

Polymers in Sustainability

OCN-c1ccc(cc1)-c2ccc(cc2)NCO
HO-CH₂-OH
polyurethane

OH
CH₂O
Bakelite

polystyrene (PS)

C=Cc1ccccc1

Neoprene

ClC=C

POLY·MER

MANY

PARTS

polylactic acid (PLA)

THIS BAG IS 100% COMPOSTABLE & ONCE DISCARDED IN SOIL OR COMPOST WILL DISAPPEAR HARMLESSLY WITHIN WEEKS

CC(O)C(=O)O

butadiene polymers and copolymers

C=CC=C

polycarbonate

HO-c1ccc(cc1)C(C)(C)c2ccc(O)cc2-CO₂-c1ccc(O)cc1

polyvinyl chloride (PVC)

ClC=C

polytetrafluoroethylene (PTFE)

F=C(F)F

cotton

cellulose

rayon

OC1OC(O)C(O)OC1O

Nylon

HO₂C-C6H4-CO₂H
H₂N-C6H4-NH₂

LDPE

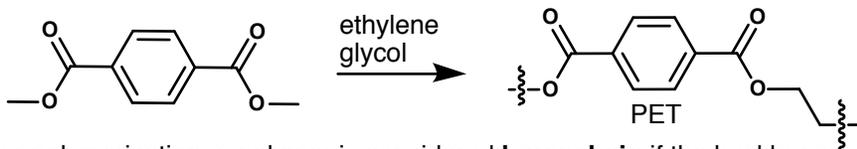
polyethylene (PE)

C=CC

HDPE

Terms to know:

- **Polymers** are macromolecules synthesized from simpler molecules called **monomers** through a process called **polymerization**.
- Some monomers, including ethanol, are **monofunctional**. Others, are **difunctional**, including *p*-hydroxybenzoic acid. A functionality of at least two is required to form polymers by methods other than alkene addition or ring-opening polymerization. Higher functionality leads to branching.
- An **oligomer** is a low molecular weight polymer of only a few monomers.



- After polymerization, a polymer is considered **homochain** if the backbone consists of a single atom type (through alkene additions), or **heterochain** if there is more than one atom type in the backbone (*i.e.* polyesters, polyethers). The **average degree of polymerization (DP)** refers to the average total number of structural units per molecule in a given sample. This is related to both chain length and molecular weight.
- If a polymer is made from more than one type of monomer, it is called a **copolymer**. Depending on their distribution, these can be **alternating** or **random copolymers**.

-A-A-A-A-A-A-A-A-	Homopolymer
-A-B-B-A-B-A-A-B-A-B-	Random copolymer
-A-B-A-B-A-B-A-B-A-B-	Alternating copolymer
-A-A-A-A-B-B-B-B-	Block copolymer
-A-A-A-A-A-A-A-A- B-B-B-B-B-B-	Graft copolymer

- **Telechelic polymers** have reactive end group for further reaction. They are often used in the preparation of block copolymers, bringing the two 'blocks' together.
- **Crosslinking** describes the formation of covalent bonds between **linear** or **branched** polymers to form **network polymers**. These polymers cannot flow past one another, melt, or be molded, and are therefore called **thermoset polymers** (rubbers).
- **Thermoplastic polymers** are usually linear, but they can have some crosslinking or branching. They can be melted and reformed with heating.

- **Other polymer** types include star polymers, comb polymers, ladder polymers, semi/step ladder polymers, polyrotaxanes, polycatenanes, and dendrimers.

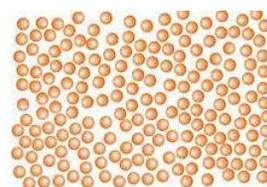


- **Rheology** in general terms refers to the science of deformation and flow. In relation to polymers, it encompasses the **viscoelastic properties** and mechanical performance of a final polymer product. This is affected by monomer type and sequence, method of polymerization and processing, polymer tacticity, and more.
- The **Young's modulus** is a measure of polymer stiffness and its ability to withstand changes in length/tension. It is temperature dependent.
- The **glass transition** of an amorphous polymer is a reversible transition from a hard, glassy, or plastic state, into a viscous or rubbery state (and vice versa).

The space shuttle Challenger exploded on a cold morning in Florida when a rubber O-ring that was operating far below its **glass transition** failed to form a proper seal



- **Polydispersity index** describes the molecular weight uniformity of polymers in a solution. A **monodisperse** solution contains polymers of uniform molecular weight, while a **polydisperse** solution has a range of molecular weights.
- The **number average molecular weight** (M_n) is a statistical avg. molecular weight of all polymer chains; **weight average molecular weight** (M_w) takes into account the molecular weight of a chain in determining its contributions.



monodisperse

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

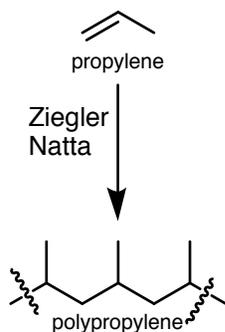
$$PDI = \frac{M_w}{M_n}$$



polydisperse

Categories of Commercial Polymers:

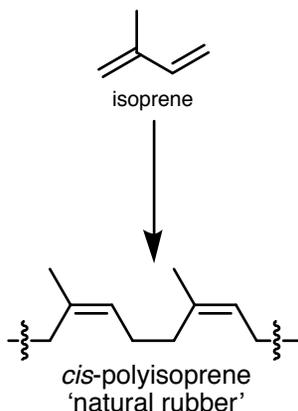
- Plastics** - 56% of total world consumption (TWC) of synthetic polymers
- *modulus* between fibers and rubber, can be thermoplastic or thermoset
 - incredibly resistant to corrosion, malleable and moldable.
 - **commodity plastics** include polyethylene, polypropylene, polyvinyl chloride, and polystyrene. They are often used in packaging or for durable goods.
 - **engineering plastics** are used in transportation, construction, electrical equipment, and industrial machinery. These include polycarbonate, some polyamides and polyesters.



polypropylene has a high thermal and chemical resistance and is commonly the material of choice for autoclaving

Rubbers/elastomers - 18% of TWC

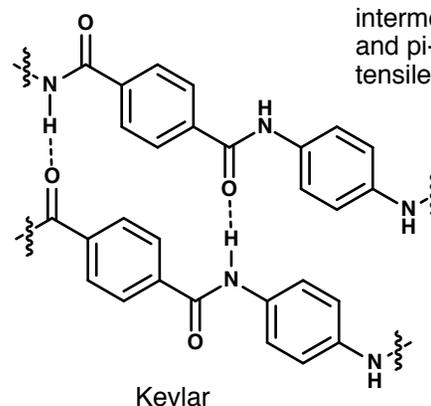
- resilient and 'stretchy', usually *thermoset*, lowest *modulus*
- viscoelastic, with very weak intermolecular bonds
- amorphous (disordered) polymers maintained above their glass transition temperature so that they remain flexible without breaking covalent bonds.
- examples include polyisoprene, polybutadiene, and nitrile rubber
- thermoplastic elastomers have properties of plastics and rubbers (styrene butadiene copolymers)



golf balls are filled with polybutadiene or polyisoprene elastomers

Fibers - 11% of TWC

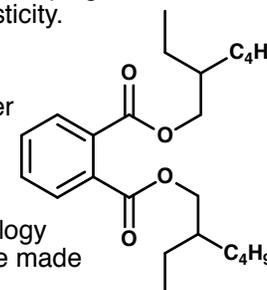
- highest strength and *modulus* polymer
- good stretchability and thermal stability
- variable properties include dyeability, chemical resistance, crease resistance
- includes **polyester**, many **polyamides** such as nylon and kevlar, and cellulose derivatives such as rayon
- some natural polyamide fibers include silk and wool, made from protein



Other categories are **coatings** and **adhesives**

- Commercial polymers are controlled for a multitude of properties depending on their purpose, including: transparency, stiffness, electrical conductance, chemical compatibility, dyeability, flexibility, thermal insulation, quiet, etc.
- These different properties can be achieved by altering the chemical properties including monomer type and sequence, chain length, level of cross-linking, polymerization and processing methods, tacticity. **Plasticizers** are molecules that change the polymer properties by helping the molecules slide past each other, allowing more flexibility or plasticity.

DEHP plasticizer
(most common)

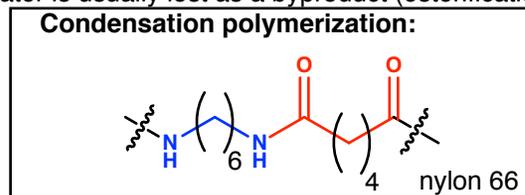
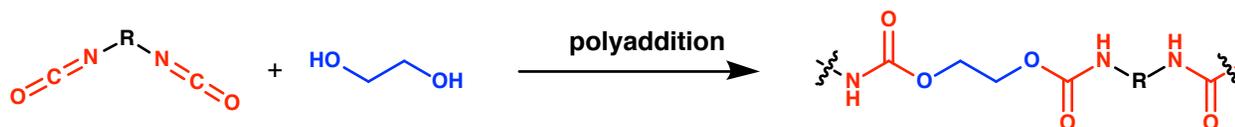


Not discussed:

- mechanical properties of different polymer types
- detailed discussion of polymer structure vs. morphology
- in depth discussion of how commercial polymers are made
- polymer characterization and property analysis

Step-growth polymerization:

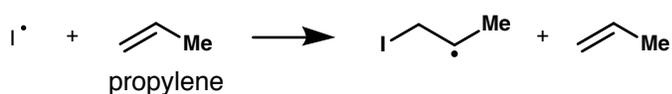
- bifunctional monomers react to form first dimers, then trimers, then oligomers separately. The polymer does not form until near complete conversion.
- polyesters, polyamides, and polyurethanes form through step-growth polymerization
- can be separated into addition reactions, in which no byproducts are formed, and polycondensation, in which water is usually lost as a byproduct (esterification)



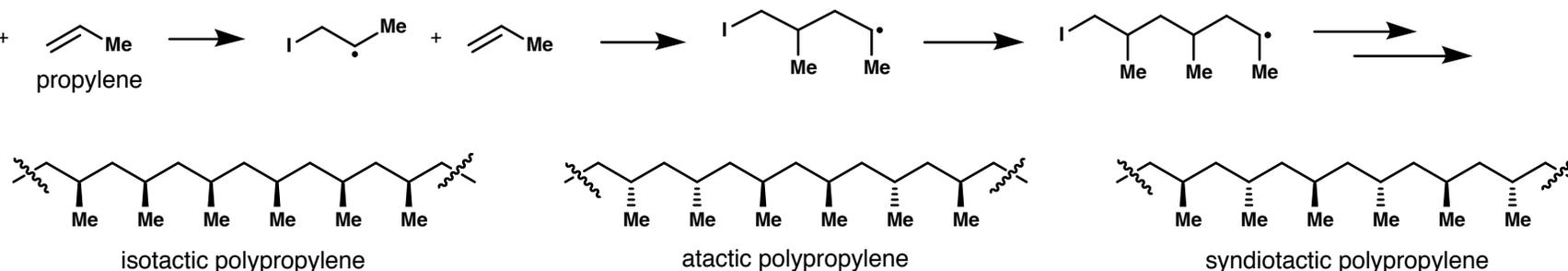
Chain-growth polymerization:

- Monomers add onto the active site of a growing polymer chain one at a time. Addition of each monomer regenerates the active site.
- An initiator is necessary to begin polymerization.
- Vinyl polymers including polyethylene, polypropylene, and polyvinyl chloride are made this way.
- Polymerization methods include free radical polymerization, ionic polymerization (cationic and anionic), ring-opening, and polymerization via catalysis.

Initiation:

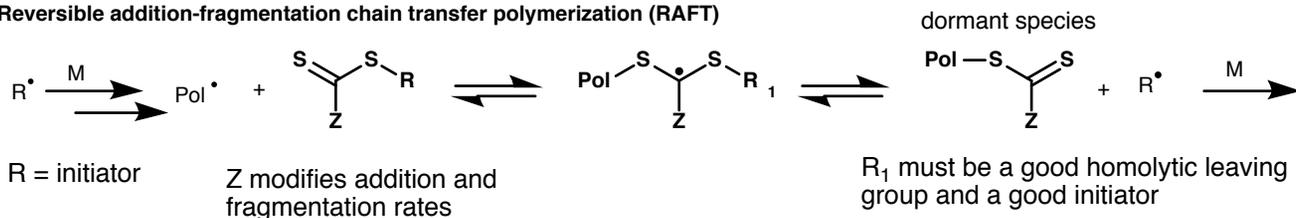


Propagation:



- Atactic polymers made via free radical polymerization, atactic and syndiotactic can be made selectively using complex coordination catalysts including the Ziegler-Natta catalyst.

Reversible addition-fragmentation chain transfer polymerization (RAFT)



- a type of living polymerization
- majority of 'living' chains are dormant
- there is ideally a rapid equilibrium between the dormant and active chains
- allows control over molecular weight and polydispersity during polymerization.

- Other polymerization methods include living radical polymerization (no chain termination), atom transfer radical polymerization, and metathesis.

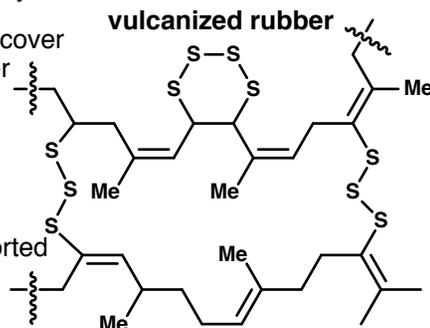
Polymer processing (molding) processes including:

1. *Mixing or compounding* includes mixing additives into polymer to achieve the desired specifications.
2. *Forming* is required to achieve the desired shape of the polymer. 2D forming includes extrusion, and coating. 3D forming includes thermoforming (heat), compression molding, transfer molding, injection molding, and rotational molding.
Extrusion is when polymers are given a controlled cross-section by softening (heat/pressure), and forcing material through an aperture (styrofoam).
3. *Finishing* includes the decoration and assembly of the polymers.

1833: Swedish chemistry Berzelius coins term 'polymer'

1839: E. Simon discovered an oily substance from the American sweetgum tree that later turned out to be polystyrene.

1840s: F. Ludersdorf and N. Hayward discover that adding sulfur to natural rubber would **vulcanize** it, irreversibly strengthening it and making it resistant to melting.



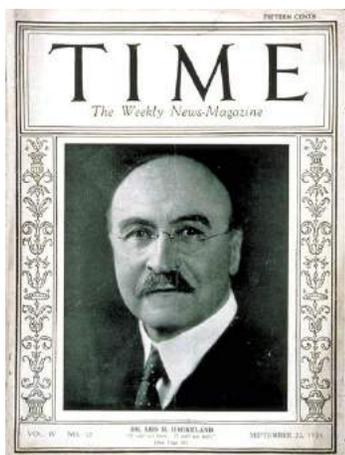
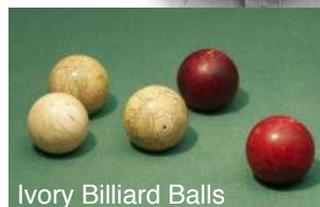
1860s: synthesis of poly(ethylene) glycol and poly(ethylene) succinate reported with correct structures

1862: Alexander Parkes creates invents nitrocellulose, termed parkesine at the time, the first truly manmade plastic.

1869: Phelan and Collender challenged inventors to develop an alternative to ivory as a material to make billiard balls.



John Wesley Hyatt further experimented with nitrocellulose and found that it could be hardened into an ivory-like solid, and was used for a short time in billiard balls.



Early 1900s: first truly synthetic polymer, a phenol formaldehyde resin was commercialized by German chemist Leo Baekeland; later termed *Bakelite* (became a replacement for billiard balls)

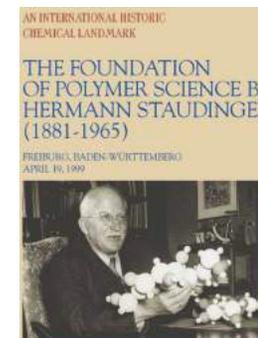
Around this time, polyester paints and polybutadiene rubber were introduced

At this time, polymer structure was not clearly defined. A prevailing theory was that polymers were aggregates of small molecules, similar to colloids, held together by a *mysterious force*. **Hermann Staudinger** attributed the unique properties of polymers to ordinary intermolecular forces between molecules of high molecular weight, linked by covalent bonds.

1930: Wallace Hume Carothers put Staudinger's theories to the test, leading to the discoveries of nylon and neoprene.

1953: Hermann Staudinger was awarded the nobel prize for his discoveries in the field of macromolecular chemistry.

"... the strength and elasticity of natural fibers depend exclusively on their macro-molecular structure."



World War 2 brought significant advances to polymer chemistry as the natural rubber-growing regions of the Far East became inaccessible to the Allies.

1955: **Karl Ziegler** discovered a coordination catalyst for initiating polymerization reactions. **Giulio Natta** applied these in a system to develop polymers having controlled stereochemistry.

1963: Ziegler and Natta win the Nobel Prize for their catalyst system. *Stereoregular* polymers have mechanical properties that are often superior.

1980s: The total volume of plastics consumed worldwide overtook that of iron and steel.

In recent years, advances in polymer science have led to the development of endless items ubiquitous to our lives today and that have improved our quality of life. Including degradable sutures, conductive polymers, high-strength aromatic fibers used in oil-drilling, thermal and oxidatively stable polymers for aerospace applications.

However, current paradigms for the generation and disposal of polymers are unsustainable. World plastic production has increased exponentially, from 2.3 million tons in 1950 to 162 million in 1993, and then to 448 million in 2015. This has recently raised many environmental concerns.

- Modern life relies on polymer materials to make clothing, houses, cars and aeroplanes. Advances in medicine, diagnostics, and electronics are possible because of polymers. Plastics improve our quality of life and even contribute to a cleaner environment as materials that enable purification of water and as polymer composites that improve fuel economy.

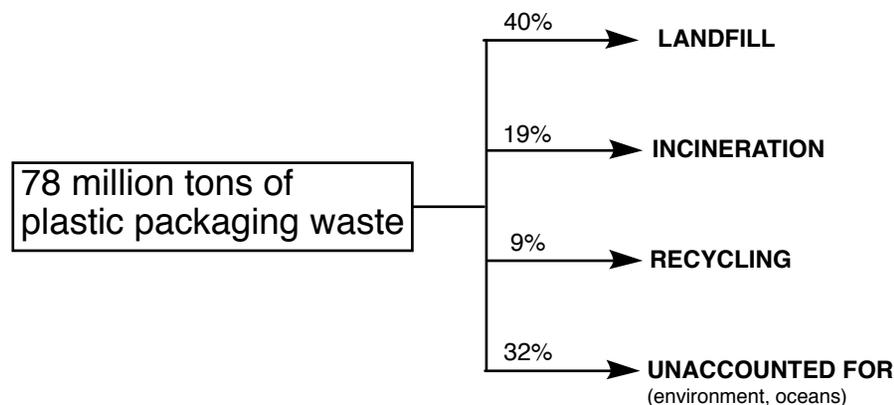
- Global plastic resin production reached 288 million metric tons in 2012, a 620% increase since 1975, but the largest market sector for plastic is in packaging (30%), materials designed for *single use* and immediate disposal. This isn't sustainable.

At present, synthetic polymers are predominantly based on petroleum:

- petroleum is a *non-renewable* resource and it is being rapidly depleted by our increasing energy and plastics demands. The rate at which these feedstocks form is much slower than the rate at which we use them.
- Waste from obtaining petroleum products is toxic and harmful to the environment
- Today, 8% of the total oil produced annually is consumed for the manufacture of polymers. By 2050, that number is expected to be 20%.

There is no end-of-life plan for most synthetic plastics:

- Synthetic polymers make up around 11% of municipal solid waste by mass. Due to their low density, they take up more space and unlike many forms of trash (food, paper), they don't degrade. They persist for millennia.
- Even 'compostable' and 'bio-degradable' plastics today cause huge problems because communities aren't equipped with the infrastructure to properly dispose of them. (i.e. PLA)

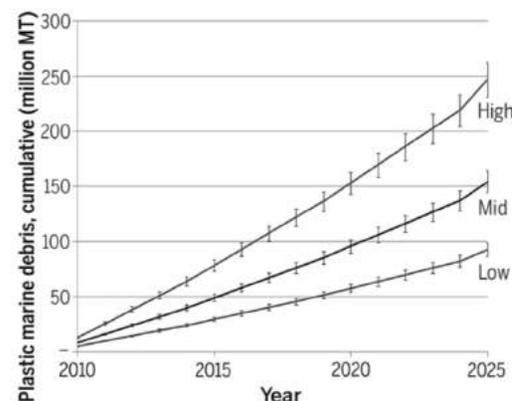


Policy changes are necessary:

- Change occurs when there are policies in place to enforce it.
- Industries aren't interested in making changes to the large scale production of polymeric materials unless they weigh favorably in a cost-benefit analysis. The benefit of a healthy planet doesn't weigh heavily. Therefore, it is important to invent ideas that are both **sustainable** and **cost-efficient**.
- In 2014, only 1.7 megatonnes of more than 300 megatonnes of polymers produced globally were bioderived. They are not yet favorable in terms of cost or material properties when compared to conventional plastics.
- A full life cycle analysis of a new product is necessary to determine if it will improve upon the sustainability of current materials; but sustainability is really difficult to quantify.

Plastic waste inputs from land into the ocean:

- 275 million metric tons (MT) of plastic waste was generated in coastal cities in 2010, with 4.8 to 12.7 million MT entering the ocean.
- Over 80% of waste that accumulates on shorelines is plastic.
- On the west coast alone, removal of plastic pollution costs over half a billion dollars annually.
- Without waste management infrastructure improvements, the cumulative quantity of plastic waste available to enter the ocean from land is predicted to increase by an order of magnitude by 2025.
- Plastics in marine environments are particularly concerning because of their persistence and effects on marine life. Weathering of plastics causes fragmentation into pieces that invertebrates ingest. These travel up the food chain and have found their way into animals.



This begs the question, have we entered the anthropocene?

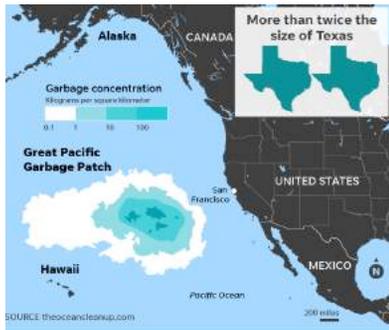
Polymers in Sustainability: Painting a Bleak Picture



Kim Preston - art



We depend on plastic.
Now, we're drowning in it.



Plastic Beach on Henderson Island

- this is an uninhabited island that collects around 3,500 pieces of trash every day
- for every square meter you walk, on average you'll find 672 pieces of trash



Pieces of plastic found in the stomach
of a single albatross chick

Some broad strategies for the development of **sustainable polymers**:

1. **Sustainable polymers from renewable resources**: upcycling of CO₂, terpenes, vegetable oils, carbohydrates and other biomass as feedstocks.

Pros:

- Reduces our reliance on non-renewable materials
- For the upcycling of CO₂, our present infrastructure for petrochemical polymers can be used. And raw materials aren't taken from agriculture.

Cons:

- No end-of-life solution, they don't necessarily degrade. (bio-PET)
- Using plant-based materials means using feedstock that we use for food
- Terpenes consistently make only low molecular weight polymers that are expensive to produce.

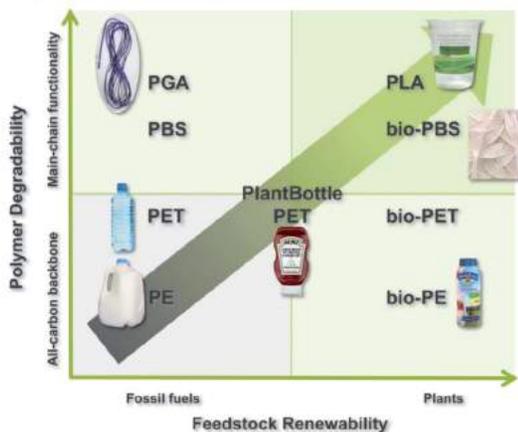
2. **Degradable materials**: to produce a plastic that is structurally sound for as long as it needs to be, yet degrades easily when its usefulness passes.

Pros:

- polymers may have an end-of-life that leaves them environmentally innocuous
- mainly derived from biorenewable sources

Cons:

- biodegradable materials fail to recover valuable feedstock chemicals
- degraded materials, especially those that don't degrade completely, can cause unintended environmental consequences (*i.e.* microplastics)
- Our current infrastructure for biodegradables is not adequate. When they end up in our recycling streams they cause contamination.
- Designing polymers that are robust in use, but degrade readily when discarded is a massive challenge.
- Biodegradability and high performance are often mutually exclusive. Materials that are durable and resistant to heat and chemicals are unlikely to degrade in a timely manner.



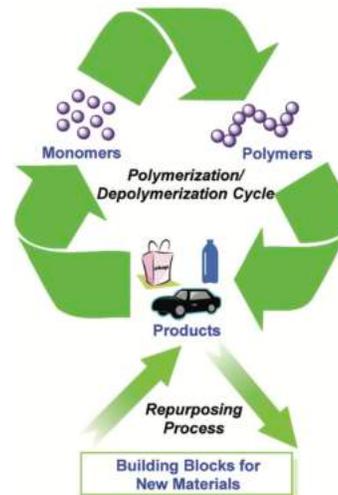
3. **Chemical recycling** (circular economy): this involves either depolymerization or repurposing of polymer waste to allow reclamation of high-value small molecules from discarded polymers. This is still very new.

Pros:

- reduce demand for finite raw materials
- minimize negative impact on the environment
- address end-of-life issue of synthetic polymers

Cons/challenges:

- polymers that can be easily depolymerized often have poor properties (Tg)
- complete feedstock recycling in depolymerization is rare
- chemical recycling is costly and energy intensive
- doesn't necessarily incorporate biorenewable resources



Industrial mechanical recycling suffers from significant quality loss and much of the material is lost all together. Chemical recycling offers a more sustainable solution and can allow for recovery of precursor building blocks in high purity.

4. **Reprocessable thermosets**:

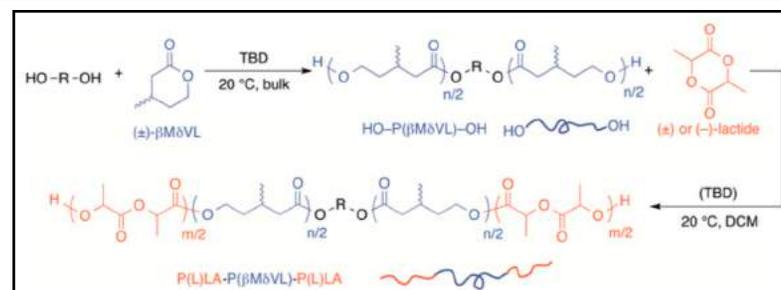
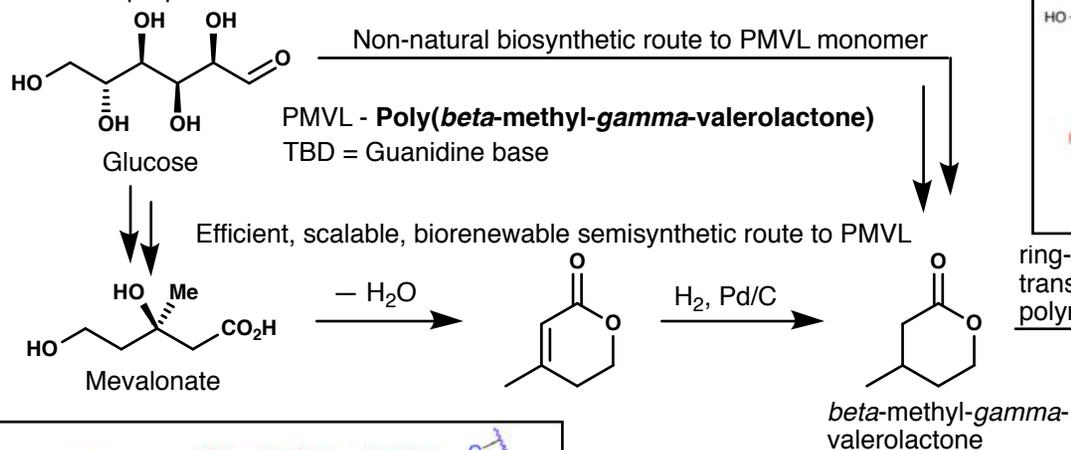
- rubbers with *reversible* covalent crosslinks

5. **Advanced catalysis for sustainable polymers**

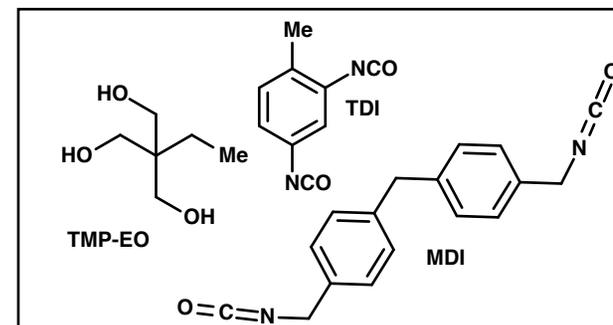
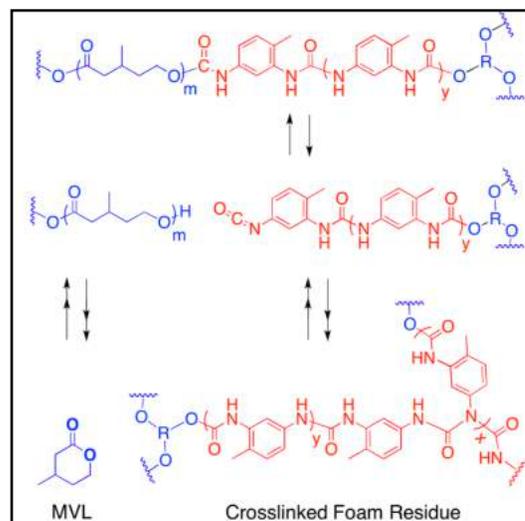
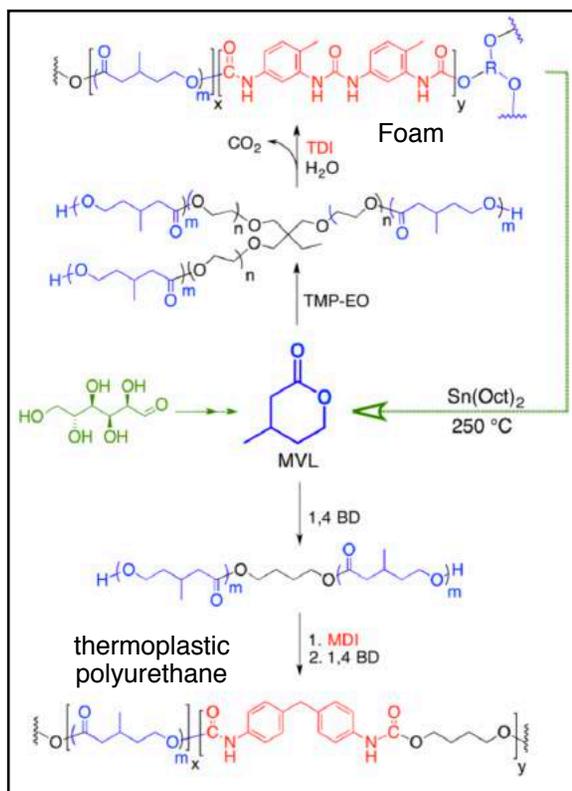
There is no panacea. Some petrochemicals are bio-degradable and not all bioderived polymers will degrade. 'Bio' doesn't necessarily mean 'green'.

Polymers in Sustainability: A biorenewable polymer that can be chemically recycled

- Development of triblock copolymers of PLA and PMVL with good thermal and mechanical properties.



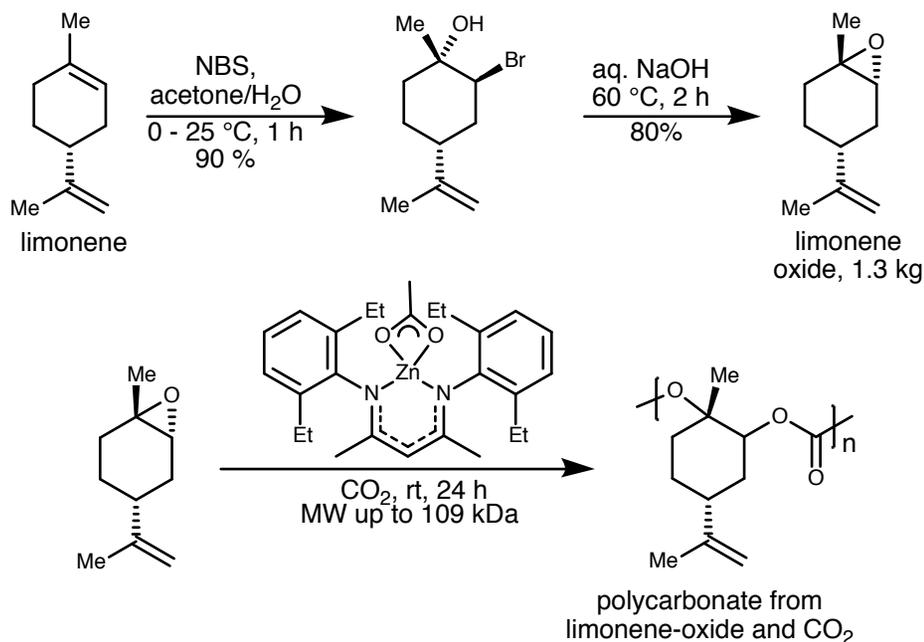
-Thermal and mechanical properties match those of commercial styrenic block polymers



- Cross-linked PMVL polyurethanes (PUs) can be chemically recycled through pyrolytic degradation, that recovers the MVL monomer in excellent yield and high purity. No addition of solvents is needed.
- TPUs are linear with urethane-rich hard segments; foams are branched networks containing polyurea hard segments. Foams are unique due to the microphase separation of hard and soft segments resulting in nanoscopic heterogeneities. Hydrogen bonding reinforces the crosslinks.
- PVML TPUs and foams exhibited excellent properties, comparable to commercial polyurethane materials
- Renewable polyols could replace petroleum derived polyols in the synthesis of TPUs and foams.

Bio-based polycarbonate from limonene oxide and CO₂ with great properties

- Conventional polycarbonate is a strong material with many applications, but it is made from toxic chemicals phosgene and bisphenol-A (BPA) that are derived from petrochemicals.
- Previous work to improve on the standard suffered from low T_g, were not biorenewable, or had poor mechanical properties.
- Limonene is an abundant terpene found in the peels of many citrus fruits, making it an optimal choice for a biorenewable monomer. Previous work from Coates and coworkers produced limonene oxide, CO₂-derived polycarbonates, but they suffered from low molecular weights (< 25 kDa).

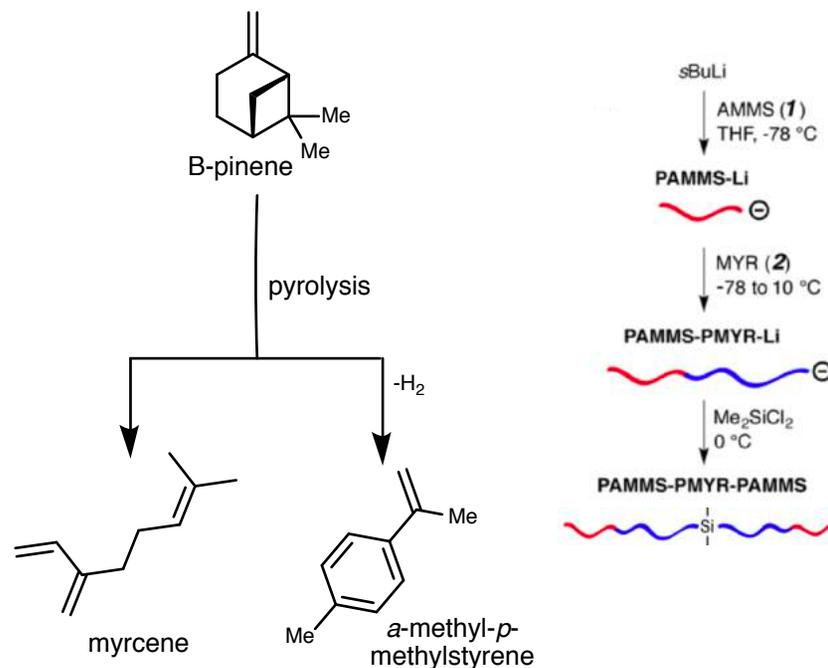


- The resulting polycarbonate can be made with high MW > 100 kDa in almost quantitative conversion (> 90%).
- Use of > 95% pure *trans* isomer, and making sure to remove all alcohol impurities, were crucial in obtaining high conversion.
- Catalyst can be removed with EDTA silica
- T_g = 130 °C; PLimC has excellent transparency and hardness.
- Would make a good 'green' coating material.

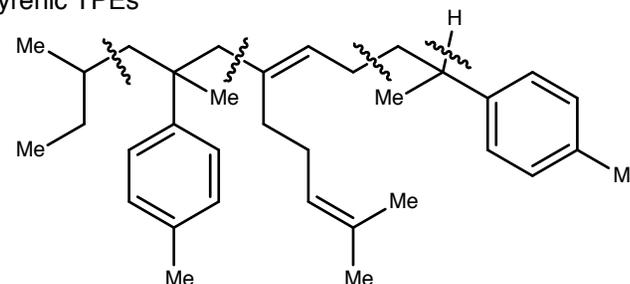
Coates and coworkers, *JACS*, **2004**, 126, 11404-11405
Hauenstein *et. al.* **2016**, *Green Chem.* 18, 760-770

Sustainable Thermoplastic Elastomers from Terpene-Derived Monomers

- Thermoplastic polymers are used in wide-ranging applications including personal care products, adhesives, footwear, asphalt, and coatings.
- Styrenic triblock TPEs have similar properties to cross-linked rubbers, but they can be melt-processed like thermoplastics.
- These are generally derived from petrochemicals.



- **ABA triblock copolymer** formed by sequential anionic polymerization, followed by dichlorodimethylsilane coupling with high efficiency.
- Polymer show improved performance at high temperature compared to current styrenic TPEs

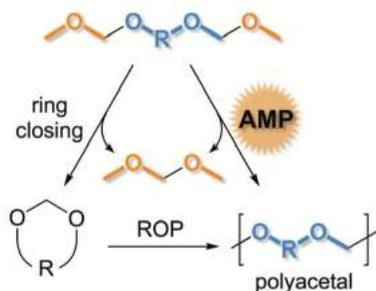


Bolton, J. M., Hillmyer, M. A., Hoye, T. R., *ACS Macro Lett.*, **2014**, 3, 717-720

Purpose: To synthesize polymers from plant-based building blocks that degrade readily and benignly in the environment.

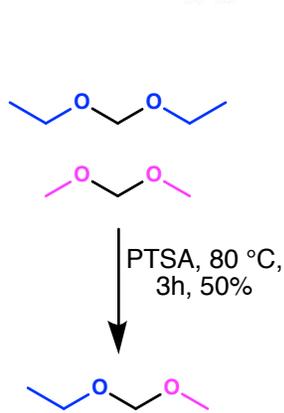
Acetal Metathesis Polymerization (AMP):

- a method to mirror acyclic diene methathesis
- Functional group metathesis polymerization also amenable to polycarbonates and polyoxalates.



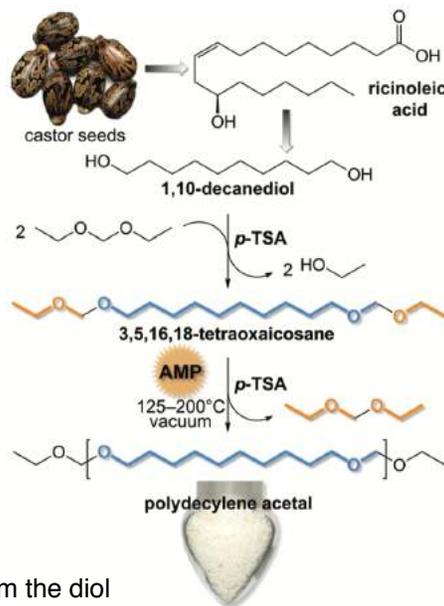
Why acetals?:

- consideration of *green birth* and *green death* imperative.
- diols easily obtained from biomass
- readily hydrolyzed under acidic aqueous conditions, congruous with conditions in a landfill.



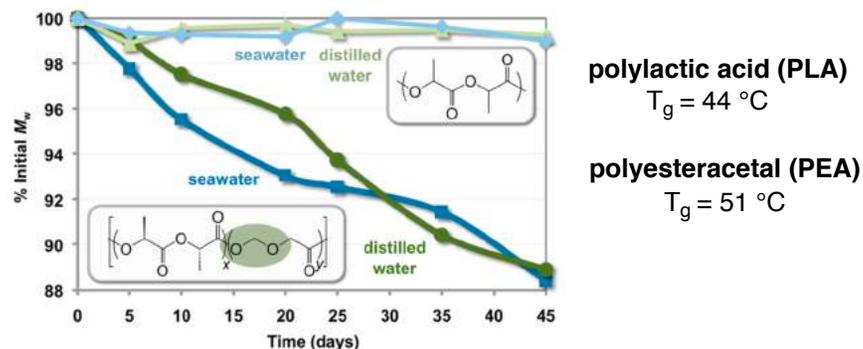
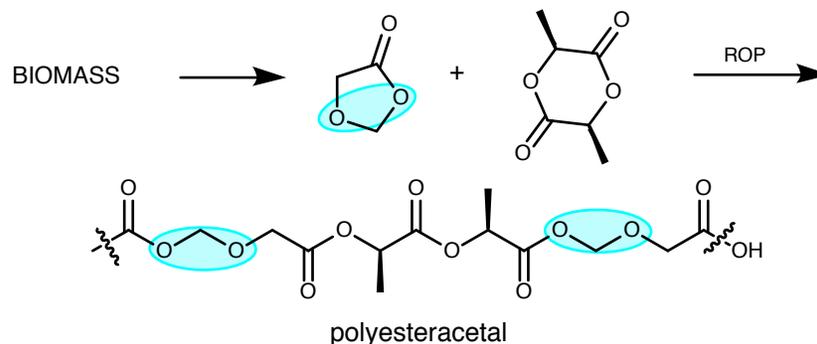
- Equilibrium of unsymmetrical acetal can be achieved rapidly from two symmetrical acetals.

- Reaction can be done in one-pot from the diol
- High molecular weight polymers can be obtained
- The polyacetals can be degraded abiotically at a rate that is comparable to that of PLA.



Improving PLA

- Polylactic acid (PLA) now stands as the most successful biorenewable synthetic thermoplastic, and it is used in several packaging markets and for beverage cups at some fast food restaurants. However its low glass transition temperature and long degradation times make its usefulness questionable.
- Additionally, the current lack of composting infrastructure make its disposal inconvenient.

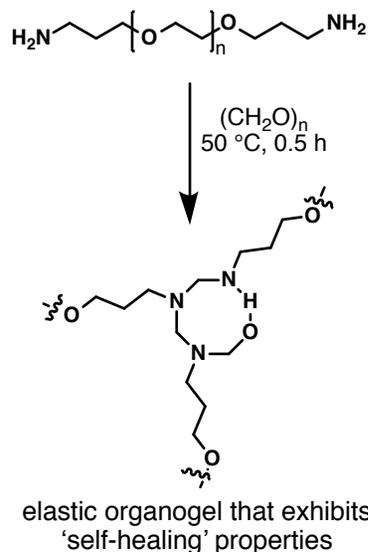
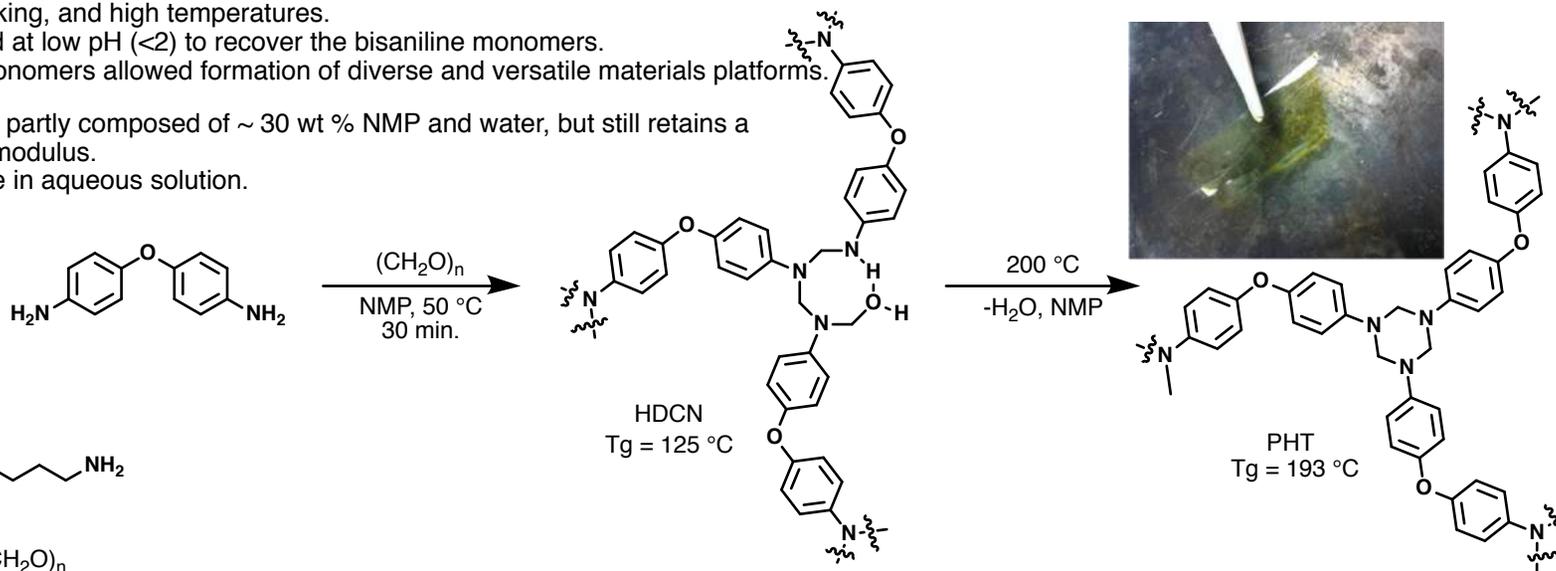


Extrapolated degradation times on the order of 5-10 years with 4 mol% acetal unit present.

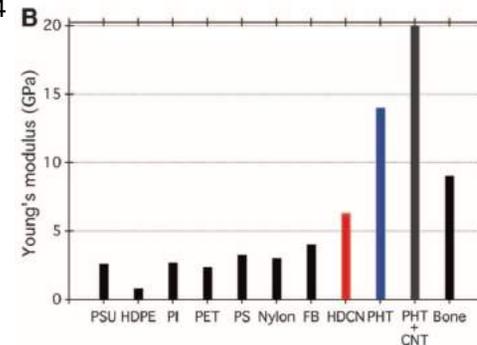
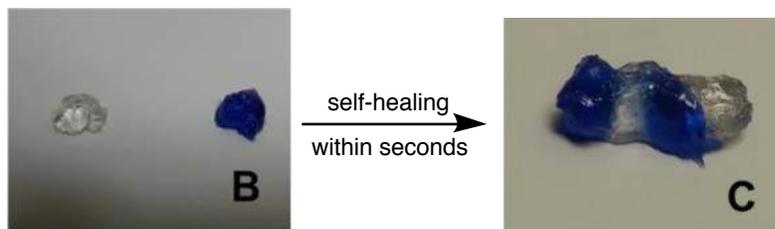
- Others have made similar PLA structures that degrade when triggered by light or certain pH levels.
- Due to fast degradation, these plastics would be most useful in single-use disposable packaging.

Recyclable, Strong Thermosets and Organogels via Paraformaldehyde Condensation with Diamines

- Nitrogen-based thermoset polymers have many industrial and commercial applications including polymer composites, adhesives, coatings, foams, and aerospace parts, but they are difficult to recycle and 're-work'.
- A simple, one-pot, low-temperature polycondensation between paraformaldehyde and 4,4'-oxydianiline (ODA) forms hemiaminal dynamic covalent networks (HDCNs), which can further cyclize at high temperature, producing poly(hexahydrotriazine)s (PHTs).
- Both materials are strong thermosets, exhibit very high Young's modulus (comparable or better than conventional thermosets), and are resistant to solvent, environmental stress-cracking, and high temperatures.
- They can both be digested at low pH (<2) to recover the bisaniline monomers.
- Using different diamine monomers allowed formation of diverse and versatile materials platforms.
- HDCN is stabilized by and partly composed of ~ 30 wt % NMP and water, but still retains a surprisingly high Young's modulus.
- ODA PHT is entirely stable in aqueous solution.



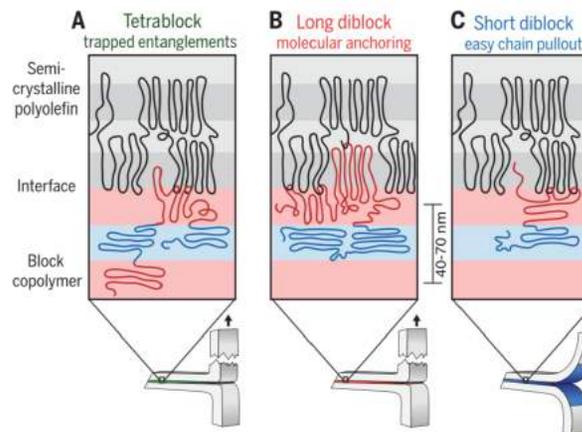
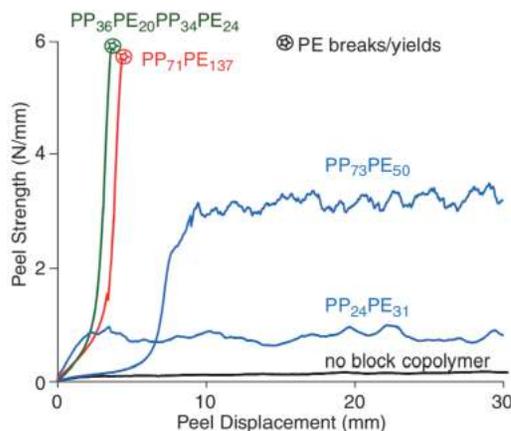
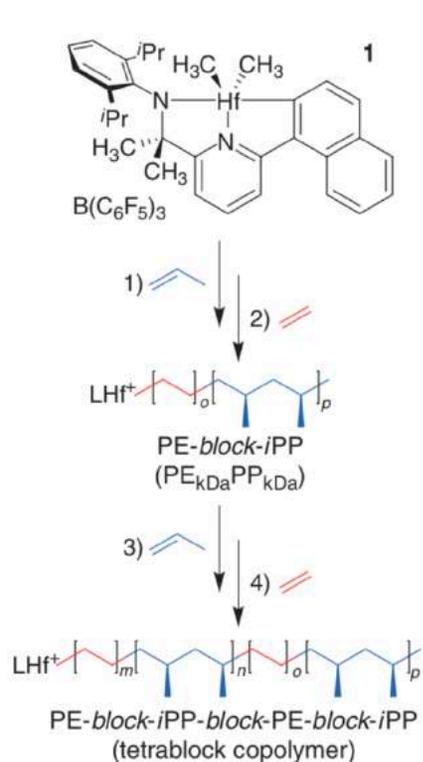
- HDCN was depolymerized in 56 minutes at pH < 2, while ODA PHT took 24 hours to be digested. They are the first easily depolymerized thermosets.
- ODA PHTs could be used in environments where robust, solvent-resistant materials are necessary; PHTs would be useful in developing recyclable microelectronics.
- The organogel formation was reversible in water after 24 hours.



Nanoindentation results indicate that the PHT is among the strongest amorphous thermosets known.

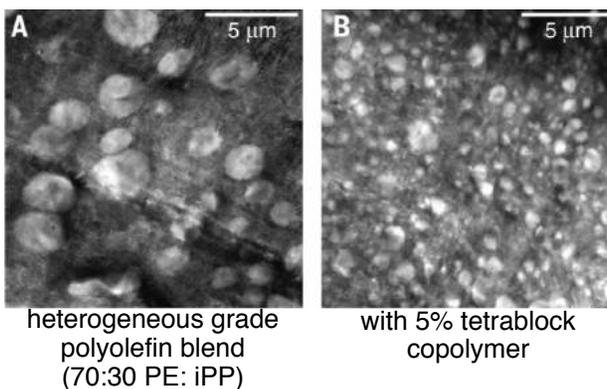
Polymers in Sustainability: Combining polyethylene and polypropylene

- Polyethylene (PE) and isotactic polypropylene (iPP) constitute nearly two-thirds of the world's plastic.
- The similar densities of PE and iPP complicate their separation in mechanical recycling of post-consumer plastics.
- Despite their common hydrocarbon skeletons, PE and iPP melts are immiscible, thus common grades of the two do not blend or adhere, making recycling of these materials difficult. Less than 5% of the value is retained when they are recycled, typically into lower-value products.
- Strategies to combine PE and iPP would have significant potential to affect sustainability and economy.
- Using a pyridylamidohafnium precatalyst and activator $B(C_6F_5)_3$, high molecular weight iPP and PE diblock and tetrablock copolymers were prepared.
- The 'living' characteristics of the catalyst system enabled precise control of block length and molar mass dispersity.



- Due to weak van der Waals interactions, PE and iPP display poor interfacial adhesion.
- To test the adhesion between PE and iPP laminates with and without the presence of block copolymers, a peel test was used.
- Laminates without block copolymers peeled apart easily.
- The blends with tetrablock copolymer exhibits considerable adhesive strength.
- Interfacial mixing during melt compression produces entangled loops that effectively stitch together the homopolymers and block copolymer films upon crystallization and cooling.

- Essentially, the copolymers act as macromol. welding flux materials that encourage the two homopolymers to mix more homogeneously.
- Increasing overall block size enhances interpenetration and the number of entanglements between the homo- and copolymers.

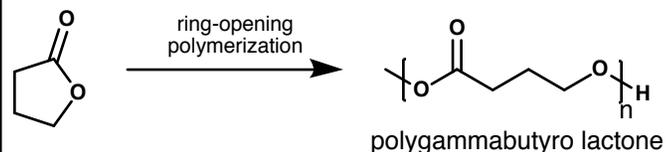


- Interfacial activity of block copolymer evidenced by a reduction in average droplet size after addition of tetrablock copolymer.
- Compared to pure iPP and PE, and a blend of the two, the block copolymers display increased ductility and strain hardening when pulled in tension at room temperature.
- This is a result of interfacial adhesion, reduced particle size, and efficient stress transfer between phases.

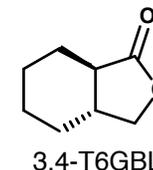
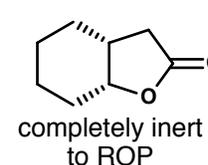
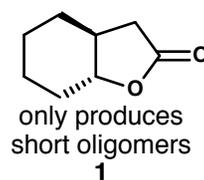
Purpose: Chemically recyclable polymers offer a solution to the end-of-use issue of polymeric materials and provides a closed-loop approach toward a 'circular materials economy'

- With specifically designed monomers, reaction conditions can be used to select the direction of monomer-polymer equilibrium, with low temperature and high monomer concentration favoring polymerization and high temperatures or dilution trigger depolymerization.

Previous work:

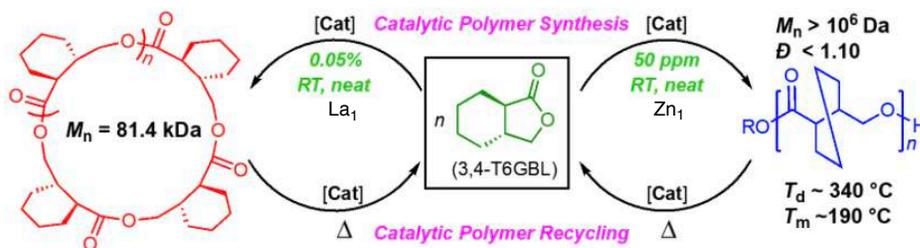


- selectively and quantitatively depolymerized back to GBL by heating at 260 °C or 300 °C
- synthesis requires energy-intensive, low temperature conditions (-40 °C)
- low thermal stability and crystallinity



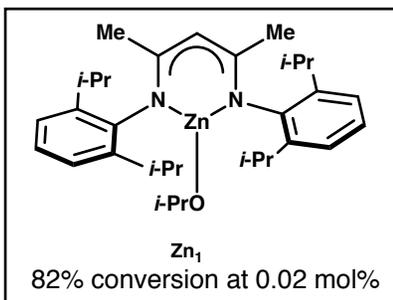
Designing 3,4-trans six-membered ring-fused gamma-butyrolactone:

- Keep GBL core to preserve complete chemical recyclability
- Increased thermodynamic polymerizability (ring-strain) could be tuned via GBL ring substituents.
- Removing gamma-substituent from **1** should increase ring strain, enhancing thermodynamic polymerizability and polymerization rate by releasing steric pressure

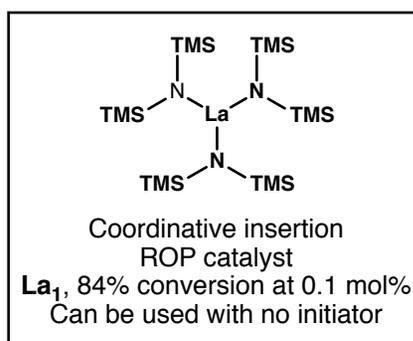


Conclusions:

- trans ring fusion renders the commonly nonpolymerizable GBL ring readily polymerizable at room temperature under solvent free conditions to yield a high MW polymer.
- The chemical recyclability of the linear and cyclic polymers was tested by thermolysis (300 °C) and chemolysis (ZnCl₂ at 120 °C), providing **full chemical recyclability** to give pure 3,4-T6GBL in every case. This was repeatable through three chemical cycles.
- Linear and cyclic polymers exhibit high thermal stability.



Initiator:
PhCHCH₂OH



Introduced solutions to three challenges in chemically recyclable polymers

1. selectivity in depolymerization
2. trade-offs between polymers' depolymerizability and their properties and performance
3. circular monomer-polymer-monomer cycle

PGBL polymers have promising applications in biodegradable medical devices.

Synthesis of pure cyclic polymers with appreciable molecular weights are critical for topology-property relationships, but generally present many challenges, making this noteworthy.

Efficient and selective degradation of polyethylenes into liquid fuels and waxes under mild conditions

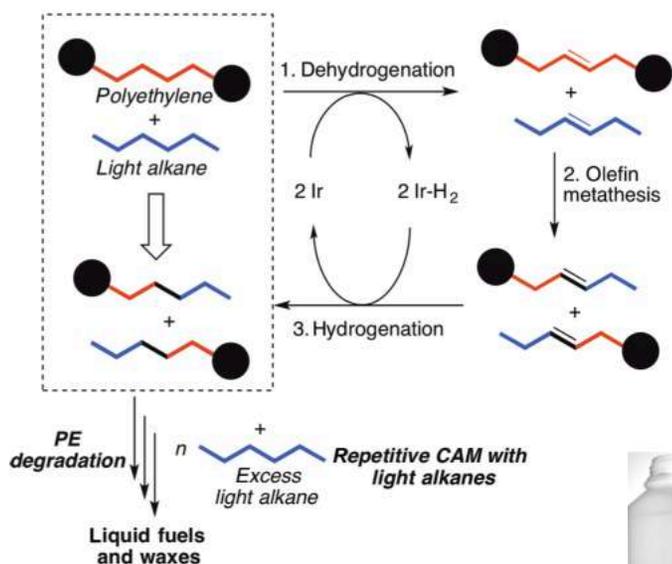
Rationale:

- polyolefins (HDPE, LDPE, LLDPE, PP) constitute more than 60% of total plastic content of municipal solid waste.
- annual production of polyethylene exceeds 100 million metric tons, but it is difficult to recycle because it is remarkably inert and difficult to degrade.
- high temperature degradation strategies are energy inefficient and result in complex product compositions.

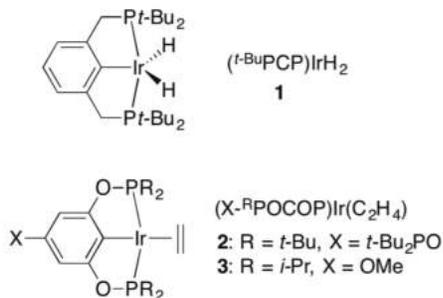
Strategy:

- polyethylene degradation based on a tandem catalytic cross alkane metathesis process involving one catalyst for alkane dehydrogenation, and another for olefin metathesis.
- large excess of 'light' alkane necessary. This also acts to dissolve the PE, forming a dilute solution of low viscosity.
- PE is eventually converted into short hydrocarbons suitable for transportation oils.
- The distribution of degradation products can be controlled by reaction time and dehydrogenation catalyst used.
- The reaction is fast, with no parent PE found after 2 hours.
- The closer the double bond is to the middle of the PE, the more efficiently the chain length is reduced.
- Combining **2** and the olefin metathesis catalyst led to a 98% conversion of PE to oils.

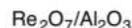
A Cross-alkane metathesis (CAM) between polyethylene and a light alkane (*n*-hexane):



Dehydrogenation and hydrogenation catalysts:



Olefin metathesis catalyst:



- Both catalysts can be recycled



Isolation



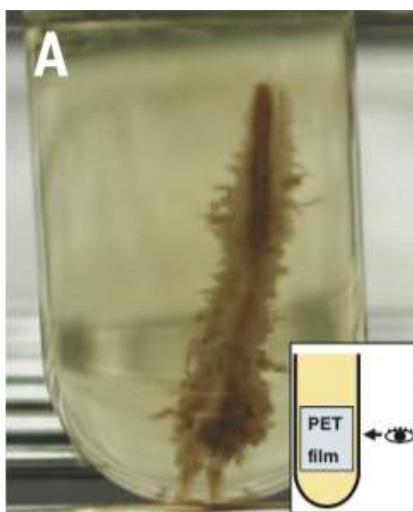
- PE waxes are used as slips, dispersants, and resins. These are difficult to make with narrow molecular distribution via ethylene polymerization

0.3 g each	8 ml petroleum ether	Isolated oil (C ₇ -C ₃₈)	Wax
HDPE plastic bottle	2/γ-Al ₂ O ₃ and Re ₂ O ₇ /γ-Al ₂ O ₃	1.8 g	2 mg
Food packaging film		0.77 g	7 mg
Grocery shopping bag		0.77 g	3 mg

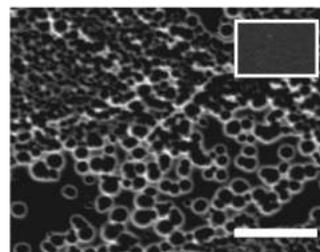
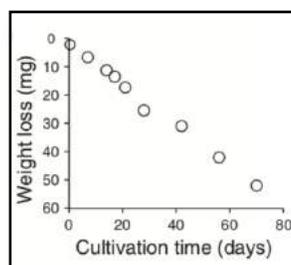
all reactions afforded alkanes in the 'diesel range'

A bacterium that degrades and assimilates poly(ethylene terephthalate)

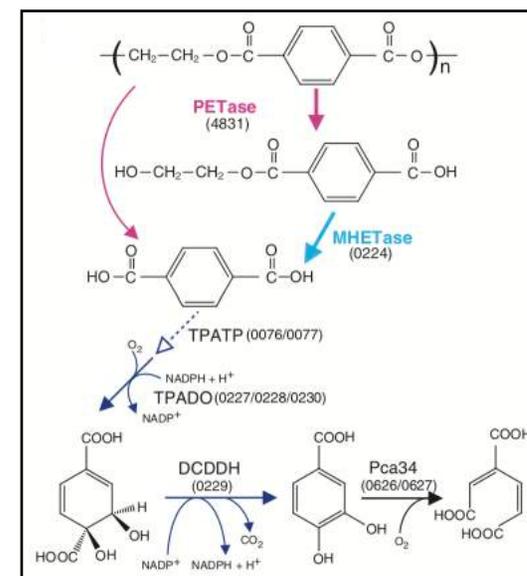
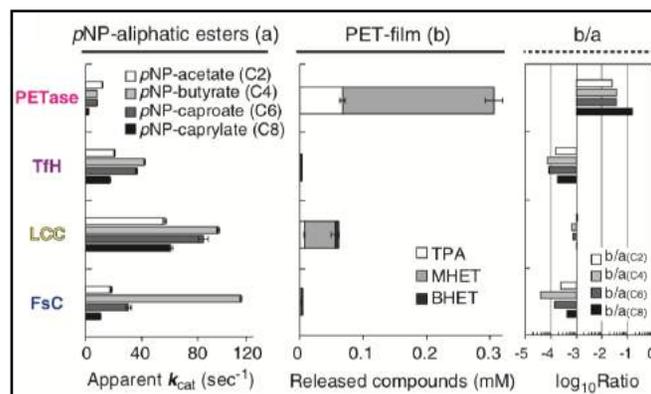
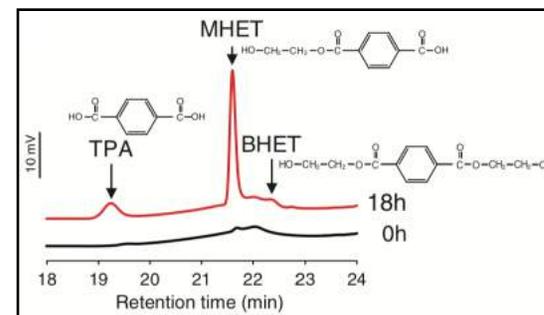
- PET is used extensively worldwide for clothing fibers (polyester), containers for liquids and foods, and in some engineering resins. It is chemically inert, generally making it resistant enzymatic biodegradation, and it is accumulating in ecosystems across the globe.
- Once identified, microorganisms with enzymatic machinery to degrade PET could serve as an environmental remediation strategy and a degradation/fermentation platform for PET recycling.
- Natural microbial communities exposed to PET (debris contaminated environmental samples at a PET bottle recycling site) were collected. Of 250 samples, one sediment sample contained a distinct microbial consortium that formed on the PET film upon culturing, and induced morphological changes to the plastic.
- A novel bacterium, *Ideonella sakaiensis* 201-F6, was isolated from the sample.
- When grown on PET, the bacteria produces two enzymes capable of hydrolyzing PET and the reaction intermediate, mono(2-hydroxyethyl) terephthalic acid.



The PET film was damaged extensively and almost completely degraded after 6 weeks at 30 °C into two environmentally benign monomers, terephthalic acid and ethylene glycol.



prominent 'pitting' on PET film



- The activity of the novel bacterium was compared to that of three evolutionarily divergent PET-hydrolytic enzymes. It was found that the catalytic preference of the novel PETase for PET film over nitrophenol-linked aliphatic esters was substantially higher than that of the other enzymes.

Polymers in Sustainability: How do we quantify sustainability?

At the United Nations World Commission on Environment and Development, **sustainable development** was defined as: *meeting the needs of the present without compromising the ability of future generations to meet their own needs*

- Sustainability can be very difficult to quantify; every solution has its own pros and cons.
- A commonly used sustainability metric is called Life Cycle Analysis (LCA): it considers the environmental aspects of a product from *cradle to gate*.

Sustainability Metrics: Life Cycle Assessment and Green Design in Polymers

- 12 commercial polymers were tested: seven derived from petrochemistry, four from biological sources, and one derived from both.
- Each was assessed using LCA methodology and for its adherence to 'green' design principles, using metrics generated for this study.

Seven plastics derived from petroleum:

1. polyethylene terephthalate (PET)
2. high density polyethylene (HDPE)
3. low density polyethylene (LDPE)
4. polypropylene (PP)
5. polycarbonate (PC)
6. polyvinyl chloride (PVC)
7. general purpose polystyrene (GPPS)

Four plastics derived from biological sources:

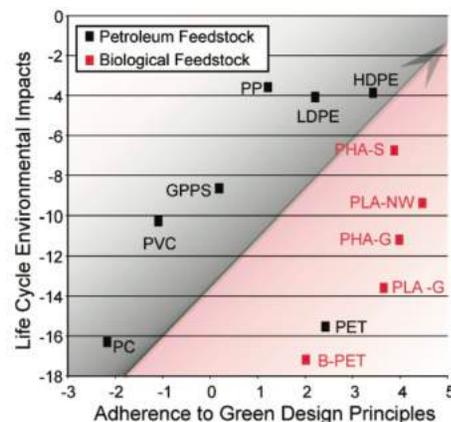
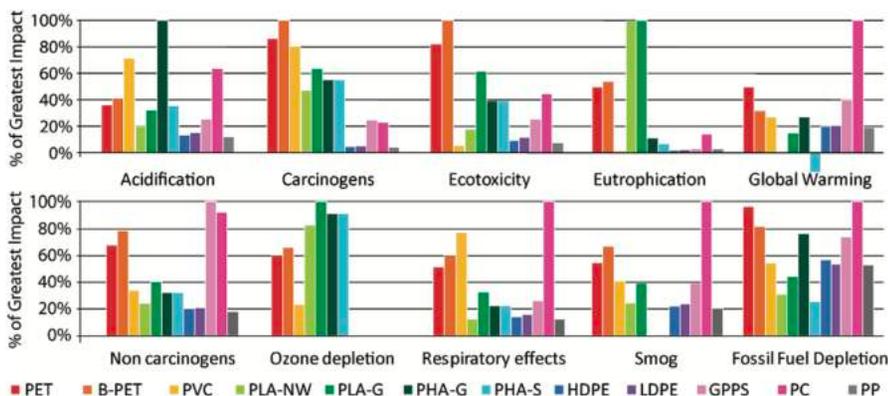
1. PLA made by a general process (PLA-G)
2. PLA made via a process reported by NatureWorks
3. polyhydroxyalkanoate from corn grain (PHA-G)
4. PHA from corn stover (PHA-S)

From petroleum and biological source: biopolyethylene terephthalate (B-PET)

Metrics for Green Design Principles	
theme	metric
avoid waste	atom economy
material efficiency	density
avoid hazardous materials/pollution	TRACI health and ecotoxicity impacts
maximize energy efficiency	Total Energy Demand
use of renewable sources	percent from renewable sources
use local sources	feedstock distance
design products for recycle	percent recycled
design to degrade	biodegradability
cost efficiency	price

Material	Overall Atom Economy (%)	Carcinogens (kg benz. eq/L)	Non-Carcinogens (kg tolu. eq/L)	Respiratory Effects (kg PM2.5 eq/L)	Ecotoxicity (kg benz. eq/L)	Energy Demand (MJ eq/L)	Cumulative % Renewable Material	Distance of Feedstocks	% Recovery	Biodegradable	Price (USD/L)
PET	80%	1.1x10 ⁻²	62.9	4.9x10 ⁻³	5.72	123.8	0%	Intern.	18%	N/A	4.13
B-PET	62%	1.3x10 ⁻²	72.7	5.7x10 ⁻³	6.98	146.2	15%	Intern.	18%	N/A	4.13
PVC	55%	1.1x10 ⁻²	31.7	7.3x10 ⁻³	0.40	82.9	0%	Intern.	0%	N/A	4.02
PLA-NW	80%	6.1x10 ⁻²	22.5	1.2x10 ⁻³	1.21	79.4	100%	R egion.	0%	Indus.	4.66
PLA-G	80%	8.4x10 ⁻²	37.5	3.1x10 ⁻³	4.31	98.3	100%	R egion.	0%	Indus.	4.66
PHA-G	48%	7.2x10 ⁻³	30.0	3.1x10 ⁻³	2.76	91.5	100%	R egion.	0%	Backyard	6.20
PHA-S	48%	1.1x10 ⁻²	30.0	2.1x10 ⁻³	2.76	91.5	100%	R egion.	0%	Backyard	6.20
HDPE	100%	6.5x10 ⁻⁴	18.7	1.3x10 ⁻³	0.65	73.4	0%	Intern.	10%	N/A	1.52
LDPE	100%	6.9x10 ⁻³	19.6	1.5x10 ⁻³	0.82	73.3	0%	Intern.	5%	N/A	1.58
GPPS	98%	3.2x10 ⁻³	92.7	2.5x10 ⁻³	1.79	92.2	0%	Intern.	1%	N/A	2.35
PC	59%	3.0x10 ⁻²	85.6	9.5x10 ⁻³	3.13	128.9	0%	Intern.	0%	N/A	5.25
PP	100%	5.8x10 ⁻⁴	16.8	1.2x10 ⁻³	0.54	67.6	0%	Intern.	0%	N/A	1.78

Life Cycle Assessment Results



Material	Green Design Rank	LCA Rank
PLA (NatureWorks)	1	6
PHA (Utilizing Stover)	2	4
PHA (General)	2	8
PLA (General)	4	9
High Density Polyethylene	5	2
Polyethylene Terephthalate	6	10
Low Density Polyethylene	7	3
Bio-polyethylene Terephthalate	8	12
Polypropylene	9	1
General Purpose Polystyrene	10	5
Polyvinyl chloride	11	7
Polycarbonate	12	11

- Over the past 50 years, the production of synthetic polymers has increased exponentially due to their many positive societal impacts and low production cost. However, this exponential increase is not sustainable in its current state for because:
 1. Current polymer production relies heavily on non-renewable petrochemicals
 2. Most plastics have no end-of-life plan or options that will leave them environmentally benign
- The long term sustainability of the polymer industry hinges on the development of new polymers that are:
 1. Derived from annually renewable resources
 2. Have sensible end-of-life options
 3. Are competitive from both performance and cost perspectives
- The strategy of chemically recyclable polymers shows a lot of promise

“In light of this, we should not accept the status quo because designing a better alternative is daunting. We conclude with what we believe is an apt aphorism, and one that is likely familiar to any student of rheology, *everything flows*. Change is more than possible — it is inevitable.”

citations

Reviews:

- Schneiderman, D. K., Hillmyer, M. A. *50th Anniversary Perspective: There is a Great Future in Sustainable Polymers*, *Macromolecules*, **2017**, 50, 3733-3749
- Zhu, Y., Romain, C., Williams, C. K. Sustainable polymers from renewable resources *Nature*, **2016**, 540, 354-362
- Hong, M., Chen, E. Y.-X. Chemically recyclable polymers: a circular economy approach to sustainability, *Green Chem.*, **2017**, 19, 3692-3706
- Meier, M. A. R. and coworkers, *Chem. Eur. J.* **2016**, 22, 11510-11521 (Biomass-derived monomers and polymers)
- Mülhaupt, R. Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality, *Macromol. Chem. Phys.*, **2013**, 214, 159-174

Historical info, definitions, basics:

- American Chemical Society National Historic Chemical Landmarks. Foundations of Polymer Science: Herman Mark and the Polymer Research Institute. <http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/polymerresearchinstitute.html> (accessed July 18, 2018)
- Polymer Chemistry: An Introduction, 3rd Edition, by Malcolm P. Stevens
- Ziegler, *et. al.*, *ACIE*, **1955**, 67, 541; Natta *et. al.*, *JACS*, **1955**, 77, 1708

Papers:

Waste inputs and sustainability metrics:

- Jambeck J. R., *et. al.*, Plastic waste inputs from land into the ocean, *Science*, **2015**, 347, 6223, 768-771
- Tabone, M. D., *et. al.*, Sustainability Metrics: Life Cycle Assessment and Green Design in Polymers, *Environ. Sci. Technol.*, **2010**, 44, 21, 8264-8269

New Methods:

-

-

Photos:

- Planet or Plastic (National Geographic): <https://www.nationalgeographic.com/environment/planetorplastic/>