

# **Applying the principles of green chemistry to achieve a more sustainable polymer life cycle**

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## **Abstract**

This mini-review highlights how many of the principles of green chemistry can be used to make polymers more sustainable. The use of renewable feedstocks has grown enormously in recent years including use of bio-derived monomers and modifications of natural polymers such as carbohydrates. Polymers are also being designed to allow entry into the circular economy especially where triggered depolymerization (e.g. catalytic recycling to monomer) can occur, which can allow easy separation from other plastics in a mixed waste stream. Computational studies and reaction monitoring are useful in identifying and understanding reactivity trends for polymer synthesis and degradation. Solvent-free reactions, including mechanochemistry, can be employed to reduce process mass intensity and environmental impacts. Use of standard polymer degradation conditions (e.g. ISO standards) and life cycle assessments, in particular hot spot analyses, should be encouraged in order to accelerate progress in this important field.

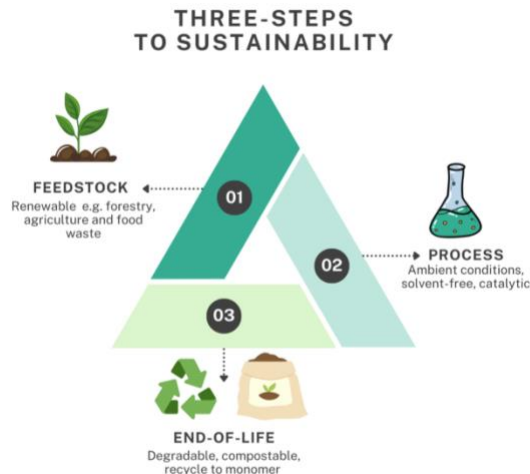
## **Keywords**

Renewable  
Degradable  
Reaction monitoring  
Circular Economy  
Catalysis  
Carbon Dioxide  
Biomass

## **Highlights**

- Many principles of green chemistry can be applied to polymer chemistry
- Beginning and end of life-cycles need to be considered for sustainable polymers
- Closing the loop will allow new low carbon-footprint plastics economies to emerge
- Enormous scope to develop new sustainable materials, catalysts and polymer systems
- Efforts to use standards and life cycle assessments are needed so comparisons can be made and necessary changes can be accelerated

## Graphical Abstract



### 1. Introduction

Chemists worldwide celebrated the 25<sup>th</sup> anniversary of the principles of green chemistry in 2023 and even though progress has been made, system-wide changes are needed.[1-3] Jessop and MacDonald have recently emphasized the role that hotspot-driven research can play in accelerating the rate at which improvements can be made.[4] This approach, which can be used to identify and select research projects, could be applied to 'green' polymer chemistry by highlighting the most harmful stage in a polymer's life cycle. Green Chemistry had its roots in synthetic organic chemistry, which led to impactful changes on how pharmaceutically active compounds were prepared and reduced their environmental burden,[5] similar changes can be envisaged for polymer chemistry. The focus of this review will be on the application of green chemistry principles to polymer systems, Figure 1, and highlight ways in which polymer life-cycles can be made more environmentally benign.[6]

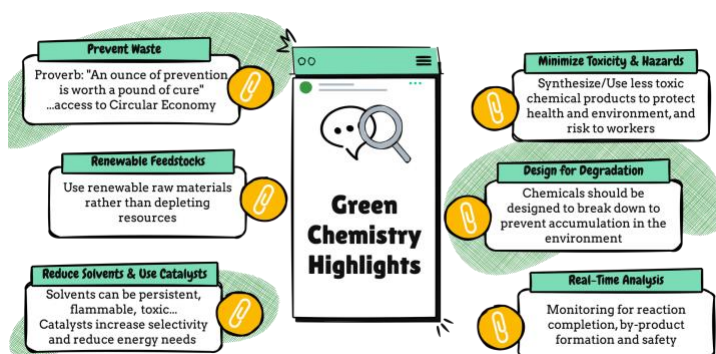


Figure 1: Some of the principles of green chemistry that can be used within the field of polymer chemistry.

There is a clearly a need for plastics in the modern world from low cost packaging materials through to high-value electronics and biomedical applications. However, the environmental cost of plastics has been in the spotlight for the past few decades due to the environmental persistence of the polymers produced at the largest scale, including polyethylene, polypropylene, polystyrene and poly(ethylene terephthalate), PET.[7] These materials gradually break down in the environment and lead to the formation of microplastics, which can enter the food chain and have been found even in the remote arctic environment.[8] Plastic pollution significantly impacts the critical situation concerning the planetary boundary for novel entities,[9] which can no longer be ignored. This has led to unprecedented research efforts focused on developing a more environmentally-benign plastics industry.[10]

## 2. Design for Degradation

Design of degradable polymers can follow two main approaches: (i) design for biodegradation so accumulation in the environment is prevented, or (ii) design for recycling to monomer or repurposing in order to reduce carbon footprints and costs whilst allowing entry into a circular economy.[11] In addition to the polymeric macromolecules, it is also important to consider the effects of polymer additives such as plasticizers, fillers and pigments.[12] In some cases additives can be potentially toxic and environmentally-persistent compounds such as halogenated flame retardants. We have recently reported the use of biochar as an additive (filler and pigment) that increased the rigidity of poly( $\epsilon$ -caprolactone),[13] and we imagine that more bio-derived materials will be used as additives in polymers moving forward. In some cases, addition of bio-sourced fillers, e.g. nanocellulose, can boost degradation of biodegradable polymers.[14, 15]

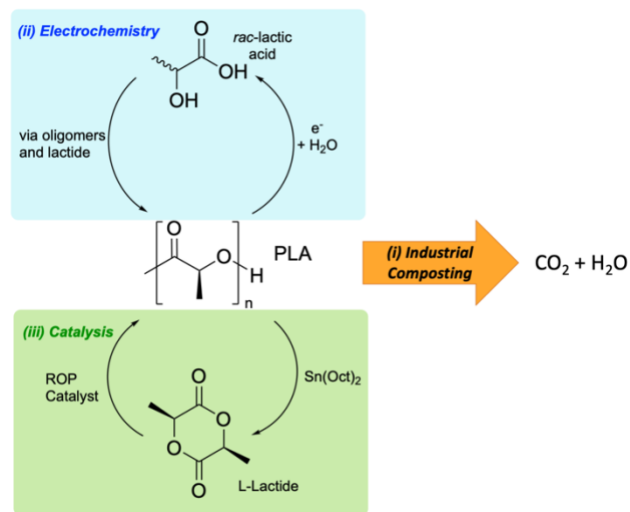


Figure 2: Poly(lactic acid) can be (i) composted industrially, or recycled to monomer via (ii) electrochemistry and intermediate lactic acid [18] or (iii) solid-state catalysis,[19]  $\text{Sn}(\text{Oct})_2$  = tin(II) octoate.

## 2.1. Biodegradation and environmentally-relevant degradation

In some cases, materials are designed for easier biodegradation i.e. they contain bonds that are more susceptible to hydrolysis. In particular, the most commonly discussed degradable polymers all contain ester linkages: poly(lactic acid), Figure 2, poly(hydroxyalkanoates), poly( $\epsilon$ -caprolactone), poly(butylene succinate) and poly(butylene terephthalate) copolymers. Hydrolysis can occur due to enzymes present within bacteria and fungi. Furthermore, these microbes can evolve naturally or by human design to degrade some commercially-relevant polymers especially polyesters. The BOTTLE consortium based in the USA has made significant progress in developing enzymatic processes for recycling poly(ethylene terephthalate).[16] New polymers, poly(imide-esters), have been made from bio-feedstocks and are inherently degradable in water [17]

## 2.2 Chemocatalytic Degradation and other chemical approaches

While poly(lactic acid), PLA, poly( $\epsilon$ -caprolactone) and other polyesters are degradable in industrial composting sites, new polyesters (and closely related polymers) have been designed for chemical recycling to monomer.[11] Chemical recycling to monomer is needed as current mechanical recycling of polymers can lead to less desirable polymer properties in the recycled polymer compared with the original virgin material. In this regard, a recent paper has been published on depolymerization of PLA to lactic acid using electrochemistry and real waste materials could also be electrolyzed.[18] It is exciting to think that this approach might be extendable to other polymer systems. Another approach to recycle PLA described using 0.01 mol% commercial tin catalyst under solid-state conditions at 160 °C to yield 92% cyclic lactide monomer.[19] Importantly, the catalyst could be recycled and the team were also able to depolymerize waste coffee cup lids to monomer in excellent yield. A similar solid-state catalytic approach could also be used to depolymerize poly(cyclohexene carbonate) to cyclohexene oxide and carbon dioxide. Catalyst activity could be screened on a small scale (100-200 mg polymer) using a Thermogravimetric Analyzer (TGA),[20] and could be scaled up to 2.00 g of polymer.[21]

Most efforts towards polymer recycling have focused on polyolefins and polyesters, as these classes of polymers are produced in the largest quantities worldwide. However, a recent review has focused on the degradation of oxygenated polymers (polyethers and polysiloxanes).[22] In this area, Miller and co-workers have reported the depolymerization of poly(dimethylsiloxane), PDMS, in the presence of catalytic NaOH to yield a cyclic monomer that can undergo ring-opening polymerization under acidic conditions.[23] This work highlights that some polymers can be depolymerized and repolymerized using simple catalyst systems, and not all depolymerizations will require extensive catalyst optimization. However, this system was designed initially using a computational approach to identify the optimum diol to use in the process and such approaches could be beneficial elsewhere.

Due to the outstanding mechanical properties of ultra-high molecular weight poly(ethylene), it is challenging to replace it with a degradable or depolymerizable material. Coates and co-

workers have developed a route to ultra-high molecular weight poly(dioxolane),  $M_n > 1,000$  kDa.[24] In their earlier report, chemical recycling to monomer was reported using relatively mild heat (140-150 °C) using 2 mol% camphorsulfonic acid.[25] They also showed that pure monomer could be recovered from a mixed plastic waste stream including polyolefins, poly(vinyl chloride) and polyesters.

### 3. Use of Renewable Feedstocks

This is a 'hot' topic in polymer chemistry at the moment, Figure 3.[26] However, in addition to targeting desirable polymer properties, it is important to pay attention to the origin of feedstock. In order to be sustainable, and not compete with food production or lead to habitat destruction and biodiversity loss, by-products from other industries should be prioritized e.g. lignin from forestry and paper industries, chitin from seafood processing discards. Our group and others have proposed the development of a marine biorefinery to yield a range of products including biopolymers from ocean biomass.[27] In this regard, it can be useful to think about what green chemistry methods can be used in extracting the value-added products e.g. vegetable oils can be used as environmentally-friendly solvents to extract pigments from waste crab shells.[28] However, there remain significant unmet challenges such as 'green' decolourization methods to yield the near-white chitin that market demands. Ionic liquids and mechanochemistry have played an important role in processing bio-sourced carbohydrates especially chitin and cellulose.[29, 30]

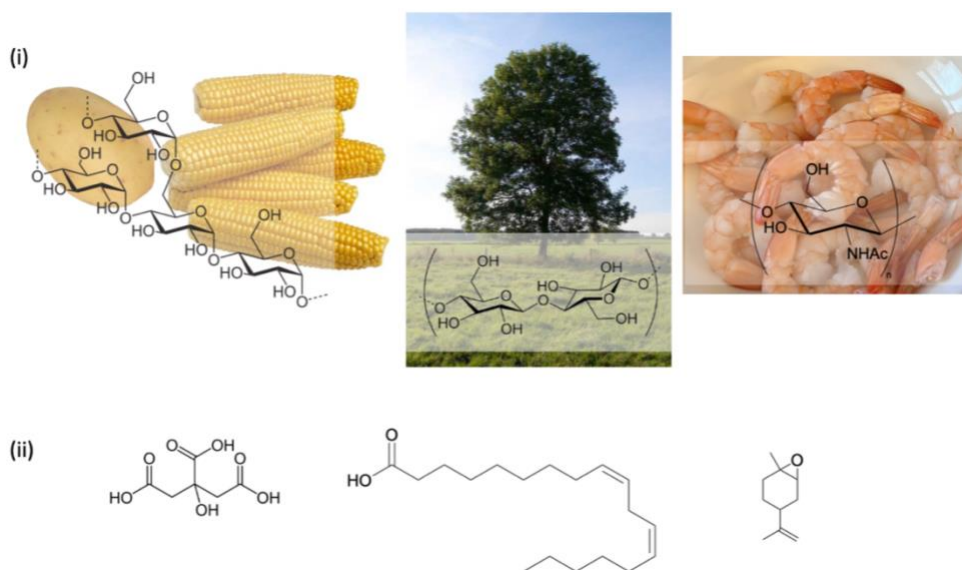


Figure 3: Select renewable polymers and monomers. (i) Left to right: Starch, cellulose and chitin. (ii) Left to right: citric acid, linoleic acid and limonene oxide

### 3.1. Biopolymers

Cellulose, hemicellulose, lignin, starch, chitin, chitosan and alginic acid are just some of the biopolymers that can be extracted from natural feedstocks. Some of these are used directly or they can be modified for a range of applications. For example, chitin can be deacetylated to produce chitosan and the resulting chitosan can be tailored regarding its molecular weight by mechanochemical treatment using phosphoric acid.[31] Mechanochemistry has also been used to produce functional biopolymers from chitosan.[32] These examples highlight the employment of green techniques in modification and processing of biopolymers. It is also worth noting that seaweed aquaculture has been highlighted as an important tool for meeting global sustainability targets.[33] In addition to yielding alginic acid and other carbohydrates, it fixes atmospheric carbon dioxide, counteracts ocean eutrophication and provides habitats to ensure marine biodiversity. Biopolymers can also be transformed to produce monomers e.g. starch to lactic acid to PLA, and hexoses produced via hydrolysis of starch or cellulose can be converted to 2,5-furandicarboxylic acid (FDCA). FDCA has been used instead of terephthalic acid in the manufacture of polyesters with properties similar to PET.

### 3.2. Bioderived monomers

In addition to monomers made from carbohydrates such as lactide made from starch obtained from maize, many other molecules e.g. citric acid,[17] have been sourced from nature and used to make polymers, Figure 3. In our own research, we have been exploring triglycerides and fatty acids e.g. linoleic acid. An excellent review has been published on making biobased polymers and networks from vegetable oils.[34] Inspired by such studies, we used oil isolated from fish processing waste to make non-isocyanate polyurethanes.[35] In addition to the oil, we used carbon dioxide to make the intermediate organic carbonates and a commercial, crosslinking amine (Cardolite NC-540), which is prepared from waste cashew nutshells. Terpenes, which can be bio-sourced, are also being widely studied as monomers. Some are used directly but others are modified in some way. For example,  $\alpha$ -pinene from pine sap was isomerized to yield  $\delta$ -pinene that underwent ring-opening metathesis polymerization to give hydrocarbon polymers ( $M_n > 70$  kDa,  $T_g \sim 100$  °C).[36] Limonene can be obtained from waste citrus fruit peels and then converted to limonene oxide. This bio-derived epoxide can then be used to make polycarbonates,[37, 38] and polyesters.[39]

### 3.3. Carbon Dioxide

Use of carbon dioxide as a co-monomer to produce polycarbonates has attracted significant attention as it uses a waste, polluting gas and also allows the replacement of toxic reagents (e.g. phosgene) in the synthesis of polymers.[37, 40] At first these carbon dioxide-derived polymers were an academic curiosity but in the past twenty years they have been commercialized by many companies worldwide to produce polyols for polyurethane synthesis. More recently, Nozaki has pioneered the synthesis of polymers from carbon dioxide and butadiene, Figure 4.[41]

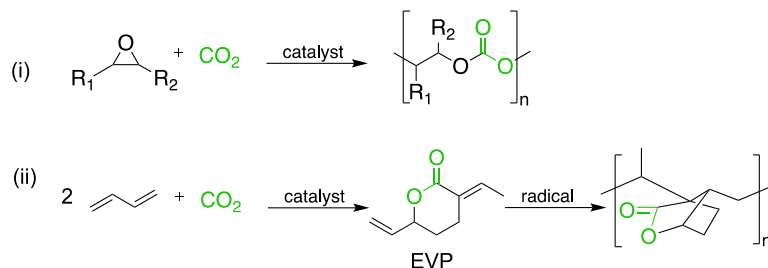


Figure 4: Copolymers of carbon dioxide formed with (i) epoxides and (ii) butadiene via intermediate EVP (3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one).

In order to diversify the properties of the resulting polymers, post-polymerization modifications have been investigated to yield tailor made materials including self-healing polymers.[38] The two most extensively studied reactions fall under the title of click reactions: thiol-ene and alkyne-azide couplings.

### 3.3.1 Earth Abundant Element and Non-Metal Catalysts

In this area, our group has been targeting catalyst systems containing earth-abundant elements: iron [42] and aluminum.[43] In some cases, the activity of these compounds may be less than desired but valuable insights can be obtained regarding structure-activity relationships.[44] We then extended our research to include non-metal catalysts in particular we studied  $\text{BPh}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  alongside suitable co-catalysts to produce cyclic and polycarbonates.[45] We have also made block copolymers, poly(carbonate-co-ester), via initial copolymerization of anhydrides in the presence of excess epoxide and once the was consumed, carbon dioxide was added to form the carbonate block.[39] Some of the most active boron-containing catalysts for these reactions include ionic tags and multiple Lewis acid sites within a single molecule.[46] This field has recently been reviewed.[47]

### 3.1.2 Tandem Catalytic, One-pot Route to Modified Polymers

As boranes and frustrated Lewis pairs are known to facilitate a wide array of catalytic reactions, we thought a tandem catalytic approach might be possible to yield functional polycarbonates. We found that a one-pot reaction could be performed between vinyl cyclohexene oxide, carbon dioxide and silanes to produce silylated polycarbonates.[48] In the course of this reaction, we used online IR spectroscopy to monitor kinetics in situ and this highlighted that an increase in temperature was needed to conduct the hydrosilation reaction in the presence of the polymerization co-catalyst.



## Conclusions

The principles of green chemistry should not only be thought of as an organic chemist's toolbox although that is where they have perhaps been most widely used to date. They can be applied across all chemistry disciplines. During recent years, plastics and therefore polymers have been the focus of growing concern due to the persistence of many in the environment and the subsequent impact that they then have on biodiversity and all life on earth. Therefore, at this time, polymer chemistry is particularly suited to a 'green revolution'. [10] Metal-catalysed polymerization reactions have long been established and the use of renewable feedstocks to produce new materials has grown exponentially in recent years. Some of this has been aided by the employment of green chemistry techniques such as mechanochemistry and in situ reaction monitoring. Plastics designed to be degradable and part of the circular economy are being investigated at an accelerated pace. However, there are gaps in our knowledge and also criteria need to be laid out to allow easy comparison of related systems. This could include life-cycle assessments or other sustainability metrics, or improved adherence to best practices e.g. use of ISO test conditions to measure biodegradability. [49]

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## Declaration of interest:

None

## Author contributions:

Writing (original draft and reviewing): F. M. Kerton

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*This review highlights some of the challenges and opportunities in the area of biodegradable plastics, and also describes policies and standards that might impact commercialization of new materials.*