
MSD Materials Sciences Division

# Material Transformations: Fundamental Challenges and Opportunities

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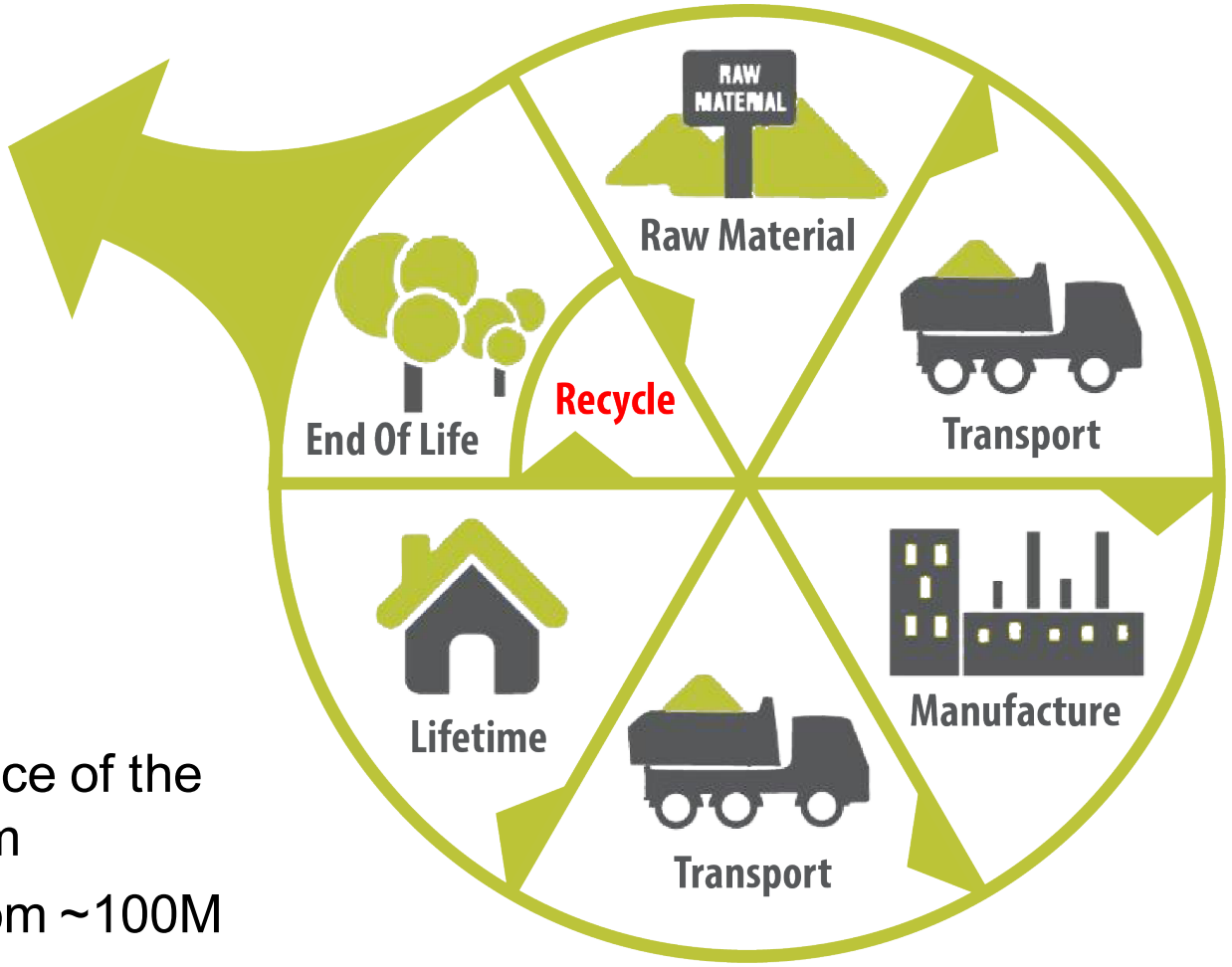
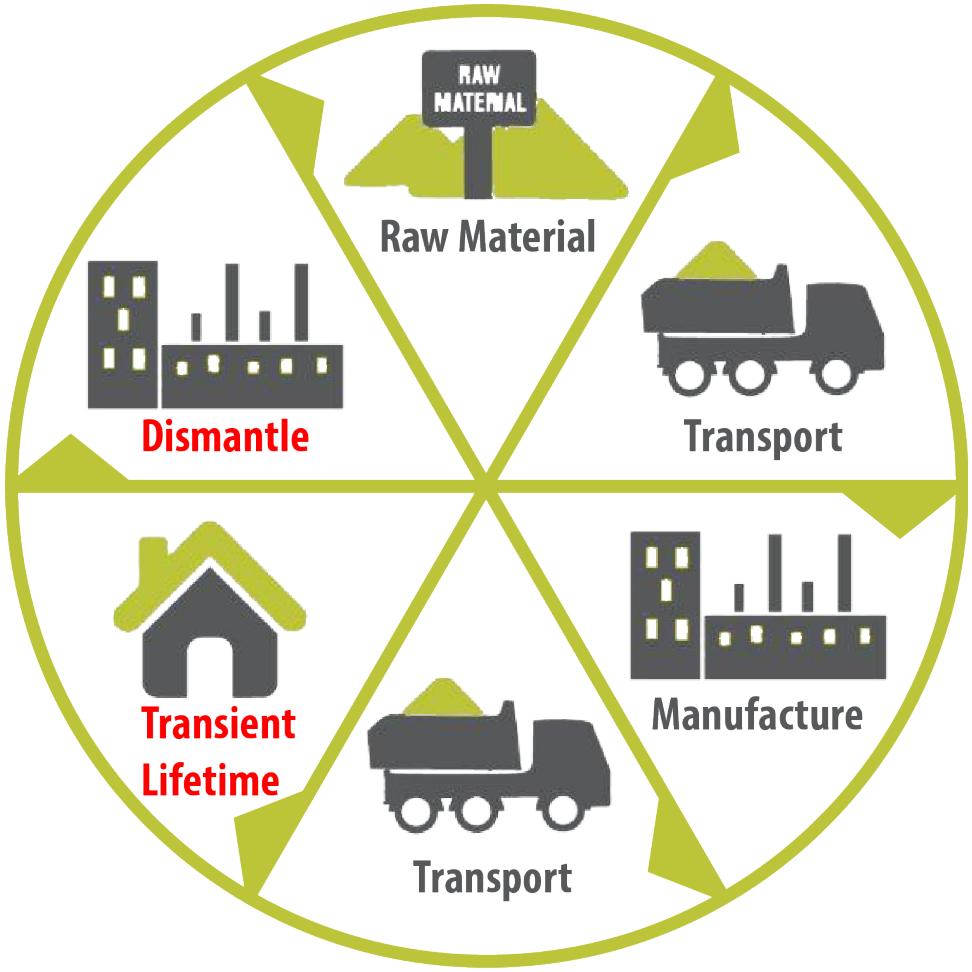
# Materials Life Cycle for Plastic and Global Impact




- Plastic refuse is the face of the modern waste problem
- Only ~2% recycled from ~100M tonnes produced per annum

# Subverting the Stagnant Materials Life Cycle for Plastic via Controlled Chemical Transformations

- ***Can we make plastic and composite materials with lasting and desirable value:***
  - Prescribed lifetime in the environment without losing performance
  - Retention of properties and performance following disassembly (i.e., real Raw Materials)
  - New life after processing

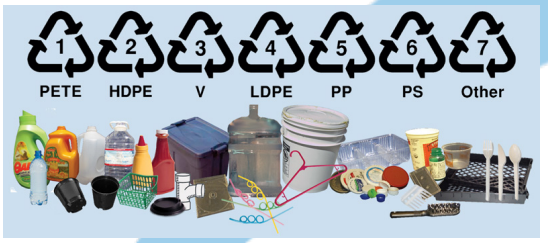


# Chemical Transformations at a Glance

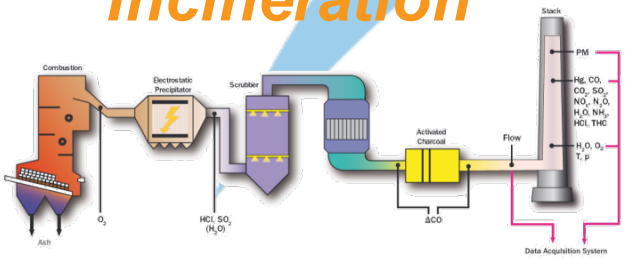
## Recovery


## De-Polymerization

## Separations

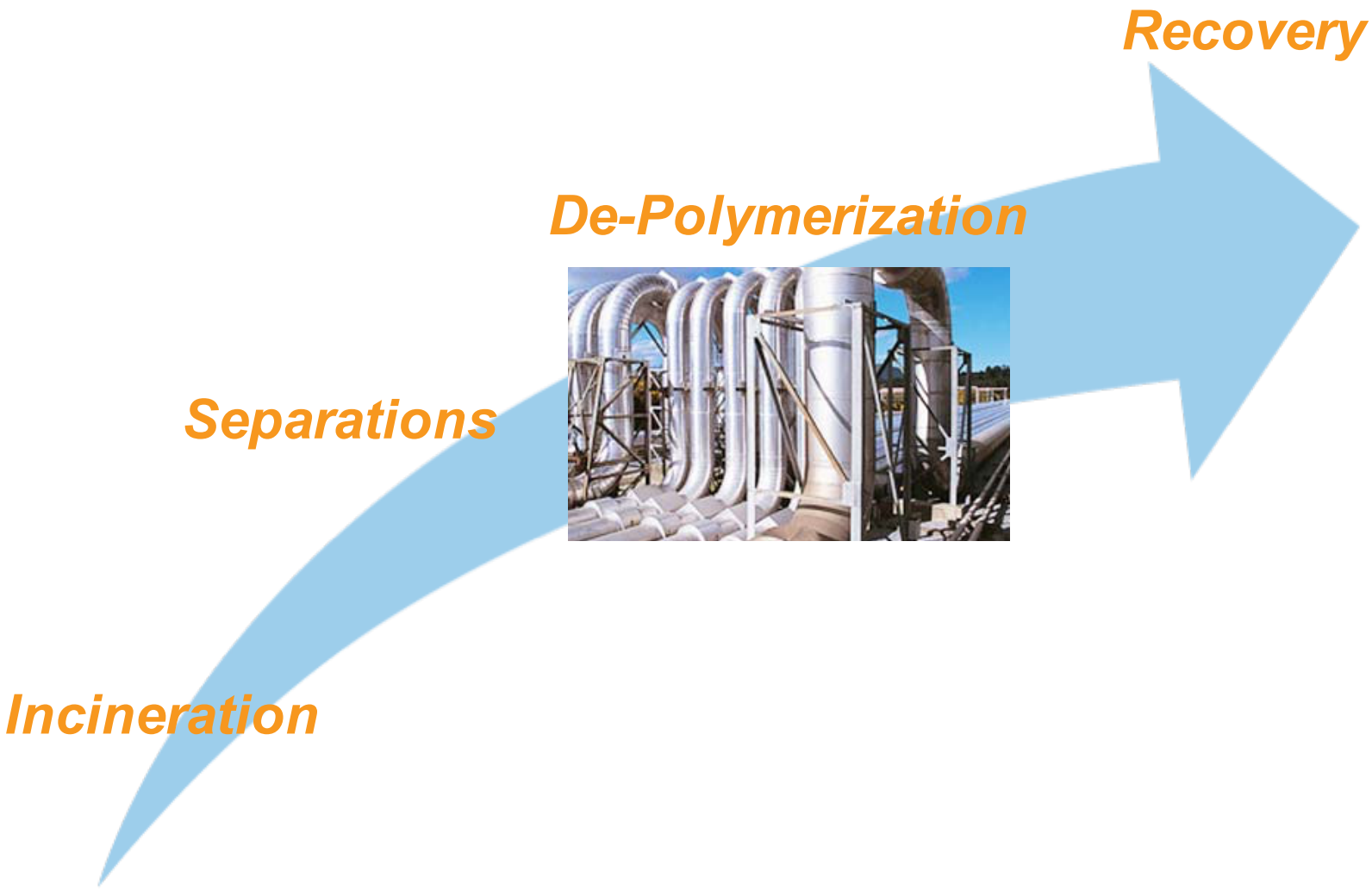



## Incineration



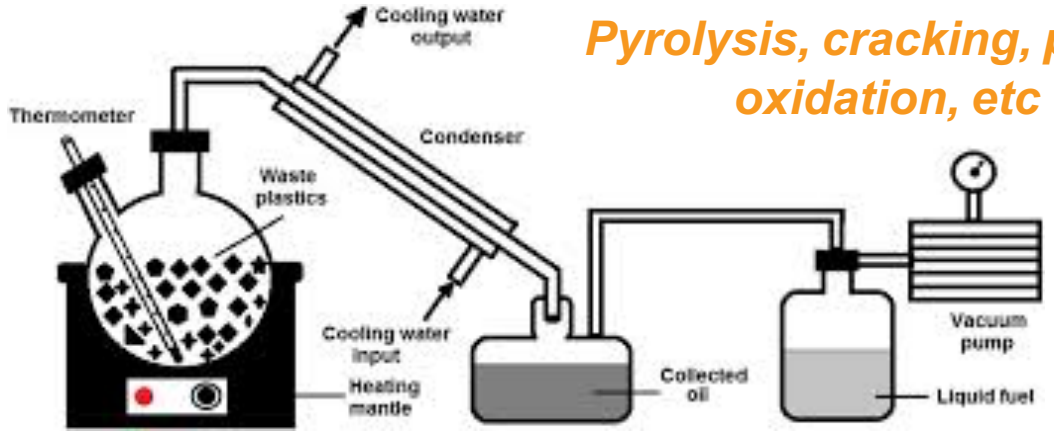

**Opportunities in Catalysis, New Materials, and Processing**

# Chemical Transformations at a Glance



# Strategies to Direct De-Polymerization

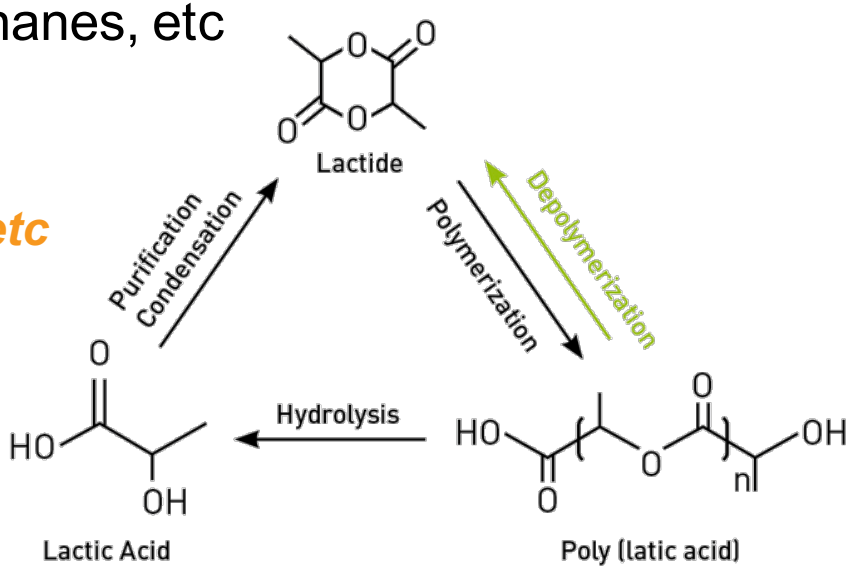
- Polyolefins



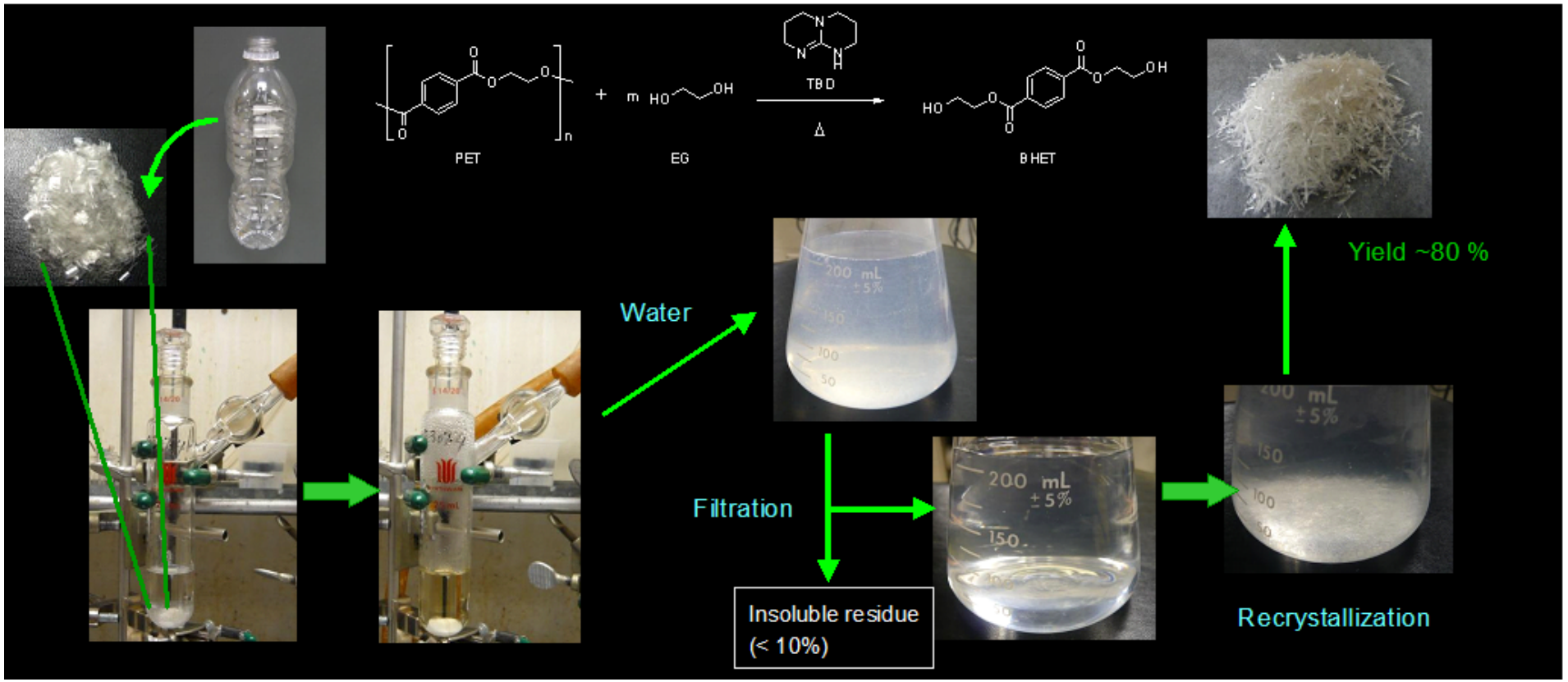

***Pyrolysis, cracking, partial oxidation, etc***

- Polyesters, polyamides, polyurethanes, etc

***Hydrolysis, glycolysis, etc***



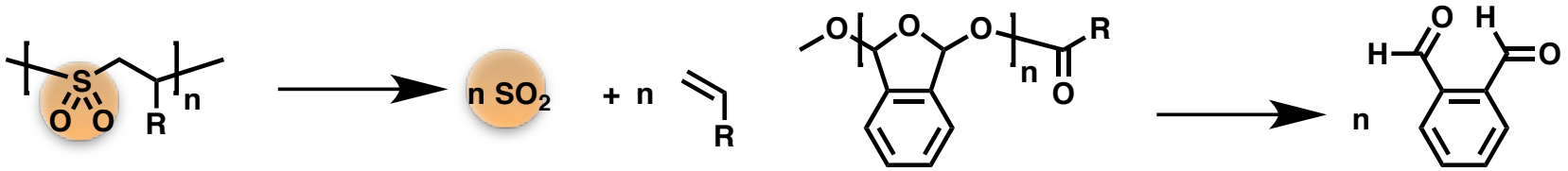
# Advanced Catalysts for PET De-Polymerization

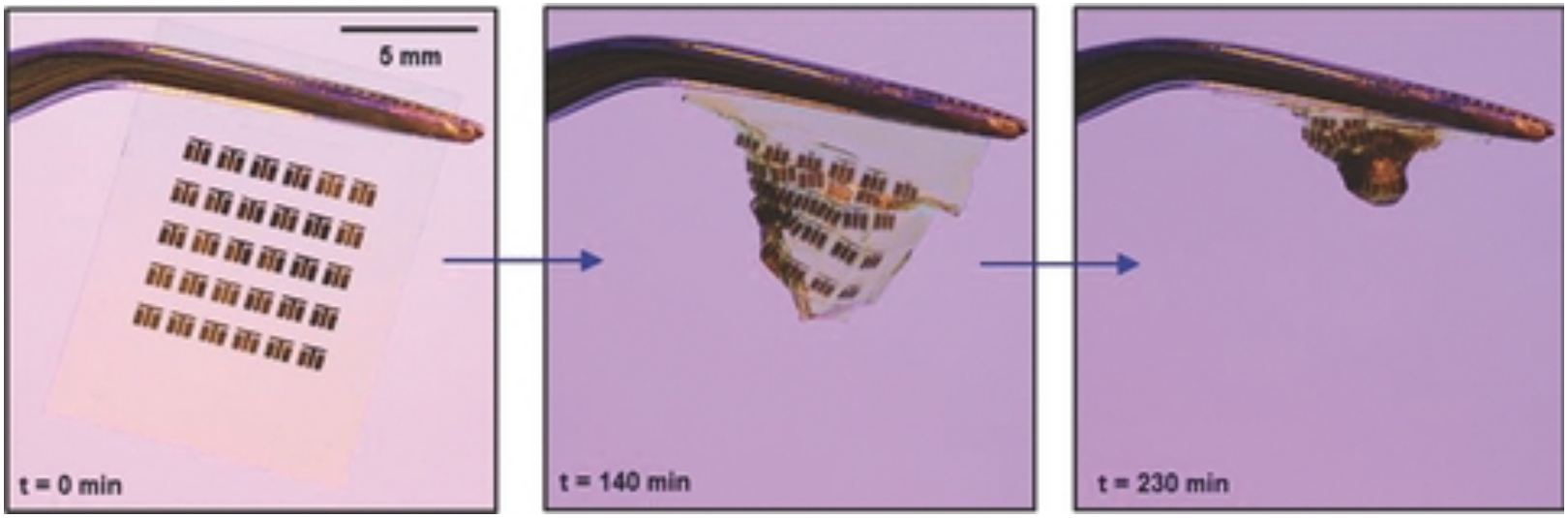



Hedrick, et al. *J. Polym. Sci. A Polym. Chem.* **2011**, *49*, 1273.
Horn, et al. *J. Phys. Chem. A* **2012**, *116*, 12389.

# Unconventional Strategies for De-Polymerization

- New (or re-purposed) polymer chain architectures that have triggered degradability



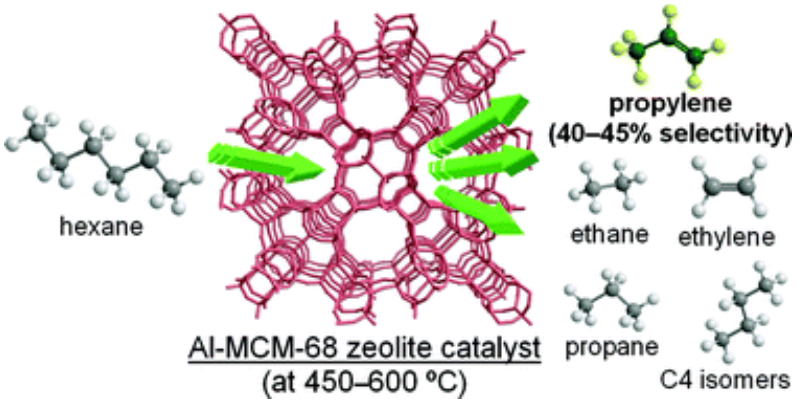



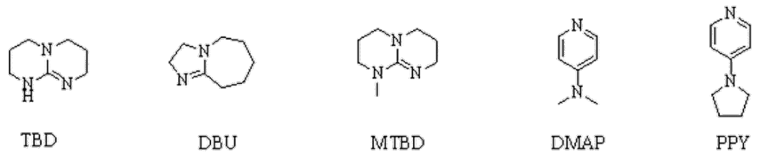


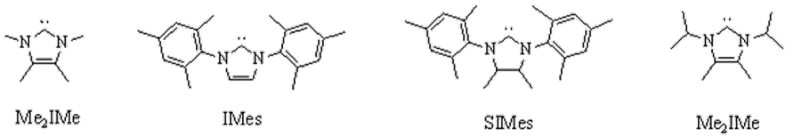
Goodwin, et al. *ACS Macro Lett.* **2015**, *4*, 907.
Moore, et al. *ACS Macro Lett.* **2015**, *4*, 665.
Moore, Rogers, & White et al. *Adv. Mater.* **2014**, *26*, 7637.

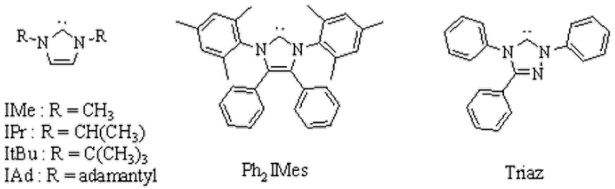
# Basic Research Needs in De-Polymerization

- ***New catalysts*** that provide more energy efficient chemical transformations for de-polymerization
  - ***Heterogeneous:*** high turnover, high surface area, selective, low-temperature operation, recyclable, earth-abundant, etc
  - ***Homogeneous:*** high turnover, functional group tolerant, isolable, inexpensive, etc
- ***New polymeric materials*** that have programmed degradability to usable monomers or high-value liquid fuels with specific chemical structures
- ***Accelerating discovery*** on both fronts likely aided by strategic development and application of a materials genome



# Chemical Transformations at a Glance

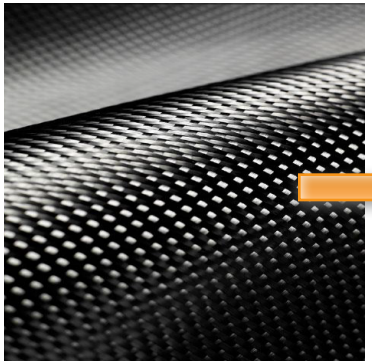
***Recovery***


***De-Polymerization***

***Separations***

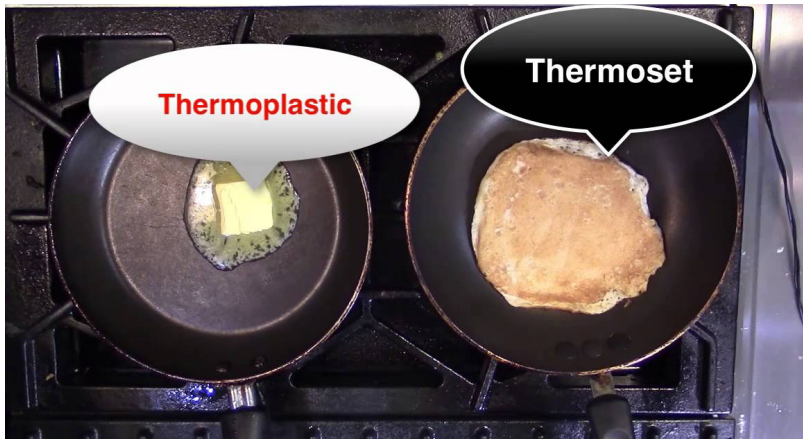
***Incineration***

Particularly important for high-value filler materials



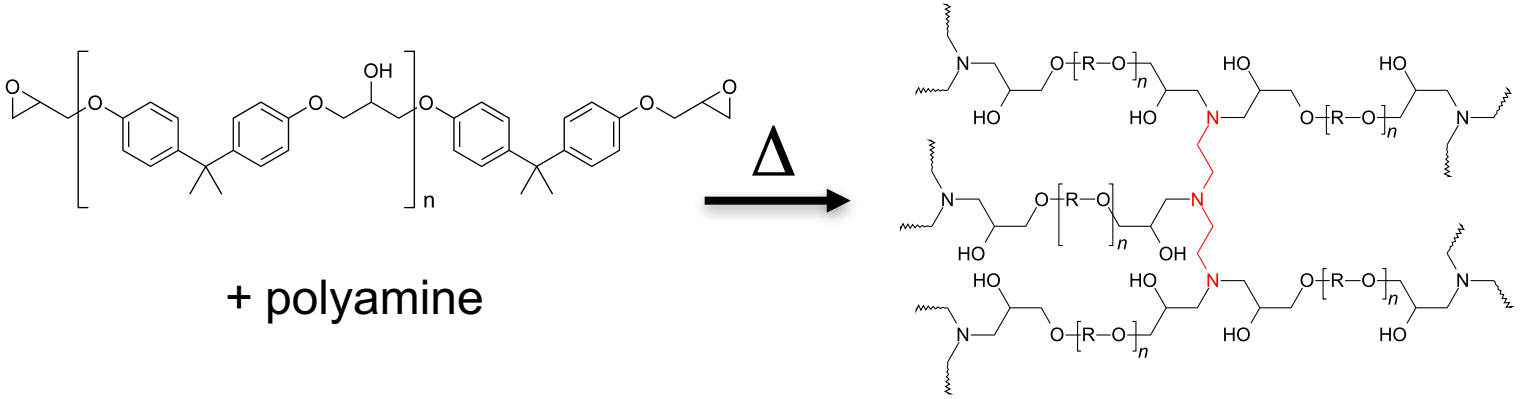
# Strategies to Direct Recovery

- Recovery efforts aimed at ***thermosets***
- Thermosets are synthetic materials that strengthen when heated, but cannot be remolded thereafter upon reheating
- ***At end of product life, they enter waste stream***; all value added is lost
- Thermosetting plastics comprise approximately ***20% of the world's polymer production by volume***, accounting for ~22M tonnes per annum
- ***New polymer chemistries are needed to transform these materials into a recoverable and recyclable commodity***

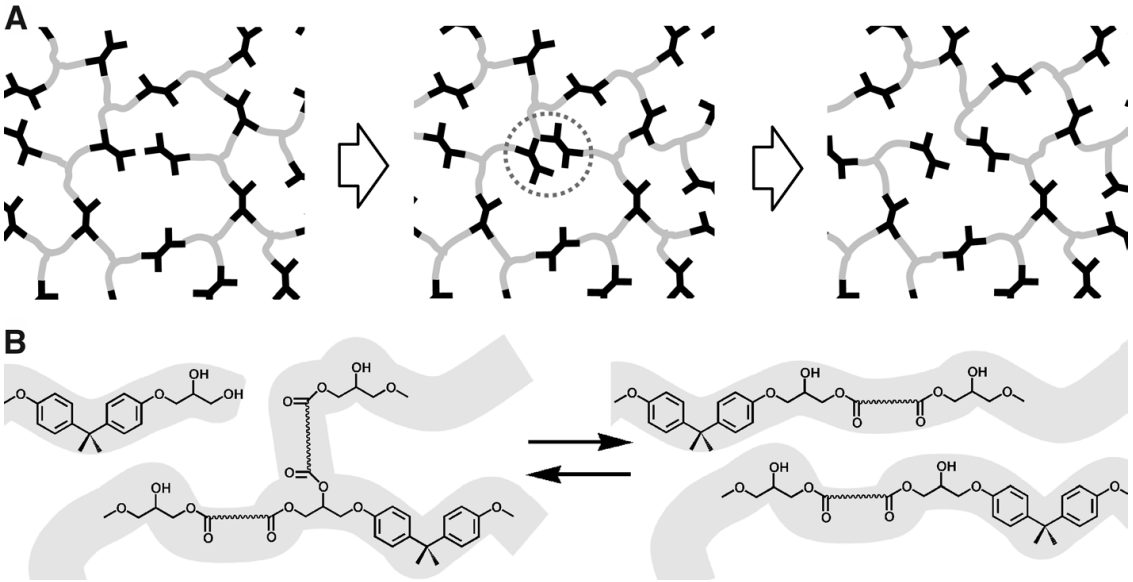



# Toward Recoverable Thermosets

- ***Conventional:*** Static Covalent Polymer Networks



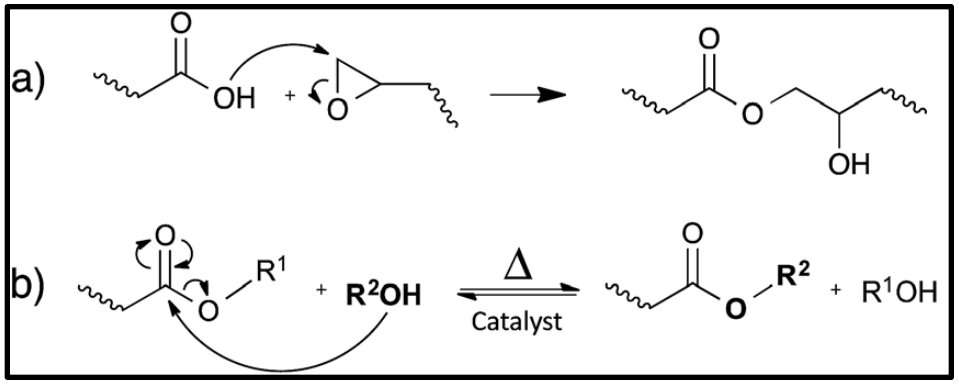

- ***Breakthrough:*** Dynamic Covalent Polymer Networks



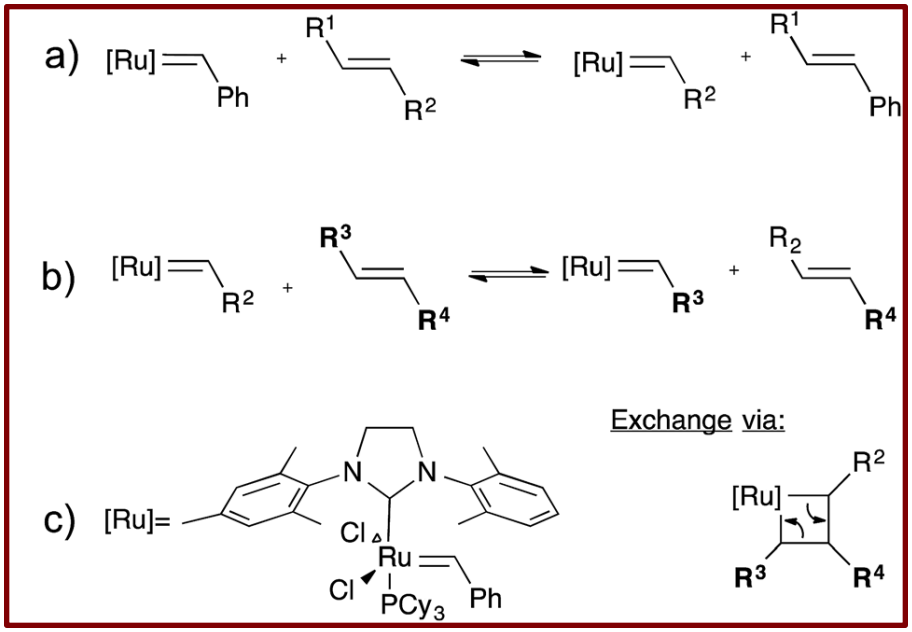

**Vitrimers:** Leibler et al. *Science* **2011**, *334*, 965; Guan, et al. *J. Am. Chem. Soc.* **2012**, 134, 8424; Du Prez et al. *Nature Chem.* **2013**, *6*, 815; Dichtel et al. *J. Am. Chem. Soc.* **2015**, *137*, 14019; Ji, et al. *Adv. Mater.* **2016**, *28*, 156.

# Vitrimers as a Versatile Matrix-Design Strategy

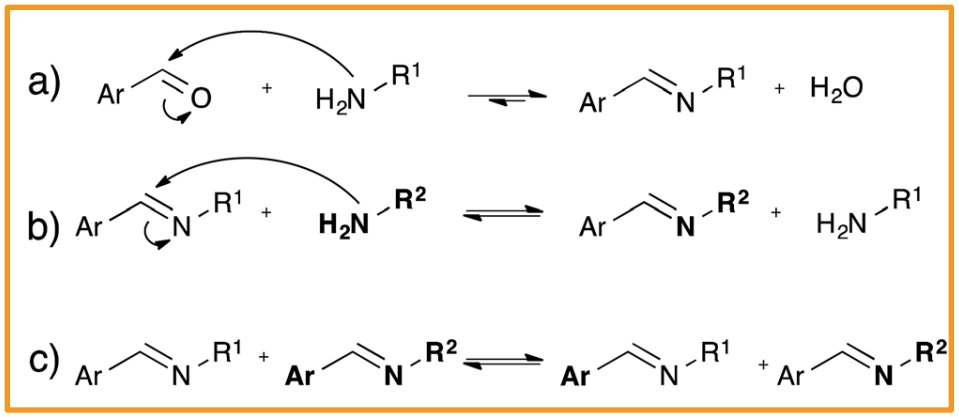
## Polyesters



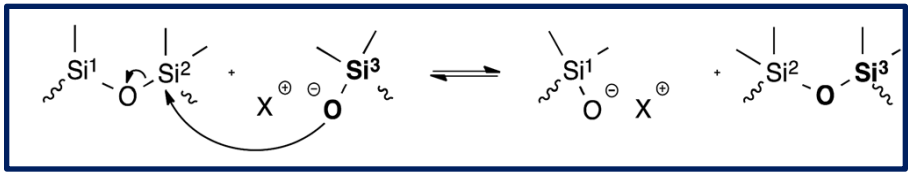

## Polyolefins




## Polyimines

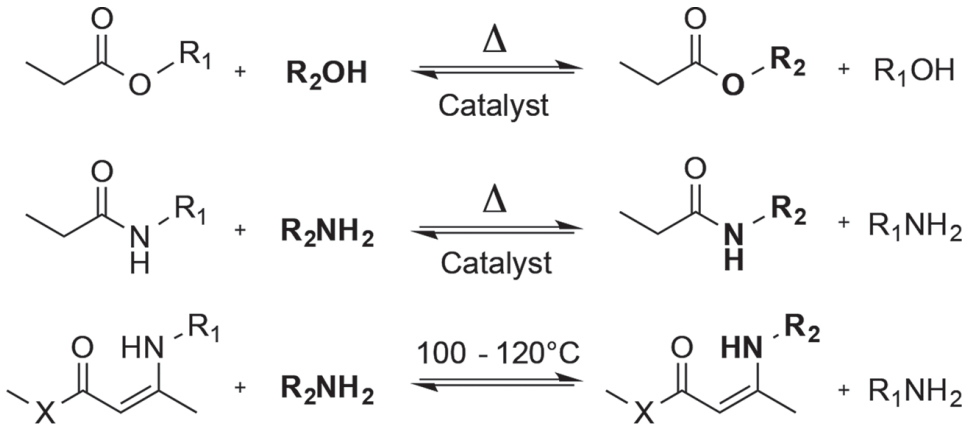



## Polysiloxanes

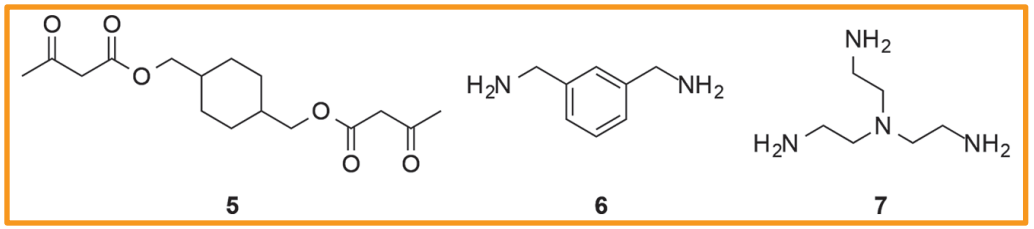



Du Prez, et al. *Chem. Sci.* **2016**, *7*, 30.

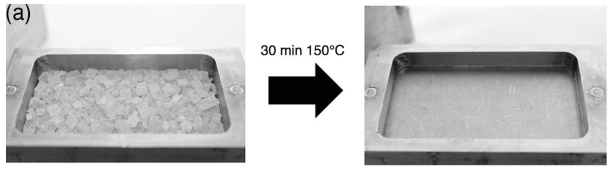
# Vitrimer Ageing and Impact on Performance

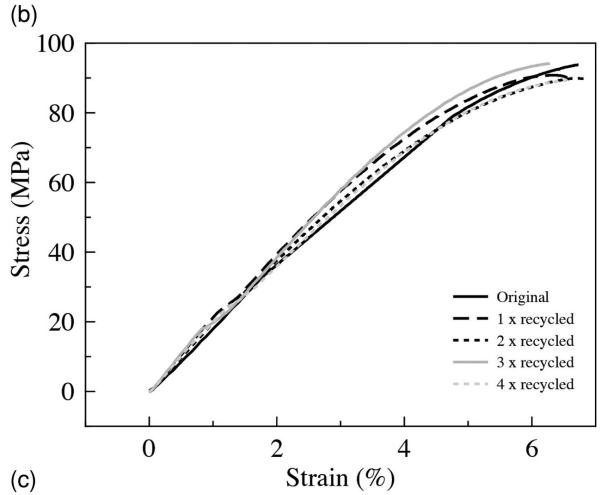


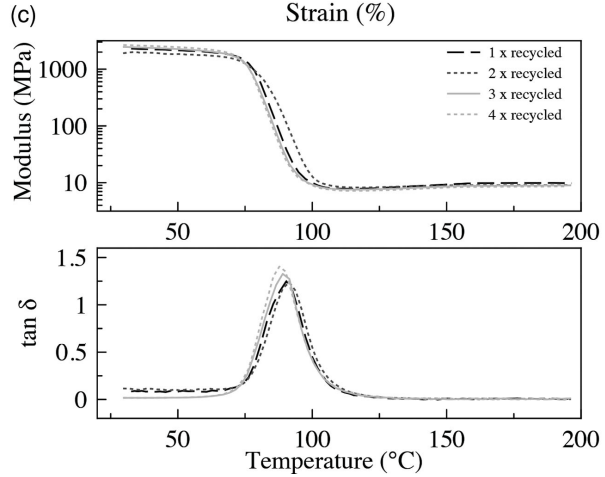

X = $CH_2$: vinylogous amide
X = O: vinylogous urethane



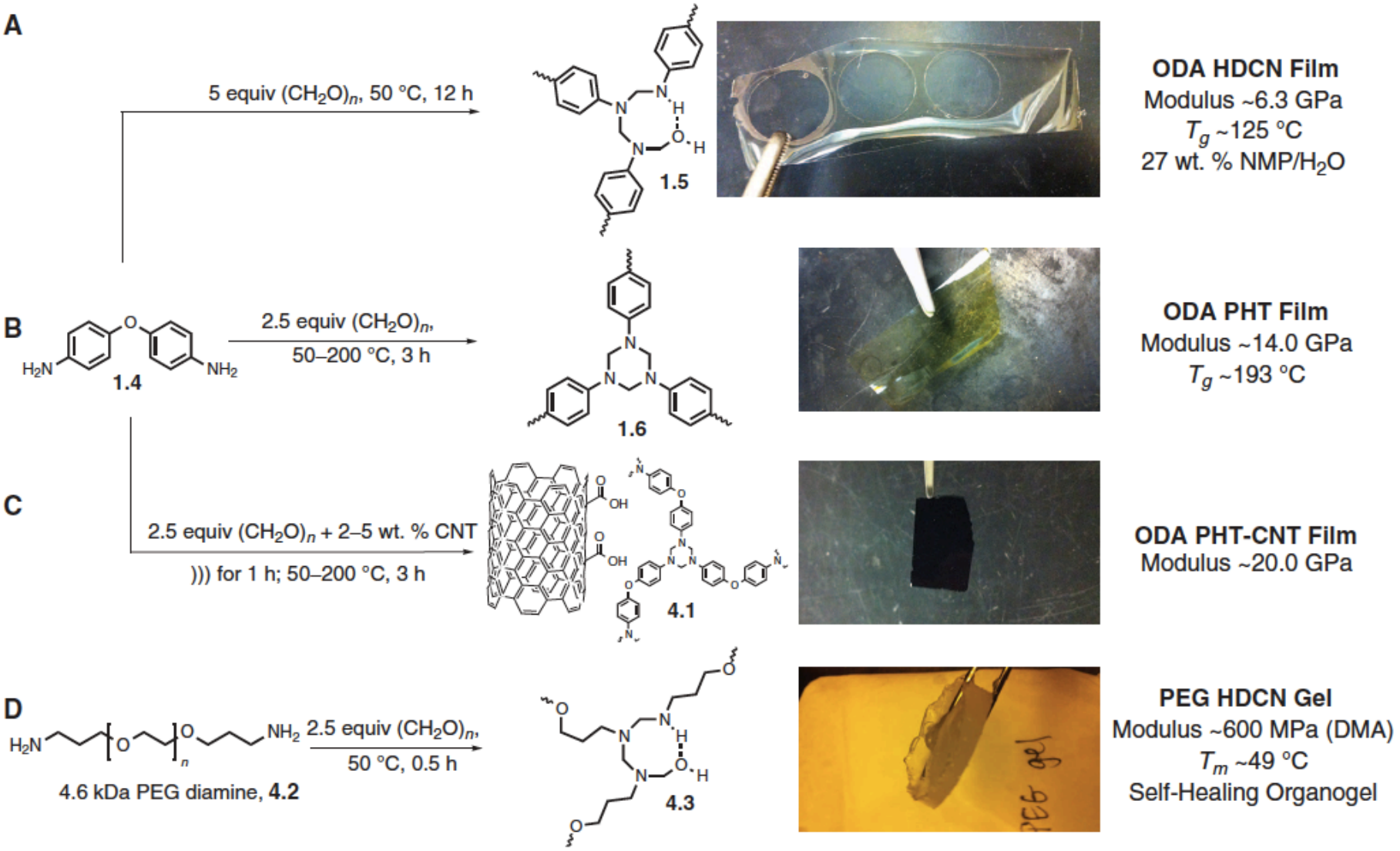

Du Prez et al. *Adv. Funct. Mater.* **2015**, *25*, 2451



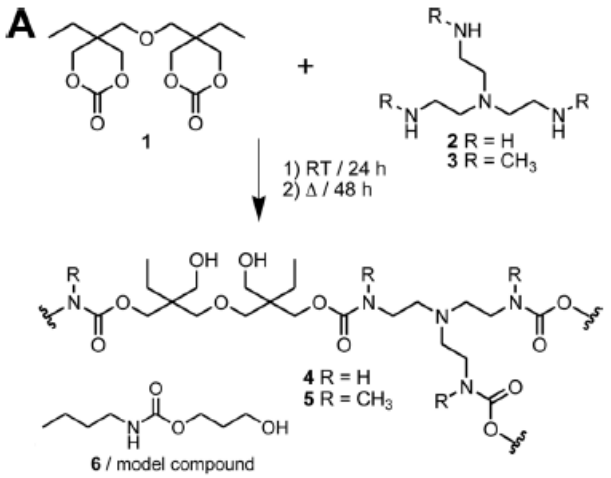
# Advanced Composites Using Vitrimers

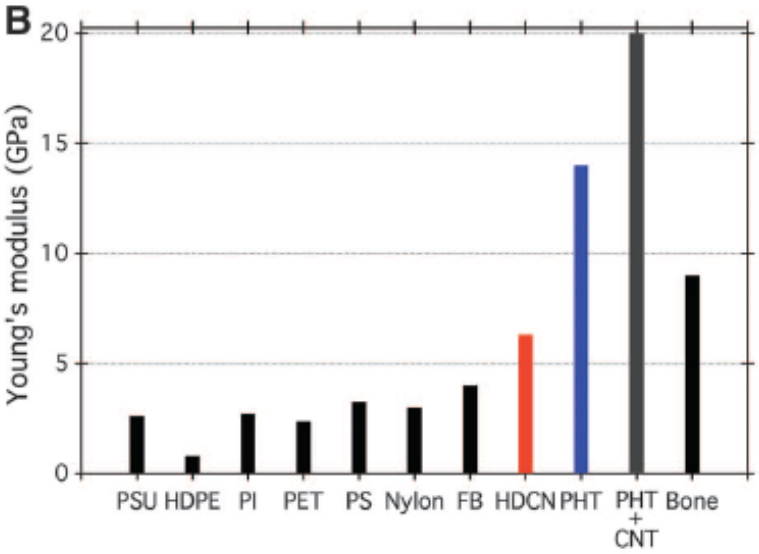



Hedrick, et al. *Science* **2014**, *344*, 732.

# Basic Research Needs in Recovery

- ***New vitrimers*** spanning all thermosetting chemistries, catalyst free and catalyst-dependent chemical transformations, controlled dynamics of reconfigurability, scalable, etc
- ***High-performance vitrimer composites*** with properties matching or exceeding conventional thermosetting plastics and composites – well-controlled interfacial chemistries, blending, molding, rheology, mechanical, etc.
- Less energy- and time-intensive vitrimer and vitrimer-composite ***processing*** - solution & solid state
- Molecular understanding of ***vitrimer ageing***



# Barriers to Innovation and Adoption

- Economics of recycling do not make business sense in the U.S. due to public policy

  ***Cost > Performance > Environment***

- Difficult to change a 50-year materials paradigm when short-term interests by industry and investors trump long-term benefits of a paradigm shift in the life-cycle of advanced materials
- Capital intensity in the U.S. has been difficult for research labs and small businesses alike. Most of the work in this area is being done in Europe and China, where there are increasingly strict rules on landfilling and incineration
- ***Public-Private partnerships may play a critical role in accelerating adoption***

*Mallinda, LLC*


*Connora Tech*

# Outlook and Challenges for a Sustainable Advanced Materials Cycle

- Prevent the creation of waste at the source by material and design innovation
- Materials designed to disassemble into reusable molecular building blocks when their useful lifetimes have expired
- Use reversible bond formation in materials by design to tune properties and persistence from collective interactions across multiple length scales and time scales

*Image: Connora Tech*