National Science Foundation | NSF Center for Sustainable Polymers

Sustainable Polymer Framework (SPF 2020)

Preface

This document is a result of National Science Foundation feedback encouraging the NSF Center for Sustainable Polymers (CSP) to develop a framework by which its members can assess their contributions to sustainable polymer innovations. The Sustainable Polymer Framework (SPF 2020) seeks to holistically define a sustainable polymer so that CSP members can identify one or more aspects of their project that meets this definition. Our goal is to introduce an integrated systems-thinking approach that considers the interconnection of all criteria and their net impact across the environment, economy, and society.[1]

The current production and use of fossil-derived polymers in society is not sustainable.[2] Most dire is the consequence of persistent plastics pollution on land and in waterways, which is a result of societal adoption of single-use packaging, failure of adequate disposal systems, lack of recycling pathways and capabilities, and chemical compositions that makes plastics difficult to degrade. Research efforts by the CSP aim to address these global challenges and parallel many of the 17 United Nations Sustainable Development Goals (UN SDGs). For example, target actions involving sustainable polymer science can be found in UN SDG Goal 6: Clean Water and Sanitation; Goal 12: Responsible Consumption and Production; and Goal 14: Life below Water.[3]

The 12 Principles of Green Chemistry[4] provide guidance in the design of new polymers and have an integral presence in the SPF 2020 descriptions. As researchers begin new projects, they should use the framework at the earliest stages and take time to evaluate how they work, design, assess, and communicate their research. That is not to say every experiment performed must strictly adhere to SPF 2020 criteria. The ability to pursue scientific curiosity towards fundamental insight and serendipitous discoveries may require deviation from green chemistry in order to lead to knowledge useful in steering sustainable polymer research.[5] Nevertheless, recognizing aspects of basic research that can be better aligned with the principles of sustainability and safety is important and every effort should be made to work within the guidelines provided.

SPF 2020 comprises four major pillars that characterize the lifecycle of a sustainable polymer: **1. Feedstock**, **2. Process**, **3. Intended Use**, and **4. End-of-Use**. Each of these pillars has three sub-categories representing various green and/or sustainable strategies for accomplishing the primary goal. CSP members can associate their individual projects with one or more sub-categories, recognizing that they are not weighted equally; that is, there is not a direct correlation between the number of categories met and the sustainability of a polymer. Overall, the tiered Sustainable Polymer Framework is meant to encourage focused advancement in fundamental research in the various sub-categories while maintaining a broader vision of the interconnected systems that define a sustainable polymer.

Pillar 1: Feedstock

In order to meet sustainability goals, researchers should consider the potential impact of their choice of feedstock on the environment, on society, and on the economics of polymer production. Sustainable sources of feedstock include bio-derived small-molecule monomers, polymeric materials found in nature, by-products of other chemical or industrial processes, any of which could be transformed to polymers, materials used as fillers or plasticizers for polymers, or recyclable polymers.

In line with the directives of the 12 Principles of Green Chemistry, priority should be given to using feedstocks derived from renewable, rather than depleting non-renewable resources. However, in some instances sufficient synthetic polymeric materials already exist, and existing polymer products or waste products from chemical or other industries can serve as feedstocks without depleting resources. A combination of these efforts to source feedstocks either renewably or through a circular economy of reuse will assure that there is a sustainable source of the polymers that benefit society without compromising the health of the planet or humans.

RENEWABLE FEEDSTOCK

Today, most polymers are synthesized from natural gas or petroleum, which are considered to be depleting resources. Use of biomass has proven to be a successful alternative as illustrated by the most successful industrial bioplastic on the market, poly(lactide), derived from plant starches of corn or sugar beets. Other plant-derived monomers from plant sources, such as limonene, menthol, and isosorbide, have been used to produce novel homopolymers with tunable properties. Biopolymers found in starch, cellulose, and chitin have also been exploited to make renewable, and in some cases, biodegradable materials.

Renewable does not always equal sustainable and a thoughtful life cycle analysis should be considered when advancing a polymer to the stages of development.

WASTE FEEDSTOCK

New biodegradable plastic materials have been made from by-products of other industries. Examples include the use of lignocellulose from wood fibers from mills, cellulose acetate from agricultural processes, bagasse from sugar extraction, organic waste such as lactic acid from bakery scraps and tall oil fatty acids from pulp processing. Use of waste by-products addresses green principles related to pollution prevention as well as a circular economy.

RECYCLED FEEDSTOCK

Plastics, like PET, have been recycled for decades. Yet the addition of dyes and other additives prevent the recycling of these plastics into raw materials of equal quality. Additionally, certain combinations of copolymers prevent recycling due to the inability to separate isolated monomers. New technologies aimed at facilitating the ease of recycling homopolymers as well as copolymers and polymers with additives would provide regenerated feedstocks that avoid the need for isolation or synthesis of new monomers and adds to a circular economy.

Pillar 2: Process

The way in which sustainable polymers are synthesized and reprocessed is directly related to the carbon footprint of the material in question. Three essential considerations include using non-hazardous materials, improving energy and resource efficiency, and waste prevention. The majority of the 12 Principles of Green Chemistry align closely with these three subcategories:

NON-HAZARDOUS

Often, synthetic processes require the use of substantially hazardous compounds posing danger to both humans and the environment. Processes that adhere to Green Chemistry Principles 3 (Less Hazardous Synthesis), 5 (Benign Solvents and Auxiliaries), and 12 (Inherently Benign Chemistry for Accident Prevention), maximize the use of non-hazardous reagents in syntheses and processes. Chemical hazards are identified using the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) developed by the Occupational Safety and Health Administration (OSHA). In this system, physical, health, and environmental hazards are characterized. These tools should be used to assess the hazards of a chemical process to minimize any identified hazards through substitutions or eliminations whenever possible.

A large contribution to the mass of all materials used in a chemical process is often the solvent. Therefore, significant effort has been made to develop green chemistry solvent selection guides that provide alternatives to hazardous solvents.[6] These tools should be used in considering suitable solvent replacements to minimize waste and hazardous waste.[7]

ENERGY/RESOURCE EFFICIENT

Chemical transformations often require the use of energy intensive process conditions. Heating or cooling reactions at temperatures far from ambient conditions requires significant energy. Aligning with Green Chemistry Principle 6 (Design for Energy Efficiency), processes should be designed to run as close to ambient conditions as possible. For example, step-growth polymerizations often require high temperatures and low pressures to produce high molecular weight polymer with desirable properties, such as in the synthesis of commercial poly(ethylene terepthalate). A more sustainable way to make such a polymer would utilize catalysis to allow for the polymerization to take place under ambient temperature and pressure, thus avoiding the use of energy for heating and vacuum.

Water can be an important resource used in a chemical process. Applications include the use of water as a solvent, coolant, extraction medium, washing, transfers, dilutions, and more. A chemical process should be designed to minimize water use and the production of water waste effluent that needs to be treated. Resource efficiency should also be considered when choosing a catalyst or reagent. Of the 118 elements of the periodic table, 44 are determined to have limited availability in the foreseeable future.[8] Nine, including helium, are considered endangered in the next 100 years. A systems thinking approach also considers the environmental justice cost of how a mineral is mined or recycled in impoverished or technologically underdeveloped economies.

WASTE PREVENTION

Green Chemistry Principles 1 (Prevent Waste), 2 (Atom Economy), 8 (Reduce Derivatives), and 9 (Catalytic (vs. Stoichiometric)) all represent ideas that lead to waste prevention in a synthetic process. Importantly, all steps in a synthetic process can lead to the generation of waste, including purification of starting materials, the synthetic step involving the chemical transformation of interest, and the purification step(s). As an example, polymers are often purified by repeated dissolution in a good solvent and precipitation from a poor solvent. This activity alone can contribute greatly to the carbon footprint of a polymer, as resources and energy are required to produce and recover the relatively large amounts of solvents used during purification. For this reason, a holistic metric that considers the mass of all chemical inputs into a given product relative to the mass of product obtained is a desirable way to quantify waste prevention. Thus, the process mass intensity (PMI), defined below, is an easily calculated number that captures principles 1, 2, 8, and 9 in a high-level and simply understood way.[9]

$$PMI = \frac{total\ mass\ in\ a\ process\ or\ process\ step\ (kg)}{mass\ of\ product\ (kg)}$$

Examples of processes that prevent waste, resulting in lower PMI values, are those that have inherently high atom economies, are solvent-free, avoid the use of derivatives, and/or use catalysis rather than stoichiometric reagents. Importantly, PMI has been shown to correlate with global warming potential in terms of kg of CO_2 produced per equivalent of drug in GlaxoSmithKline’s development portfolio,[10] demonstrating the ability of PMI to gauge the sustainability of a given process in terms of waste prevention. CSP researchers should calculate a PMI, even at the early stages of their research, and continue to use it as a metric of progress with an ultimate goal of strategic design for a low PMI.

Pillar 3: Intended Use

Sustainable polymeric materials must be environmentally friendly, and they should also have properties that are both functional and competitive with current commercial materials. That is, a new polymeric material may be derived wholly from renewable resources and degradable, but if it cannot perform the function of its intended use or be economically viable, it will not contribute to the sustainable plastics economy. Additionally, sustainability can be intrinsically designed to specific intended use scenarios. For example plastic bottles could be designed to be reused versus one-time use.

In considering the intended use, it is also highly important and in line with Green Chemistry Principles that safety, in terms of human and environmental toxicity, be a primary consideration in design. Use of modern predictive models and evaluations of interconnected systems will avoid the unintended consequences that have historically plagued the chemical industry. Though safety in “intended use” may not be forefront in a discovery stage of a project, it must be an end goal of a polymer that is characterized as sustainable.

COMPETITIVE PROPERTIES

Consumers and materials suppliers will not readily adopt sustainable solutions that are not competitive with or better than existing materials. While changes to societal expectations and behaviors are possible when there is both attractive supplier offerings and consumer demand, they usually involve long time horizons of years to decades.

Benchmarking sustainable solutions against existing options in terms of key application properties is an important first step. An analysis that anticipates primary, secondary, tertiary, etc. potential use demands/impacts should be considered. For example, a soda bottle must obviously maintain its CO_2 content at room temperature, but it must also do so in a hot car that approaches 70 °C.

ECONOMICALLY VIABLE

Once a new polymer material with competitive properties is discovered, the economic viability of the polymer and its related processes and potential applications should be assessed. Important factors to consider are feedstock availability/cost, processing costs, transportation requirements, and product market. For example, compatibility with established processing techniques will lead to lower costs and more rapid adoption. In addition, any intended use that requires consideration of a new business model or transportation mechanism will likely be more costly and more difficult to implement. Use of techno-economic tools can provide insight into economic viability.

SAFE-IN-USE

Green Chemistry Principle 4 states that a chemical product should be designed to have minimal toxicity while effective in desired function. New advances in *in silico* modeling of toxicology are increasingly available to assist in predicting whether a chemical, such as a polymer, or additive will be harmless.[11] Lessons from BPA, vinyl chloride and flame retardants highlight the importance of evaluation of safety in polymeric materials, from synthesis to end-use. To aid with this analysis, it is helpful to think of every process and environment the material will encounter over its lifespan, from feedstock handling to a given application to discard/reuse scenarios. As an example, new biodegradable materials may be attractive, but identifying and understanding the potential toxicity, bioaccumulation, etc. of degradation by-products is also essential.

Pillar 4: End-of-Use

Motivated by green chemistry and circular economy, researchers should design sustainable polymers that at the End-of-Use have minimal environmental impact and economic loss. The approaches used for recapturing value of the polymers will depend on the applications and full life cycle, drawing crucial connections to the other three SPF 2020 pillars of sustainability. Select sustainable "End-of-Use" approaches include chemical recycling, biodegradation and reprocessing, as described below.

CHEMICALLY RECYCLABLE

A chemically recyclable plastic and/or polymer is capable of being processed and broken down into small-molecule components that can be used as raw material feedstocks for other chemical processes, including monomer and polymer synthesis. The major approaches include:[12]

- Depolymerization: controlled chemical or thermal depolymerization of polymers back to either monomers or short fragments that can be recombined into new polymers.
- Feedstock recycling: thermal processes that convert polymers into simpler molecules by applying heat to break their covalent bonds. Such processes include pyrolysis, gasification or thermal cracking.

BIODEGRADABLE

A biodegradable polymer is designed to break down into benign subunits (e.g. water, carbon dioxide, mineral salts, methane, and biomass) at its end-of-use through cell-mediated processes of microorganisms. Biodegradation is distinct from abiotic degradation mechanisms such as hydrolysis, oxidation or photo-oxidation which might occur to polymers in certain environments which may or may not result in benign subunits.[13] Additionally, the use of pro-degradant additives to degrade otherwise non-biodegradable polymers to lower molecular weight "biodegradable" components[14] should not be confused with biodegradable polymers.[15] Overall, the desired degradation mechanism(s) should ultimately result in benign subunits.

Environmental conditions play a significant role in whether a biodegradable polymer will break down within an acceptable timeframe as composting, soil, and aquatic environments present vastly different microbial communities and activity levels. Some biodegradable polymers are capable of biodegrading under a wide range of environmental conditions; for example, polyhydroxyalkanoates are degradable by composting and in soil and marine[16] environments. In contrast, polylactic acid, only degrades readily in industrial composting environments.[17] Standard methods exist which define pass/fail criteria and test methods to assess the biodegradability of polymers in different environments such as:

- Industrial composting[18]
- Soil[19]
- Marine[20] and freshwater

Consideration of local regulations is important when designing biodegradable polymers as in some markets unqualified claims of biodegradability can be considered misleading, particularly if a biodegradable plastic is disposed in locations (e.g. landfills) that do not allow for complete biodegradation within a required timeframe.[21]

REPROCESSABLE

A reprocessable material can be chemically and/or thermally treated in order to be reshaped and reused. Unlike a chemically recyclable polymer, which is broken down into small molecules, a reprocessable material retains the majority of the chemical linkages (polymer structure). Example approaches include:

- Reversible crosslinks: use of triggerable crosslinks within thermosetting materials that are designed to dissociate and allow the material to regain its thermoplastic properties for recovery and reuse.
- Compatibilizers: use of additives that enable mixtures of incompatible polymers to be recycled and processed together without loss of desirable material properties.

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