Sustainable Development of Polymers for a Circular Plastics Economy

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How is plastic made?

- Plastics are made of **polymers**
- **Mono**mers become **poly**mers by a repetitive chemical reaction
- **Different monomers** lead to **different physical properties**: melting temperature, flexibility, strength, etc.
- **Metal catalysts** are often used to reduce energy input and control molecular-level structure

Challenges in Plastic Recycling

Mechanical Recycling

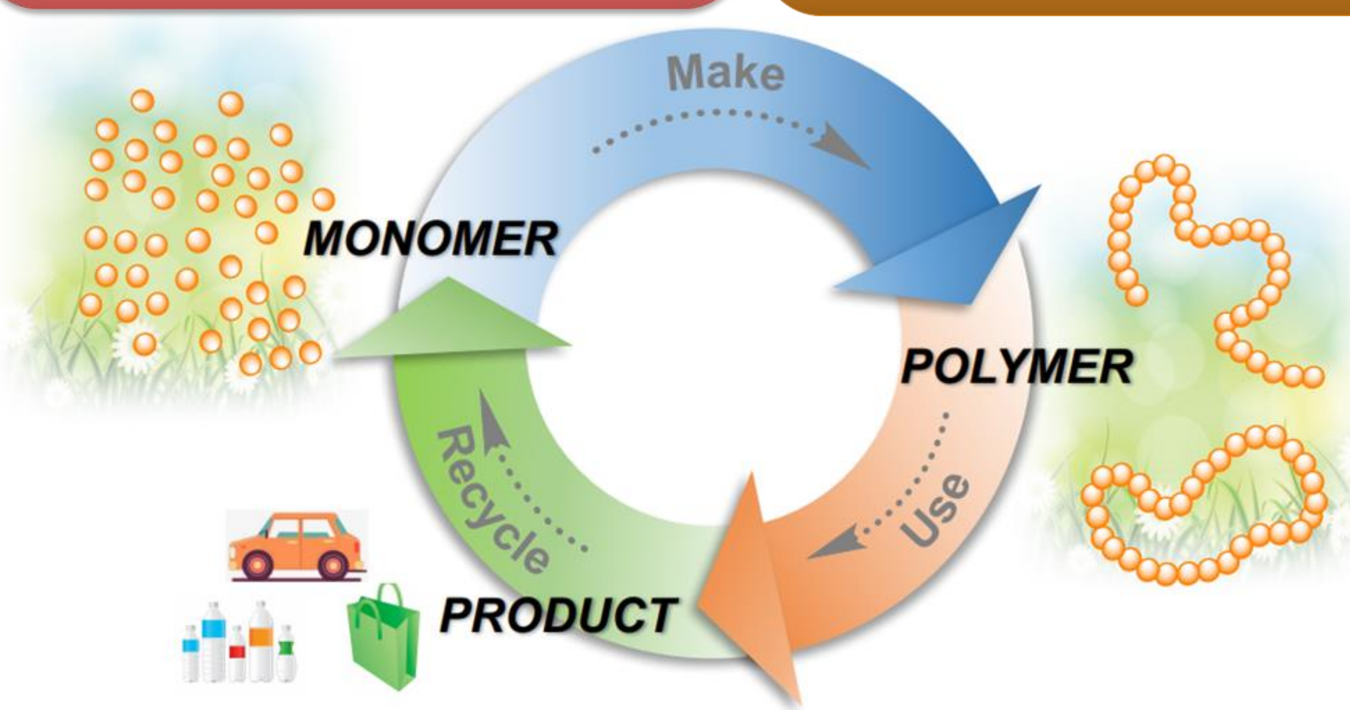
+ material recovery
+ well established
- cost vs. quality
- extension of linear economy

Incineration

+ energy recovery
+ out of landfill/ocean
- material value lost
- toxic/polluting emissions

Biological Recycling

+ carbon neutral
+ reduce pollution/waste
- no material or energy recovery
- select materials, controlled environments may be required



Chemical Recycling

+ virgin quality material regenerated
+ less raw materials
- energy input vs. material output
- select materials, nascent stage

Objective

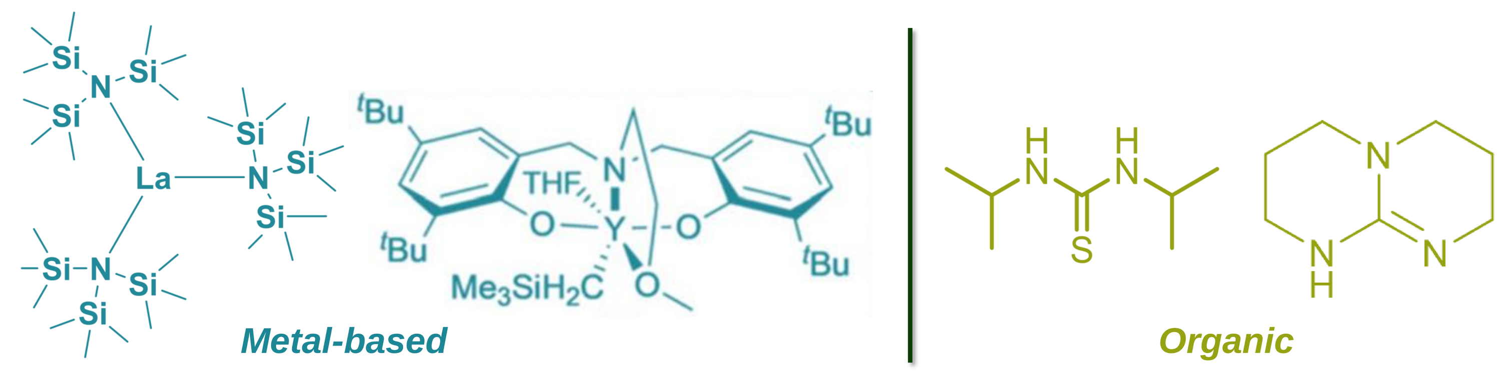
To prepare and chemically recycle a plastic material with green catalysts and methods

What was known:

- Monomers with the **'gene' for full chemical recyclability** can be (de)polymerized by metal-based catalysts.
- Organic (**metal-free**) **catalysts** have demonstrated **sustainability & performance advantages**: *economic, environmental, polymer applications*

What we aimed to discover:

- **Efficient**, metal-free catalyst systems to make and completely disassemble polymers
- **Advantages** over metal catalysts
- **Mechanical properties** of the recyclable plastic material

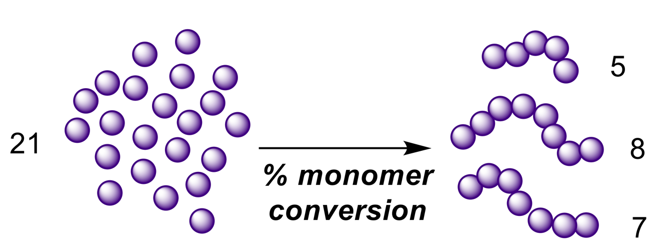


Design & Results

I. Hypothesis-driven search for the best catalyst system

- Reaction rate
- Structural control (molecular weight & uniformity)
- Depolymerization (100%)
- Compare to metal catalysts

	TU	TU-1	TU-2	TU-3
Base	pK_a	13.4	16.8	~20
DBU	13.9	14%	13%	6%
BEMP	16.5	6%	61% 7.70 kDa, $Đ$ = 1.04	70% 8.22 kDa, $Đ$ = 1.04
IMes	18-24	8%	67% 9.06 kDa, $Đ$ = 1.08	83% 10.8 kDa, $Đ$ = 1.11



molecular weight: *# monomers in chain*
dispersity: uniformity of chain length

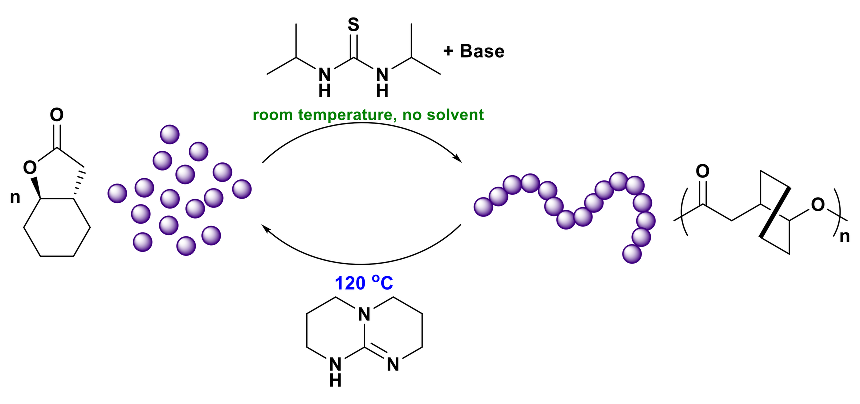
	U	U-1	U-2	U-3
Base	pK_a	13.8	16.1	18.7
DBU	13.9	73% 8.14 kDa, $Đ$ = 1.08	68% 7.08 kDa, $Đ$ = 1.08	20% 3.56 kDa, $Đ$ = 1.40
BEMP	16.5	69% 7.45 kDa, $Đ$ = 1.07	81% 9.74 kDa, $Đ$ = 1.10	82% 10.1 kDa, $Đ$ = 1.09
IMes	18-24	65% 5.88 kDa, $Đ$ = 1.08	80% 10.2 kDa, $Đ$ = 1.11	81% 9.50 kDa, $Đ$ = 1.12

no gelation occurred | gelation within 24h | gelation within few hours or minutes

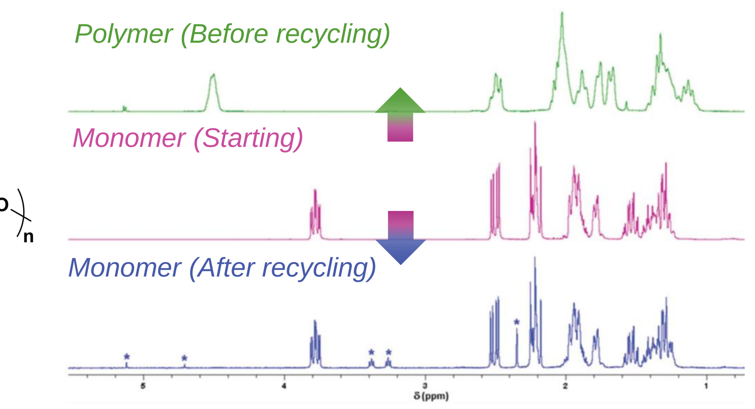
II. Scale-up best performing system

- Produce large quantities for mechanical testing
- **Dynamic Mechanical Analysis (DMA)**: How do material properties change with heat? i.e., what temperature is the plastic [melt] processable?
- **Tensile analysis**: how far and with how much force can the material be stretched?
- Compare data to other plastics

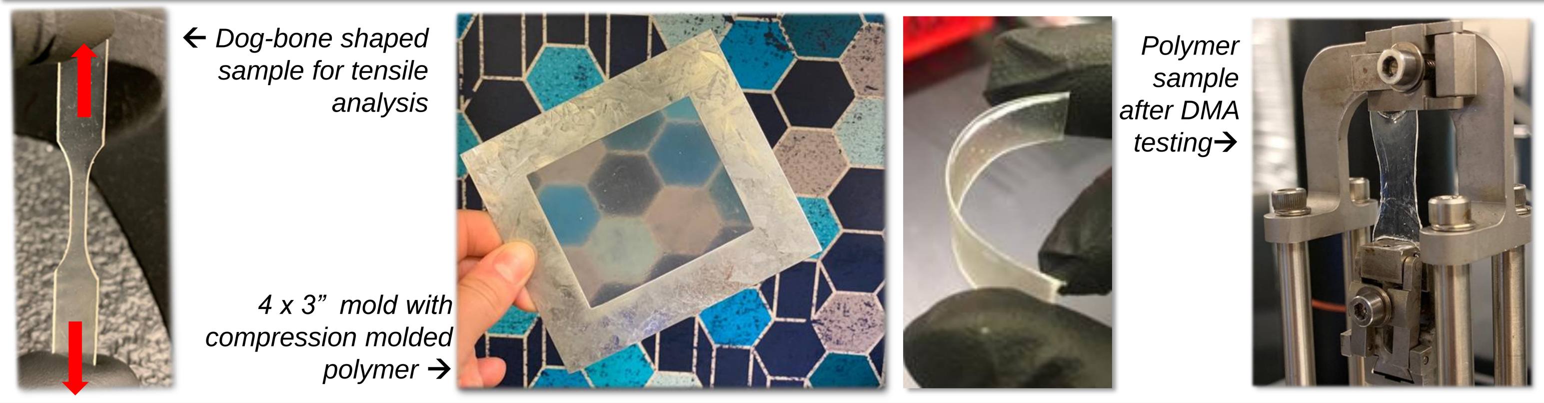
Results

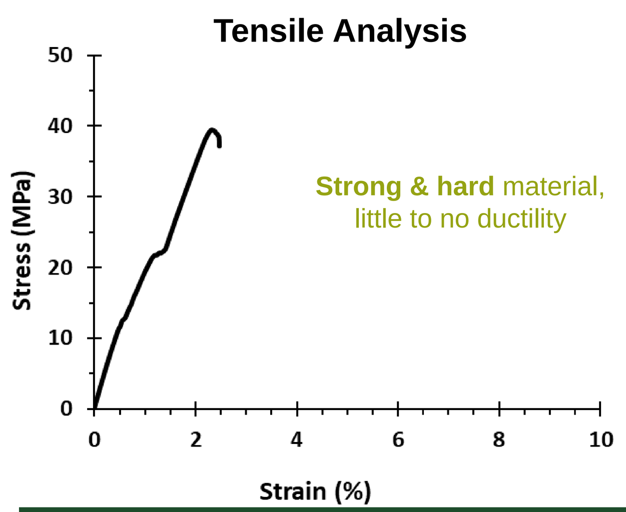


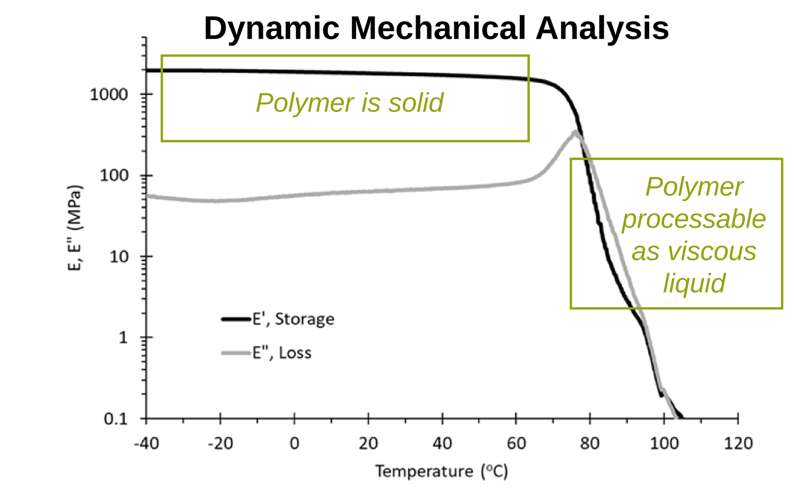
Forward and reverse polymerizations with optimal organic catalysts



*^{1}H NMR evidence for chemical recyclability; *signals from catalyst or solvent*







Conclusions & Ongoing work

- **Organic catalysts led to several advantages:**
  - Higher **yield**
  - Higher molecular weight (good for mechanical properties)
  - Less purification required (**less waste**)
  - **Increased thermal stability** (no metal contamination)
- **Methods could be scaled up to prepare large samples for mechanical testing**
  - Structure/property relationships of recyclable monomer/polymer systems being studied in Chen lab/start-up company, SusMer
- **International collaborators are evaluating the plastic**
  - As a **packaging material** (gas barrier properties)
  - As a **membrane material** (water purification)

References & Acknowledgments

- Professor Eugene Chen, Dr. Jianbo Zhu
- Szekely Group (collaborators) – KAUST, Saudi Arabia
- Sardon Group (collaborators) – BERC-POLYMAT, Spain

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