Chemical Upcycling of Polymers: A Basic Energy Sciences Perspective

NAS Workshop on Emerging Technologies to Advance Research and Decisions on the Environmental Health Effects of Microplastics

January 27-28, 2020

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Office of Basic Energy Sciences
Basic Energy Sciences

BES supports fundamental research to **understand, predict, and ultimately control matter and energy** at the electronic, atomic, and molecular levels in order to provide the **foundations for new energy technologies** and to support DOE missions in energy, environment, and national security. The BES program also **plans, constructs, and operates major scientific user facilities** to serve researchers from universities, national laboratories, and private institutions.

**Materials sciences & engineering** – exploring macroscopic and microscopic material behaviors and their connections to various energy technologies

**Chemical sciences, geosciences, and biosciences** – exploring the fundamental aspects of chemical reactivity and energy transduction over wide ranges of scale and complexity and their applications to energy technologies

**Scientific User Facilities** – the largest collection of facilities for electron, x-ray, and neutron scattering in the world

[https://science.osti.gov/bes/](https://science.osti.gov/bes/)
Core Research Divisions

Chemical Sciences, Geosciences, and Biosciences
- Ultrafast chemistry
- Chemistry at complex interfaces
- Charge transport and reactivity
- Reaction pathways in diverse environments
- Chemistry in aqueous environments

Materials Sciences and Engineering
- Quantum materials
- Theory, modeling & simulation
- Nano- and meso-scale science
- Advanced instrumentation
- Materials synthesis

SUPPORTED RESEARCHERS
~6,200 Ph.D. scientists ~2,100 students supported

$787 MILLION RESEARCH BUDGET

OVER 1,100 CORE RESEARCH PROJECTS
Basic Energy Sciences: Scientific User Facilities

- Available to all researchers at no cost for non-proprietary research, regardless of affiliation, nationality, or source of research support
- Access based on external peer merit review of brief proposals
- Coordinated access to co-located facilities to accelerate research cycles
- Collaboration with facility scientists an optional potential benefit
- Instrument and technique workshops offered periodically
- A variety of on-line, on-site, and hands-on training available
- Proprietary research may be performed at full-cost recovery

Unique research facilities and scientific expertise for ultra high-resolution characterization, synthesis, fabrication, theory and modeling of advanced chemical and materials systems

$934 MILLION
Scientific User Facility Operating Budget

$369 MILLION
Facility Upgrades, Construction Budget

http://www.science.osti.gov/bes/suf/user-facilities
Upcycling of Polymers to Revolutionize the Lifecycle of Plastics
Plastics are Essential in Today’s World: Versatile, Durable, Light Weight, Cost Effective, …
The Plastics Challenge is Recognized Globally

Many recent examples of the call for action

Scientific community begins advancing new approaches to reduce plastic waste

Depolymerization of Waste Plastics to Monomers and Chemicals ...

Albertsso, Hakkarainen, Science, 2017, 358 (6365), 872

Monsigny, Berthet, Cantat, ACS Sustainable Chem. Eng. 2018, 68, 10481

Garcia, Robertson, Science, 2017, 358 (6365), 870

"Without fundamental redesign and innovation, at least 50% of plastic packaging items – or 30% of the market by weight – will never be reused or recycled" The New Plastics Economy – Rethinking the future of plastics (World Economic Forum, the Ellen MacArthur Foundation and McKinsey & Company, 2016)
The Plastic Challenge – Reducing Plastic Waste

Large and growing production volume

- Current annual production:
  - Global: >400 Mt (~50 kg/person/year)
  - US: >50 Mt
  - Global: ~36%
  - US: ~16%
- Cumulative production: ~8,000 Mt

Majority of used plastic is discarded

- Current amount recycled:
  - Global: ~20%  US: <10%

Significant discharge to environment

- ~32% of plastic packaging* is released to the environment
- Mass of plastics in oceans > fish by 2050

* Plastic packing is about 40% of all plastics

Estimated Fate of End-of-Use Plastics (Mt)

- ~55% Discarded into landfills/environment
- ~25% Incinerated
  - Energy recovered << energy to produce plastic
  - Unwanted byproducts produced

Mt = million (metric) tonnes = 2.2 billion pounds

Data from Geyer et al. *Sci Adv* 3(7), e1700782 (2017)
(http://advances.sciencemag.org/content/3/7/e1700782.full)
Production of polymers, the molecules that make up plastic materials, competes for fossil feedstocks with energy production

- Plastic production consumes about 4% of global oil and gas production as feedstock and an equivalent amount to transform the feedstock into products.

Production of polymers also consumes a significant amount of energy

- Energy use varies with chemical composition of polymers; production of a single plastic bottle uses about 1 kWh.
- Current PET (PETE in chart) production consumes ~1% of global energy.
- Total energy consumed to make plastics is up to 10% of energy produced globally.

Recycling reduces global energy use

- Recycling plastics uses less energy than making new plastics, currently saving the equivalent of about 2% of global energy production.

87% of plastics fall within categories 1-6.
Today’s Approaches for Reducing Plastic Wastes Have Limits

Incineration and biodegradation consume plastic – no recycling
- Incineration recovers only ~ ½ of energy saved by mechanical recycling
- Biodegradation of current plastics is slow; enhancement requires design of new polymers
- Both produce unwanted byproducts

Mechanical recycling downgrades polymers – limited future use
- The process of melting and extruding the material limits its use for polymers with lower melting temperatures

Chemical recycling – significantly increases the potential for future use
- The high stability of polymers make it difficult to deconstruct and/or reprocess
- Current energy-intensive (e.g., high-temperature) processes create simple molecular components, requiring further energy input to convert to valued products

<table>
<thead>
<tr>
<th>Recycle Code</th>
<th>Polymer</th>
<th>Major Use</th>
<th>Global Production</th>
<th>Recycle Rate (US)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PET</td>
<td>Packaging</td>
<td>10%</td>
<td>20%</td>
</tr>
<tr>
<td>2</td>
<td>HDPE</td>
<td>Packaging</td>
<td>16%</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>PVC</td>
<td>Building</td>
<td>12%</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>LDPE</td>
<td>Packaging</td>
<td>20%</td>
<td>5%</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>Packaging</td>
<td>21%</td>
<td>1%</td>
</tr>
<tr>
<td>6</td>
<td>PS</td>
<td>Packaging &amp; Building</td>
<td>8%</td>
<td>1%</td>
</tr>
<tr>
<td>7</td>
<td>Other</td>
<td>Various</td>
<td>13%</td>
<td>Varies</td>
</tr>
</tbody>
</table>

Scientific research is required to design new approaches for reducing plastic wastes

Most plastics are made from several polymers

Data from Geyer et al. *Sci Adv* 3(7), e1700782 (2017) (http://advances.sciencemag.org/content/3/7/e1700782.full)
Opportunities in Basic Science Research to Advance Chemical Upcycling of Polymers
Workshop Chair: Phillip Britt (ORNL)

Co-Chairs: Geoff Coates (Cornell Univ.)
Karen Winey (Univ. of Penn.)

Participants: 23 from universities, national laboratories, and industry

Date: April 30–May 1, 2019

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
Opportunities to Advance Chemical Upcycling of Polymers

Goal: provide foundational knowledge for designing new chemical processes and polymers to shift the paradigm of discarded plastics from wastes to a resource for making high-value fuels, chemicals, and new polymeric materials

Priority Research Opportunities (PROs) for a BES research agenda:

• Master the mechanisms of polymer deconstruction/reconstruction
  – How do we develop selective and integrated chemical processes to upgrade a discarded plastic into a desirable product?

• Understand and discover integrated processes to upcycle mixed plastics
  – How can we directly transform mixed discarded plastics to desirable products?

• Design next generation of polymers for chemical circularity
  – How can we design new polymers that have the properties of today’s polymers and enable simple reuse of the molecular building blocks?

• 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?
• Develop a mechanistic understanding of the deconstruction/reconstruction reactions to inform the design and development of next-generation plastic
  – A tandem catalytic method was developed for efficient degradation of polyethylene under mild conditions (150-175 °C) to liquid fuels.

Master the Mechanisms of Polymer Deconstruction/Reconstruction

- Develop a mechanistic understanding of the deconstruction/reconstruction reactions to inform the design and development of next-generation plastic.
• 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

• 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 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
  - Poly(diketoenamine) – a new polymer that can be recycled back into its original monomers, from mixed waste streams (Christensen, Scheuermann, Loeffler, Helms, *Nat. Chem.* 2019 11, 442-448)
- Design new polymeric materials for circularity that have properties of today’s plastics
Future Research Opportunities to Enable Polymer Upcycling and Circular Lifecycle

- Master the mechanisms of polymer deconstruction/reconstruction
- Understand and discover integrated processes to upcycle mixed plastics
- Design next generation of polymers for chemical circularity
- Develop novel tools to discover and control chemical mechanisms for macromolecular transformations
Coordination Across DOE to Advance Chemical Upcycling of Polymers

- Office of Science
  - Advanced Scientific Computing Research
  - Basic Energy Sciences
  - Biological and Environmental Science

- Office of Energy Efficiency and Renewable Energy (EERE)
  - Advanced Manufacturing Office
  - Bioenergy Technology Offices
  - Vehicle Technology Office

- Advanced Research Projects Agency–Energy (ARPA-E)
• **Collection**: Develop novel collection technologies to prevent plastics from entering the ocean.

• **Deconstruction**: Develop biological and chemical methods for deconstructing plastic waste, including from rivers and oceans, into useful chemical streams.

• **Upcycling**: Develop technologies to upcycle waste chemical streams into higher-value products, which reduces energy intensity and encourages further recycling.

• **Design for recyclability**: Develop new plastics that are recyclable-by-design and can be scaled for domestic manufacturability.

• **Commercialization**: Support a domestic plastics upcycling supply chain for US companies to scale and deploy new technologies in domestic and global markets

https://www.energy.gov/eere/articles/department-energy-launches-plastics-innovation-challenge
Funding Opportunities

• Notice of Intent (NOI) for Funding Opportunity (FOA) to Advance DOE’s Plastic Innovation Challenge posted December 10, 2019

• Topic Areas:
  – Highly Recyclable or Biodegradable Bio-based plastics
  – Novel Methods for Deconstructing and Upcycling Existing Plastic Waste
  – BOTTLE Consortium Collaborations to Tackle Challenges in Plastic Waste

• EERE-Exchange.energy.gov

Workshops

• December 11-12, 2019 Plastics for a Circular Economy Workshop

• Presentations and report-outs available here:
  – https://www.energy.gov/eere/bioenergy/events/plastics-circular-economy-workshop

• Report forthcoming
EERE Plastics Efforts

FY 20: Launched Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE) National Lab Consortium

- www.BOTTLE.org; bottle@nrel.gov
- NREL, LANL, ORNL, MIT, MSU, CSU

RFPs for REMADE Institute (Reducing EMbodied-Energy and Decreasing Emissions):

- REMADE - up to $11M of federal funds for R&D projects spread across multiple areas, including recycling and recovery of plastic waste
  - https://remadeinstitute.org/project-call-documentation
FY 2020 Continuation of Solicitation for The Office of Science Financial Assistance Program

- Includes opportunities for applications aligned with research direction identified in Roundtable report
- FOA will remain open until September 30, 2020

Early Career Research Program

- Includes opportunities for applications aligned with research direction identified in Roundtable report
- Submission deadline for preapplications was January 7, 2020

Energy Frontier Research Centers

- “This FOA solicits proposals for EFRCs that will address the PRDs/PROs identified in one or more of the following four (4) reports” including the Roundtable on Chemical Upcycling of Polymers
- “Applications in this topical area [polymer upcycling] should propose research that addresses at least two of these PROs”
- Submission deadline for preapplications was January 16, 2020
Office of Science Graduate Student Research (SCGSR) Program

Prepare graduate students for STEM careers critically important to the DOE Office of Science mission. (~100 - 120 participants)

- Graduate students conduct a part of their graduate thesis research at a DOE lab with a collaborating principal investigator.
- Award terms range from 3 months to 1 year and can begin any time between the earliest and latest start dates specified in the solicitation.
- Graduate students pursuing Ph.D. degrees in areas of physics, chemistry, material sciences, biology (non-medical), mathematics, engineering, computer or computational sciences, or specific areas of environmental sciences that are aligned with the mission of the Office of Science are eligible to apply for the supplemental research awards provided by the SCGSR program.
- Specific areas of interest deemed to be of high program priority/workforce need. The areas may change slightly from year to year, depending on program determinations of workforce need.
- Applications open February 2020, applications due May 2020

### Award Benefits:

- A monthly stipend of up to $3,000/month for general living expenses
- Reimbursement of inbound/outbound traveling expenses to/from the DOE laboratory of up to $2,000.

(Award payments are provided directly to the student.)

### Eligibility:

- U.S. Citizen or Lawful Permanent Resident
- Qualified graduate program & Ph.D. Candidacy
- Research aligned with a SCGSR priority research topic
- Establishment of a collaborating DOE laboratory scientist at the time of application

See website for details: [https://science.osti.gov/wdts/scgsr](https://science.osti.gov/wdts/scgsr)
Polymer upcycling – turning discarded plastics into high-value products

- Efficiently couple selective deconstruction of polymers into molecular intermediate with synthesis of new products
- Selective deconstruction of polymers to chemicals and fuels
- Chemically modify intermediates to synthesize new polymers or create other new, high-value products
- Chemically modify polymers directly to create new plastics

Circular lifecycle – greatly extending the useful lifetimes of polymers

- Design new polymers and plastics that have desired properties but deconstruct easily
- Build on knowledge of chemical upcycling to design integrated chemical processes that enable large number of cycles of deconstruction and reassembly

Polymer upcycling and circular lifecycle will:

- Reduce accumulation of discarded plastics by using them as feedstocks for new products
- Decouple plastics from fossil feedstocks
- Decrease energy cost of plastic production