

Design for Resiliency

Achieving sustainability will arguably require the development of resilient engineered systems that mirror the dynamic attributes of ecological systems. Resilience can be defined as the capacity of a system to tolerate disturbances while retaining its structure and function [11], and has emerged as a critical characteristic of complex, dynamic systems in a range of disciplines including economics, ecology, pedology, psychology, sociology, risk management, and network theory [12]. Engineering research has emphasized resilience as recovery from perturbations, but ecological resilience also emphasizes adaptive capacity, which may lead to new equilibria [13]. Resilient systems are able to survive, adapt, and grow in the face of uncertainty and unforeseen disruptions, particularly relevant given the ‘dynamic world’ discussion earlier. While resiliency tends to increase if a system has diversity, redundancy, efficiency, autonomy, adaptability, cohesion, and strength in its critical components, a rigorous definition is difficult to find and system parameters that can be used as design specifications remain even more elusive.

The Path Forward

We can no longer deny that the unintended consequences that society is enduring are due partly to the way that we, as chemists, have pursued our craft, focusing on knowledge generated in a reductionist-only framework. ‘Unintended’ is not the same as unknown or unknowable. Knowledge is not the same as insight or wisdom informing improved future design. As Einstein said, ‘The right to search for truth implies also a duty; one must not conceal any part of what one has recognized to be true.’ If we recognize that the knowledge we are imparting is limited – and that those limitations have consequences – then are we fulfilling our duty? If the knowledge is precisely right for the reduced system but generally wrong for the integrated one, are we honoring what Einstein called our ‘right’?

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Special Issue Part Two: Big Questions in Chemistry

Science & Society

Future Directions for Sustainable Polymers

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Current practices in the generation and disposal of synthetic polymers are largely unsustainable, causing severe worldwide polymer pollution and enormous materials value loss. To address these dire environmental and economic issues, several research fronts aim to develop sustainable polymers with closed-loop life cycles.

A Definition for Sustainable Polymers

Solving the worsening polymer-pollution problems [1,2] created by the linear-economy model (Box 1) takes a ‘whole-society’ approach, requiring effort and cooperation from all relevant stakeholders. As chemistry has led to the creation of plastics that modern life and the global economy depend on, it will undoubtedly contribute key solutions to address the current polymer waste challenge. It will also lead to the creation of innovative polymers with recyclability inherently built into their material properties and performance. Researchers are combating these issues through the development of sustainable polymers (SPs), redefined most recently as ‘materials derived from renewable feedstocks that are safe in both production and use and that can be recycled or disposed of in ways that are environmentally innocuous’ [3] or ‘a class of materials that are derived from renewable feedstocks and exhibit closed-loop life cycles’ [4]. In this Science & Society article, we highlight state-of-the-art examples of sustainable polymers, emphasizing both opportunities and impeding challenges.

Traditional Classes of SPs

Plant-Based Polymers

Plant biomass (produced from CO₂ and H₂O via photosynthesis using solar energy) provides abundant, renewable resources through conversion into building-block monomers and possesses an

Box 1. The Problem of Plastic Pollution

We are living in a materials world made of synthetic polymers, which have become indispensable for modern life and the global economy. Their annual production is increasing and expected to reach ~1.12 billion tons in 2050. However, the current production and disposal of synthetic polymers follows an unsustainable economic model comprising a 'fossil, take, make, use, dispose', one-way linear framework (see Figure 1 in main text). This linear-economy model, which fails to address end-of-life issues of post-consumer polymer wastes, not only rapidly depletes finite natural resources but also suffers from tremendous economic loss and creates severe worldwide environmental consequences of worsening plastic pollution. The current practice of recycling of polymers, especially plastics (the highest production volume among all types of polymers), is largely ineffective for a variety of reasons, with only ~5% of material value recovered for subsequent use. The dire consequences are twofold: about 95% of plastic materials value (~US \$100 billion) is lost in the economy annually after a single use and ~50 million tons of plastic waste are disposed into landfills and oceans each year. If no changes are made, by 2050 the ocean is expected to contain a greater weight of plastics than of fish (<https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economyrethinking-the-future-of-plastics-catalysingaction>).

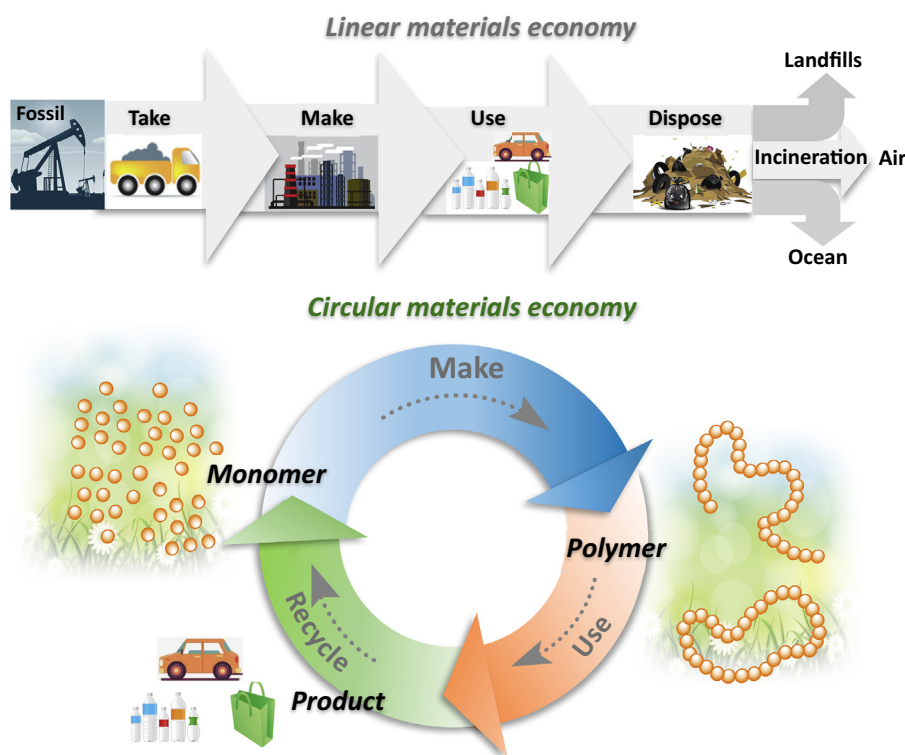


Figure 1. Illustrations of the Linear Materials Economy and the New, Circular Materials Economy Frameworks. The new framework can be established by the development of sustainable polymers with full chemical recyclability.

intrinsically negative carbon footprint. Hence, the development of plant-based polymers, such as polylactide and other renewable polyesters or polylactones, bioderived poly(ethylene terephthalate), sugar-based poly(ethylene furanoate), and renewable polycarbonate, has been directly linked to SPs and remains a highly active area [5,6].

Often, native plant resources must first be transformed into polymerizable forms. With an abundance of synthetic techniques at chemists' disposal, nearly any monomer can be prepared from a renewable feedstock. The question then becomes: how many steps away from the native resource can be used to create monomers/polymers that can still be

considered renewable? A full life-cycle assessment on such processes is informative but often impractical. At minimum, the following set of guidelines should be followed: (i) minimizing the number of transformation steps; (ii) maximizing the conversion and atom efficiencies of each step; and (iii) using catalytic reactions and 'greener'

conditions where possible. Furthermore, future research should emphasize the design of performance-advantaged, degradable, and/or recyclable plant-based polymers.

Degradable Polymers

Polymers designed to degrade into environmentally innocuous species and ultimately thermodynamic sinks (e.g., CO₂, H₂O) have the potential to establish an environmentally closed circular ecosystem. Thus, they are commonly referred to as environmentally benign materials, with already realized applications, especially in short-term products, such as polyglycolide, polytrimethylene carbonate, and polyhydroxyalkanoates used as biomedical and packaging materials [7].

Although polymers that are efficiently degradable in a controlled laboratory or microenvironment can be produced, they usually do not perform nearly as well in large-scale or natural settings such as landfills or oceans [7]. The time lapse in degradation between the environments is so large (in many cases) that degradable polymers in controlled environments can become practically nondegradable in the wild. In either case, these polymers potentially create new or unintended environmental consequences (e.g., as pollutants in our oceans). Furthermore, building-block chemicals are typically not recovered. Nevertheless, the design of polymers whose degradation is selectively triggered by external stimuli can be valuable for waste management, especially once the aforementioned challenges are overcome. When collected in compost or recycling facilities, degradable polymers can degrade into recoverable products.

Emerging Classes of SPs

In contrast to the traditional linear-economy model, a circular materials economy framework comprises 'make, use, recycle' closed-loop cycles (Figure 1). In

this sustainable system, the rate of resource regeneration is equal to or greater than the rate of resource utilization. Chemically recyclable polymers are attracting increasing attention due to their potential to preserve finite natural resources, offer a feasible solution to the end-of-life issue of polymer waste, and establish a circular materials economy [8]. Below we discuss the opportunities and challenges of three research fronts in this emerging area.

Chemically Recyclable Polymers

The design of new SPs with full chemical recyclability built into their properties is highly desirable. These SPs can be completely depolymerized into their monomers on demand with high selectivity, yield, and purity and can be directly repolymerized into the virgin-quality polymer. This process can, in principle, then be repeated infinitely. Such recyclable polymers [9] possess significant potential to achieve a circular materials economy and prevent waste at the source. For example, recent work has demonstrated that polymers incorporating the intrinsically recyclable five-membered γ -butyrolactone ring (due to both thermodynamic and kinetic underpinnings) exhibit useful material properties (similar to those of common plastics) and repeated chemical recyclability [10,11].

The realization of these SPs must address three challenges: energy cost, depolymerization selectivity, and depolymerizability/performance tradeoffs. Ideal polymers must be not only thermally and mechanically robust to be useful but also chemically recyclable (depolymerizable) with quantitative selectivity for clean monomer recovery, under cost-effective production and deconstruction conditions.

Upcycling or Repurposing Post-Consumer Polymers

Another emerging area concerns existing post-consumer polymers (especially mixed polymer wastes) and develops

innovative, economical approaches to upcycle or repurpose them into useful materials [12]. Such approaches make use of abundantly available commodity polymers as cheap feedstocks to make new or even higher-value materials, giving post-consumer polymers a new life, thereby extending their lifetime. One recent example utilizes a multiblock ethylene-propylene copolymer as a compatibilizer to effectively recycle the mixed polyethylene and isotactic polypropylene into equal or possibly higher-value materials [12].

In the upcycling or repurposing scheme, achieving value-added polymers by chemical transformations is often straightforward. Future challenges include making such processes cost-effective and, more importantly, simultaneously installing chemical recyclability to the new materials so that they will not become new waste to address after their new useful lifetime.

Reprocessable and/or Recyclable Crosslinked Polymers

Traditional crosslinked polymers with permanent chemical crosslinks are mechanically robust and highly durable materials used as thermosets and elastomers. However, they are neither mechanically reprocessable nor chemically recyclable. Recent research has developed reprocessable thermosets with dynamic covalent networks (crosslinks) that can undergo associative exchange reactions, allowing the materials to flow on heating. Such 'vitrimers' can behave like thermosets below a topology-freezing transition but can be thermally processed (at higher temperatures) like viscoelastic liquids without losing network integrity [13]. Chemically recyclable, high-performance thermosets have also been created [14].

These pioneering contributions will stimulate further developments in sustainable thermosets and address various

challenges, including: (i) polymers with enhanced creep, solvent, thermal, and chemical resistance when exposed to harsh, uncontrolled environments; (ii) thermosets that are both mechanically malleable and chemically recyclable [15]; and (iii) cost-effective processes to install dynamic crosslinks into commodity thermoplastics with wide temperature windows.

Future SPs

The development of SPs holds great potential to preserve finite natural resources and offer a feasible solution addressing critical issues created by currently unsustainable practices in synthetic polymers. Research directions commented on herein contribute towards the development of SPs from various perspectives. As an inspirational goal, SPs with full chemical recyclability built into their materials properties and performance feature a circular materials economy approach towards sustainability. Many challenges remain, however, especially energy cost, recycling/depolymerization selectivity, and recyclability and/or performance tradeoffs. Considerable future research

is required to address these challenges by the design of innovative monomer and polymer structures and the development of more environmentally benign processes (e.g., catalytic, solvent free) for their synthesis and the recycling of polymers, including mixed polymer wastes and composites.

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