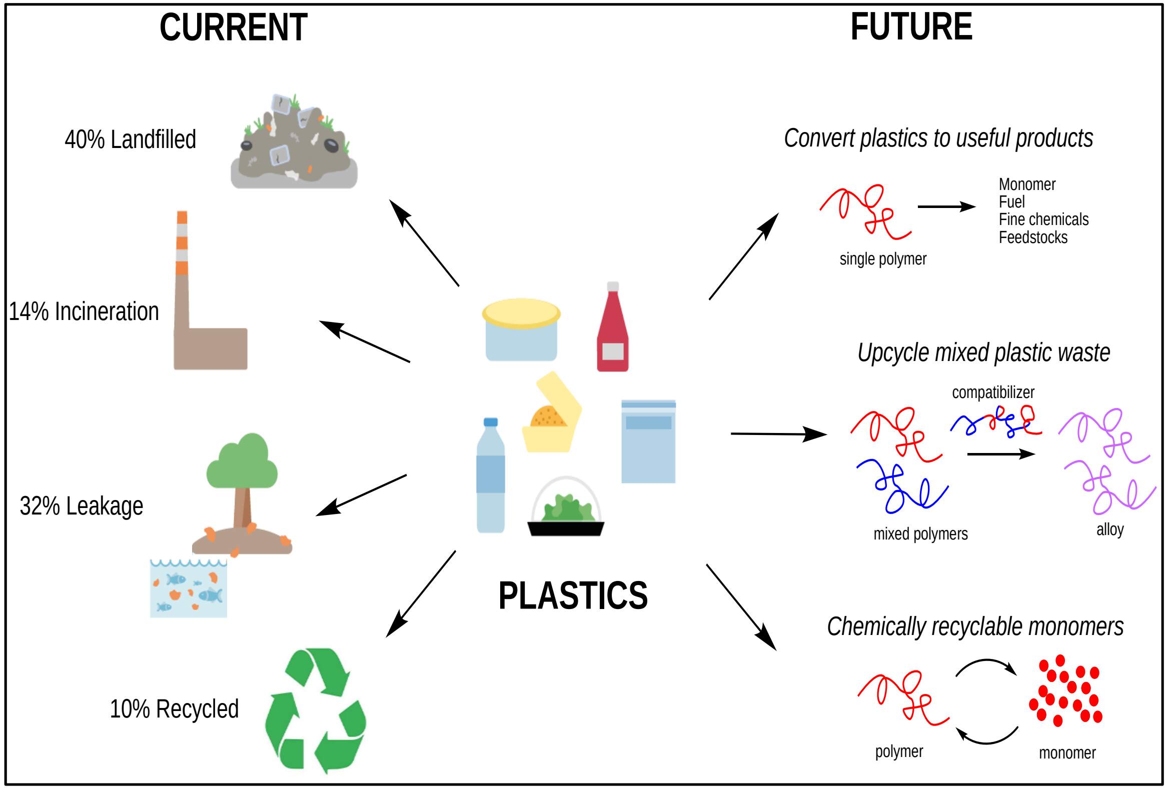
– Bryan Coughlin, University of Massachusetts Amherst

Cross-cut: Advance experimental, computational and data science approaches for upcycling of polymers

– Dion Vlachos, University of Delaware

Draft Priority Research Opportunities (PROs)

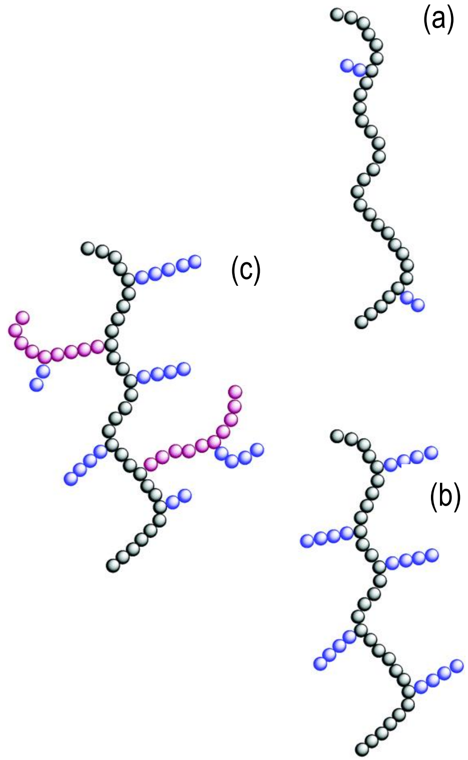
- **PRO 1:** Design reaction pathways to selectively transform single polymer waste streams into new products
- **PRO 2:** Understand and design integrated processes to upcycle mixed polymer waste
- **PRO 3:** Design next generation of polymers for chemical circularity
- **PRO 4:** Develop novel tools to discover and control chemical mechanisms for macromolecular transformations



PRO 1: Design Reaction Pathways to Selectively Transform Single Polymer Waste Streams into New Products

How do we design selective chemical transformations to convert single polymer waste streams into desirable products?

- Challenges
  - Plastics are designed to be recalcitrant: chemically and thermally stable, insoluble and high melting
  - Selective transformations of large, relatively undifferentiated repeat units in the macromolecules (e.g., cleavage and functionalization of C-C, C-H, and C-O/N bonds)
  - Feedstock is a distribution of large molecular weights, while many of the desired products are smaller and single sized
  - Additives are designed to prevent polymer degradation and improve properties (antioxidants, flame retardants, plasticizers, fillers, pigments, etc.)



(a) High Density (HD) Polyethylene (PE), (b) Linear Low Density (LLD)PE, and (c) Low Density (LD)PE.
Eselem Bungu, P. S.; Pasch, H. *Polym. Chem.* **2018**, *9*, 1116-1131

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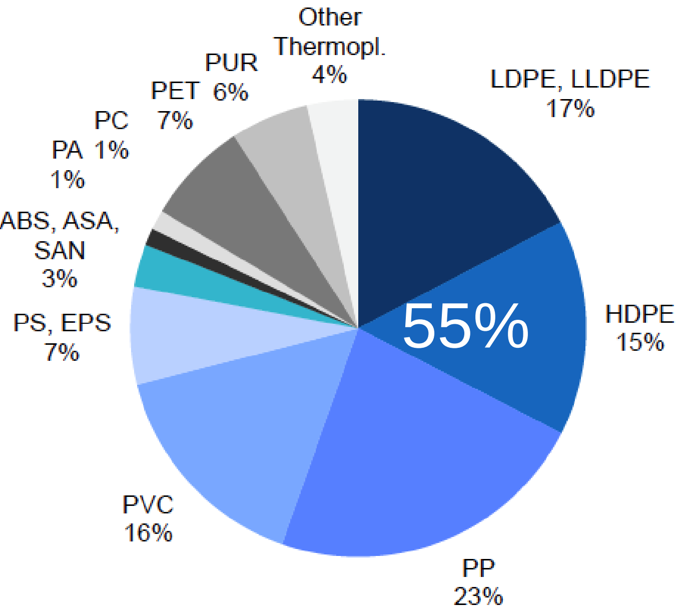
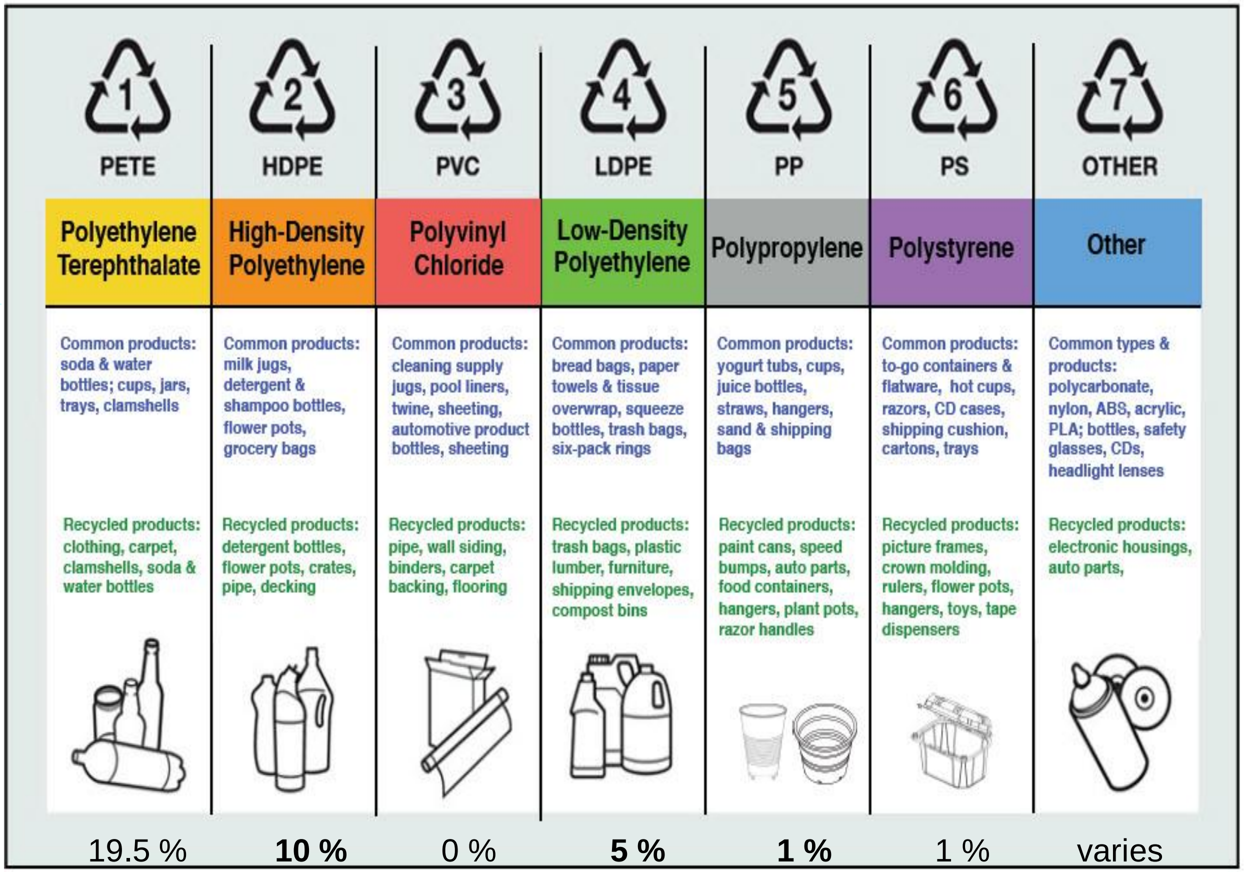
Focus on Polyolefins: Dominate Single-Use Plastics are Challenging to Recycle

Plastic production



Plastic Resin Identification Codes

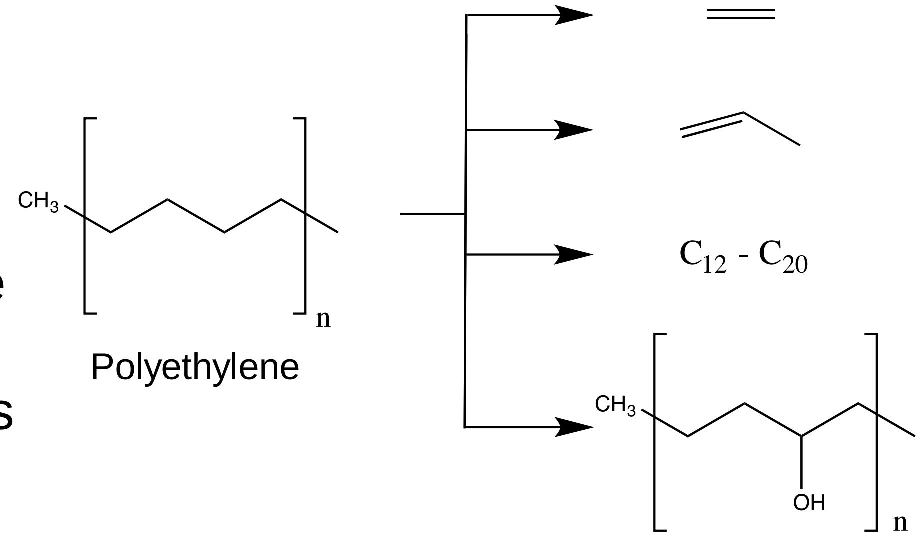


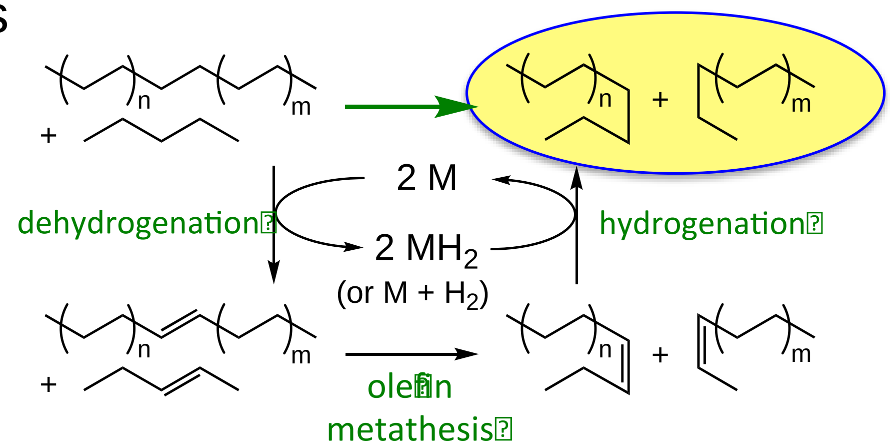
- Packaging (i.e., single use) is largest application of plastics (40%)
- Polyolefins are the dominant plastic used in packaging (69%)

https://www.bluelinelabels.com/glossary-of-resins-containers-decorating/

PRO 1: Design Reaction Pathways to Selectively Transform Single Polymer Waste Streams into New Products

- Design robust catalysts and chemical processes to:
  - Selectively react with recalcitrant bonds in polymers to produce the original monomer, a new monomer, chemical intermediates or fuels, or directly create new materials
  - Selectively functionalize polymers at a precise location
- Develop tandem reactions involving multiple catalyst to selectively depolymerize and repolymerize waste plastics



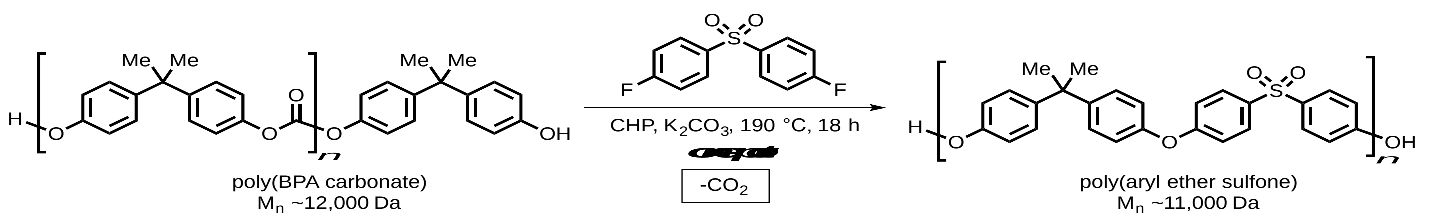


Courtesy of Alan Goldman

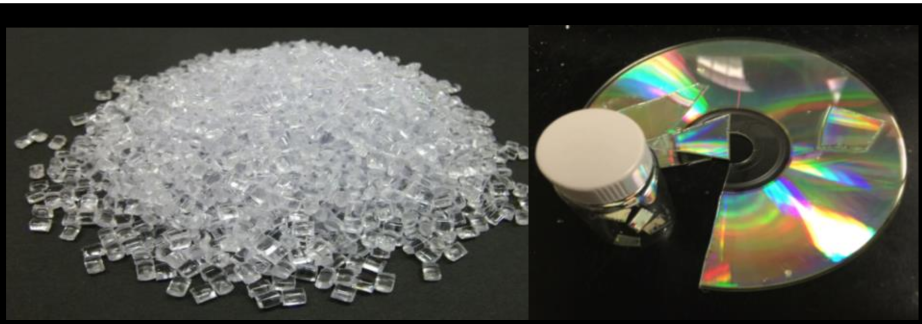
PRO 1: Design Reaction Pathways to Selectively Transform Single Polymer Waste Streams into New Products

- Develop a mechanistic understanding of the deconstruction/ depolymerization reactions to inform the design and development of next-generation catalyst or chemical process
- Develop catalysts and processes to directly react with solid polymerics and viscous polymer melts

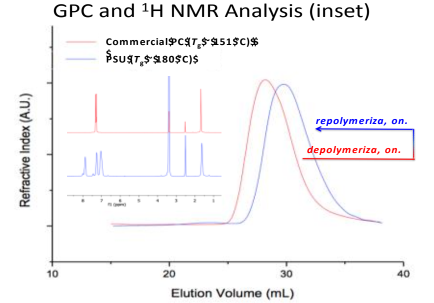
Waste polycarbonate for polysulfone production



CHP, *N*-cyclohexyl-2-pyrrolidone



GPC and [1]H NMR Analysis (inset)



With G. Jones,
Proc. Natl. Acad. Sci. 113, 7722-7726 (2016).

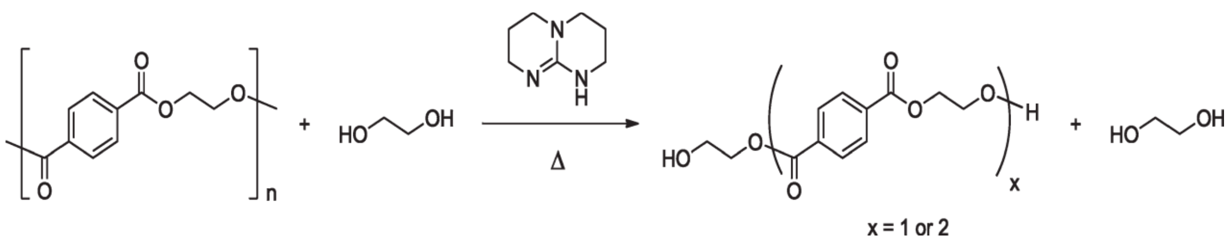
PRO 2: Understand and Design Integrated Processes to Upcycle Mixed Polymer Waste

How can we directly transform mixed polymer waste to desirable products?

- Challenges
  - Design chemical processes to extract valuable products from mixtures of waste polymers
  - Selective chemical transformations (solubilization, functionalization, depolymerization, etc.) of individual components or classes of components in mixtures of waste polymers
  - Control the compatibility between different polymer types (immiscibility, reactivities, etc.) to obtain new materials with desired materials properties
  - Presence of trace impurities and/or additives

PRO 2: Understand and Design Integrated Processes to Upcycle Mixed Polymer Waste

- Design robust catalysts and chemical processes to create unique products with high value by taking advantage of the multiple components in a waste polymer mixture
- Design processes and selective catalyst than will only react with one polymer in a complex mixture
  - IBM has developed a process (VolCat) that separates contaminants (e.g., food residue, glue, dirt, dyes, and pigments) from PET and produces pure monomer in an energy-efficient cycle



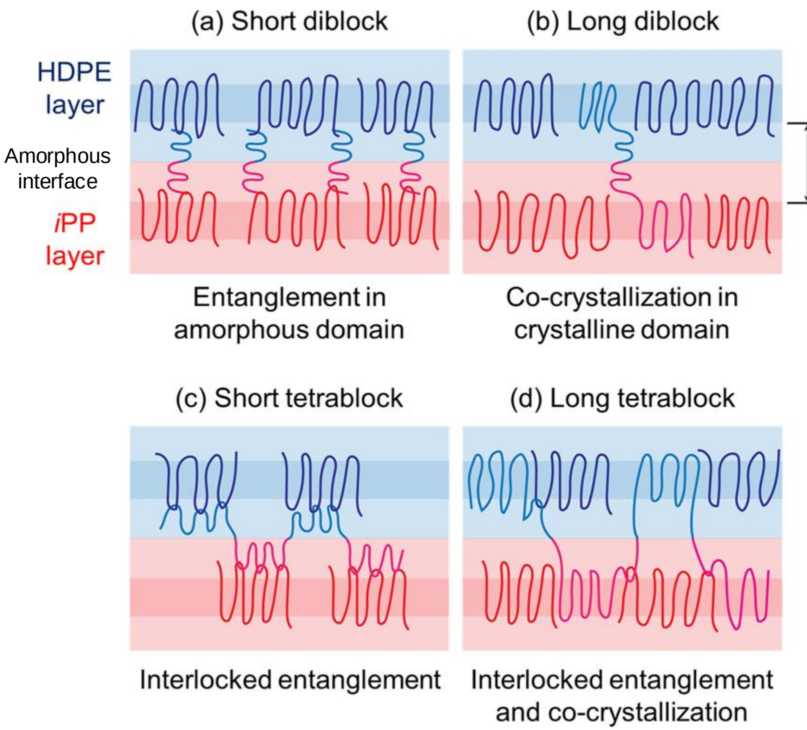
Polyethylene terephthalate (PET)

Bis(2-hydroxyethyl) terephthalate

- Design integrated catalytic transformations and separations for polymer mixtures to obtain higher-value products

PRO 2: Understand and Design Integrated Processes to Upcycle Mixed Polymer Waste

- Understand molecular interactions between complex mixtures of (immiscible) polymers through structure-property relationships to design compatibilizers (and reactive compatibilizers) to create new products
- Design tandem reaction that take advantage of a combination of chemocatalytic, biocatalytic, and thermal transformations to transform mixed polymer waste to higher value products



Xu, J. et al. *Macromolecules* **2018** *51*, 8585

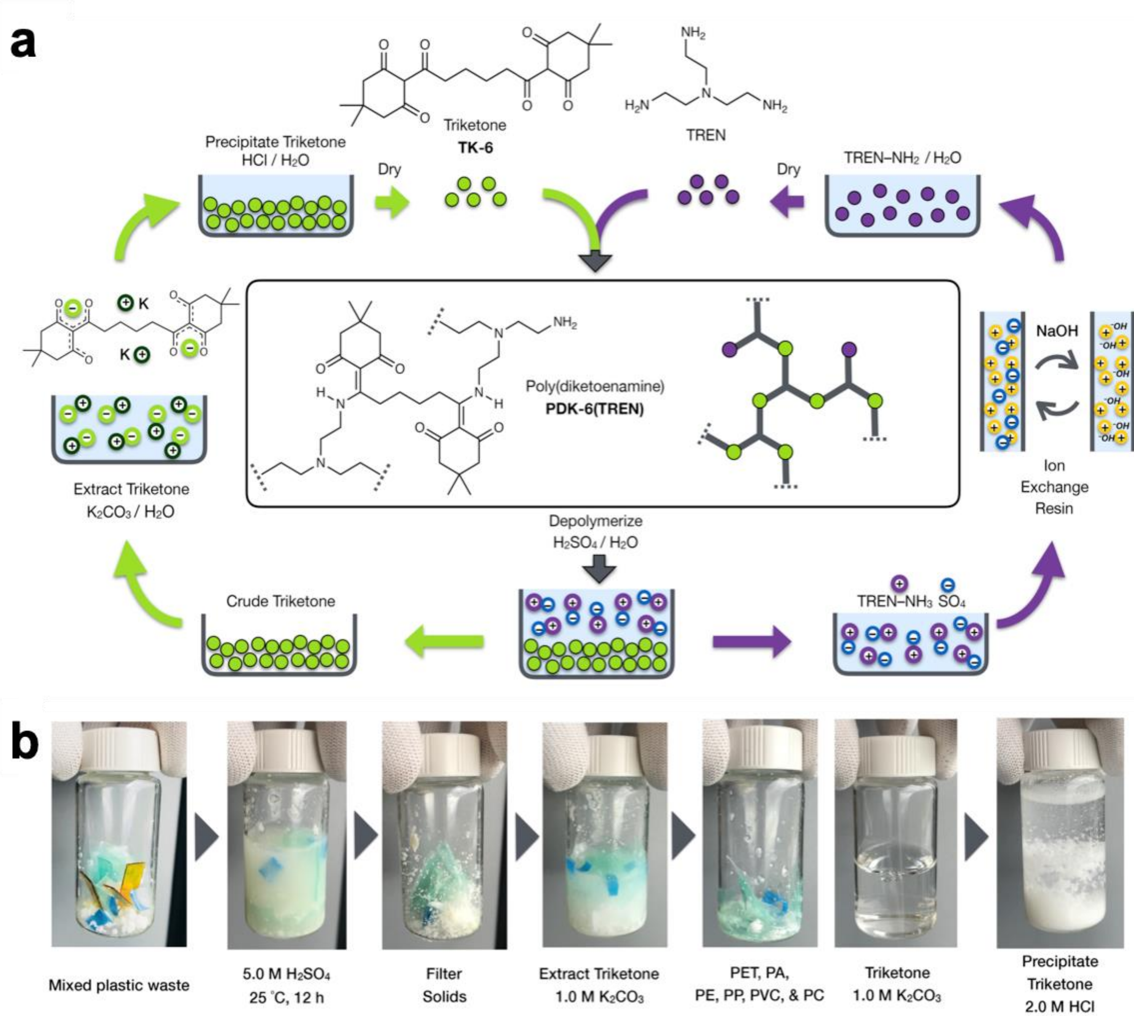
PRO 3: Design Next Generation of Polymers for Chemical Circularity

How can we design new polymers with chemical circularity that can be repeatedly deconstructed and remanufactured into polymers with desirable properties?

- Challenges
  - Design and synthesis of polymers with properties similar to or better than current materials that can be selectively depolymerized and separated from additives to yield repolymerizable virgin monomers or intermediates for chemical circularity
  - Design and deconstruction of complex multi-material products
  - Develop recyclable thermosets, which are currently not recyclable or reprocessable, with similar properties and performance to current materials

PRO 3: Design Next Generation of Polymers for Chemical Circularity

- Design and develop new strategies for depolymerization and repolymerization to achieve chemical circularity based on selectivity, tolerance to impurities, and atom- and energy-efficiency



Christensen, P. R. et al. *Nat. Chem.* **2019**, *11*, 442

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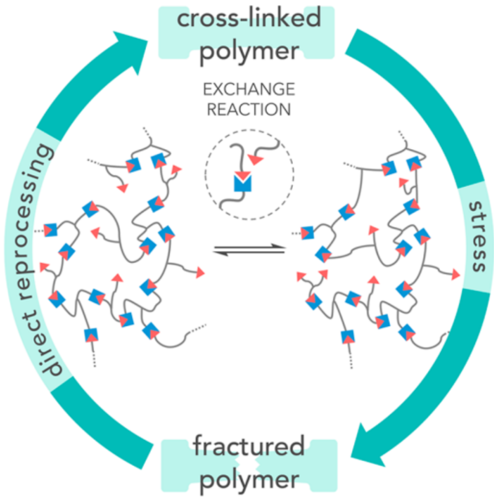
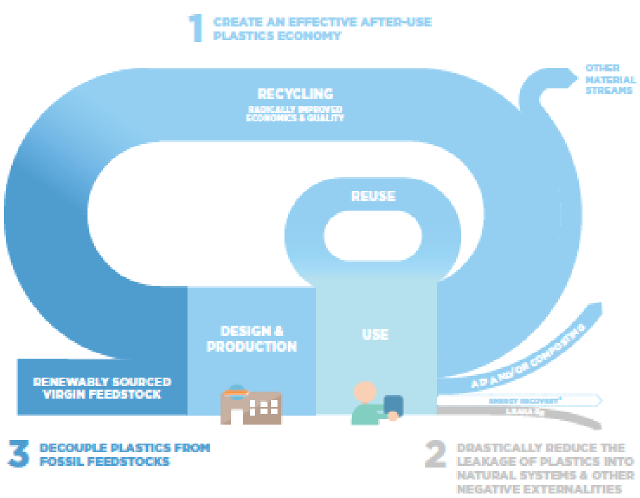
PRO 3: Design Next Generation of Polymers for Chemical Circularity

- Understand, design and develop reversible polymer chemistries that go beyond the current state-of-the-art
- Integrate renewable feedstocks into polymer designs to improve sustainability and enable biodegradability and monomer recovery for chemical circularity
- Develop strategies to depolymerize polymers in response to a stimulus (temperature, light, pressure, etc.) or embedded catalyst to enhance recovery of monomers or intermediates



Fortman, D. J. et al. *ACS Sustainable Chem. Eng.* **2018**, *6*, 11145



The New Plastic Economy: Rethinking the Future of Plastics, World Economic Forum 2016

PRO 4: Develop Novel Tools to Discover and Control Chemical Mechanisms for Macromolecular Transformations

What experimental and computational tools are needed to elucidate the macromolecular transformations of plastics in complex, non-equilibrium media?

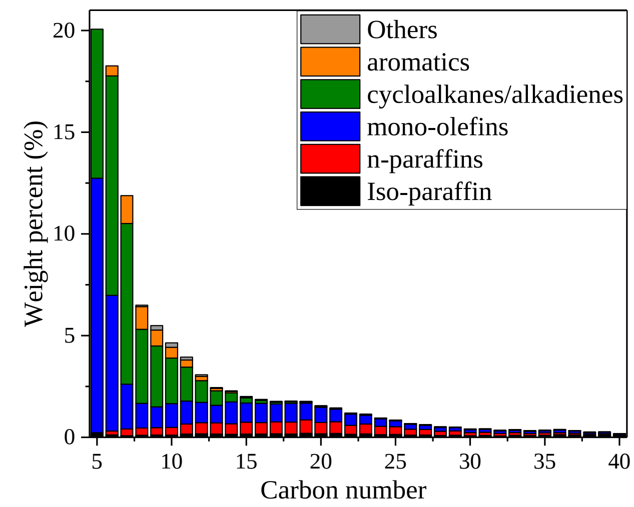
- Challenges
  - Understand and predict the fundamental interactions and reactions between plastics and their environment which span multiple length and time scales, ranging from bond breaking and making to intramolecular and intermolecular interactions among chains to conformational changes of chains to evolving interfaces as plastics begin to react
  - Understand reaction mechanisms which require experimental and computational tools that enable simultaneous, real time, in-situ or operando speciation quantification
  - Predict the structure-property relationship of macromolecules
  - Understand complex reaction networks for polymer transformations
  - Understand nonequilibrium processes and dynamics of polymer

PRO 4: Develop Novel Tools to Discover and Control Chemical Mechanisms for Macromolecular Transformations

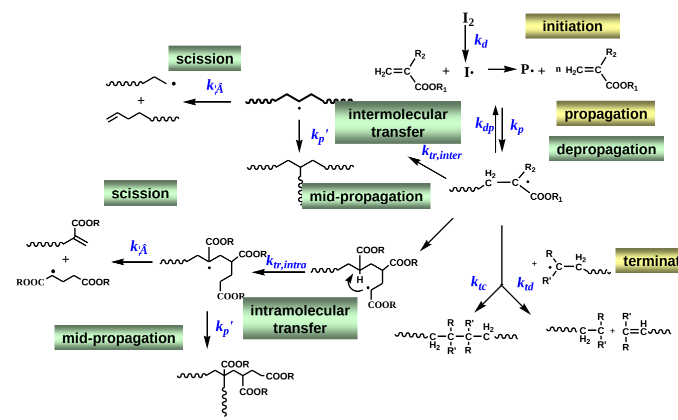
- Integrated experimental tools for in situ and operando monitoring and characterization in condensed phases
  - Analysis and quantitation of reaction intermediates for elucidation of reaction mechanisms and kinetics
  - Rheology during decomposition
  - Structure, dynamic and metastable behavior in synthesis and deconstruction by light and neutron scattering methods
- Predictive computational methods for understanding and predicting macromolecular transformations and properties including the ability to address non-equilibrium reaction/transport phenomena
  - Develop of scalable, predictive, multiscale computations for condensed phase reaction
  - Develop *smart reaction networks* that actively learn the reaction paths and are self-parameterized
  - Develop methods to study evolution of interfaces over time and space

PRO 4: Develop Novel Tools to Discover and Control Chemical Mechanisms for Macromolecular Transformations

- Integration of experimental and computational data for mechanistic validation and prediction
  - Develop methods to understand how the polymer structure and properties evolve over time
  - Develop new targeted computational and data analysis methods that permit interpretation of chemical, spectroscopic, and structural data with realistic physical models
  - Develop computational tools to combine with multimodal experimental data



Liquid products produced from pyrolysis of polyethylene (Courtesy of George Huber)



BES Roundtable on Chemical Upcycling of Polymers

Current Status

- Brochure providing a high level summary of the workshop has been drafted
- Roundtable report is in preparation
- Content of report:
  - Executive Summary
  - Introduction
  - Priority Research Opportunities
  - Summary
- Factual document prepared