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Introduction to Polymer Upcycling

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Plastics are ubiquitous in our daily life, yet drastic amounts of plastics have found their way into landfills and the environment. In 2015 alone, the global waste generated by plastic packaging was around 6300 metric tons, and global production of waste is anticipated to increase to 12 000 metric tons by 2050.[1] The elimination or reduction of the use of plastics on the consumer side is not foreseeable in the near future. Hence, methods for the disposal of new and existing waste in ways that do not negatively impact the environment, human health, and climate change is imperative. The United Nation's Sustainable Development Goals (SDGs) emphasize the need to reduce single-use plastics to ensure sustainable consumption and production patterns.[2] As part of reaching these goals, approaches to produce high value products from plastic waste, referred to as polymer upcycling, are particularly attractive.

A multi-pronged approach is needed to rapidly develop capabilities for polymer upcycling, including new polymer molecules that are more readily upcycled, new catalysis approaches for transformation of polymer-based waste to new materials and improved understanding of the complex waste streams and products of the depolymerizing and degrading polymers. In this themed collection, we include outstanding contributions in these areas, highlighting the multiple ways that we as a field must approach

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Marco A. Fraga graduated with a DSc degree in Chemical Engineering in Heterogeneous Catalysis at State University of Campinas/UNICAMP in Brazil. He joined the National Institute of Technology (INT, Rio de Janeiro) in 2000 where he is presently a senior scientist. Since 2013, he has also been engaged in high-level teaching in the Master's and Doctoral Program in Chemistry at the Military Institute of Engineering (IME, Rio de Janeiro). His research interests are in heterogeneous catalysis, green chemistry, sustainable catalysis, biomass conversion, CO_2 capture and conversion, and polymer upcycling.

polymer upcycling in concert to rapidly decrease the negative environmental impact of plastics.

Catalysis can critically contribute to the establishment of innovative processes to convert plastic waste into fuels and valued products or even back to their monomers. Different catalytic approaches have increasingly been discussed in very recent years and perspectives on understanding the chemical pathways and overcoming the challenging energy and time demands of these processes are exciting. In this collection, an original approach is first presented by Assefa and Fieser to upcycle PVC (https://doi.org/10.1039/D2TA08142C). This high volume polymer could be converted to poly(ethylene-*co*-styrene) derivatives through a tandem hydrodechlorination/Friedel–Crafts alkylation catalytic system based on silylium cations under mild conditions. The potential of this strategy is evidenced by the very high PVC conversion reached in a short timeframe and it was shown to be effective even for commercial PVC items. Conversion of polyolefins to liquid hydrocarbons is also achieved with the aid of catalyst nanoengineering as reported by McCullough *et al.* (https://doi.org/10.1039/D2TA08133D). The discussion on metal particle size is focused and the study indicates that smaller nanoparticles are more active for hydrocarbon production from plastic hydrogenolysis, bringing an important contribution to the design of robust catalytic materials.

In addition to developments in catalysis, making progress towards sustainable plastics requires new uses for upcycled high volume polymers, especially developments where the new products are themselves reprocessable. Torkelson's research group demonstrated a novel method of simple upcycling of thermoplastic polyethylene by its conversion into covalent adaptable networks (https://doi.org/10.1039/D2TA06364F), *i.e.*, polymer networks that, thanks to dynamic covalent cross-links, are recycled *via* melt-state processing. The method of polyethylene transformation into a reusable cross-linked material involved a one-pot process consisting of reactive-radical-based melt-state processing with dicumyl peroxide and bis(2,2,6,6-tetramethyl-4-piperidyl methacrylate)disulfide. The dynamic disulfide cross-links incorporated into the network assured its complete reprocessing at elevated temperature (160 °C) as a result of their fast reshuffling. The method was verified not only for virgin but also for post-consumer low-density and high-density polyethylene using plastic bags and a milk jar, respectively. The presented approach is positioned in front of the ubiquitous usage of polyethylene comprising 36% of global plastics production.[1] The elaborated method is promising for the development of covalent adaptable networks based on reactive processing of cross-linked polyethylene nanocomposites and foams as well as ethylene-based copolymers.

Another important challenge in advancing polymer upcycling is that it is a complex deconstruction process from mixed materials, which can be mixed on macro, micro and molecular scales, and with a significant amount of the deconstruction taking place in the solid or viscous liquid phases. This requires new modeling, manufacturing and material design approaches to handle the complex systems. In the work of Yappert and Peters (https://doi.org/10.1039/D2TA04628H), a modeling framework is designed to identify the mechanism taking place during catalytic depolymerization *via* different upcycling strategies. They develop a number of population balance models for mechanisms including homogeneous and heterogeneous cases and melt and solution depolymerization, which predict the evolution of the molecular weight distributions. The output of these models can be fit to experimental measurements of molecular weight distributions during catalytic

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depolymerization, aiding in developing mechanistic understanding for emerging polymer upcycling processes.

Cross-cutting research in materials chemistry is essential to rapidly addressing the challenges with plastic waste and designing solutions for economically feasible upcycling. The articles highlighted here and others in the collection offer a window into the exciting and high quality research performed towards this goal and provide hope for a more sustainable future.

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