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Sustainable Green Polymerizations and End-of-Life Treatment of Polymers

Danielle E. Fagnani, Coralie Jehanno,* Haritz Sardon,* and Anne J. McNeil**

D. E. F.

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109-1055, USA

E-mail: dfagnani@umich.edu

ORCID: 0000-0003-3373-4265

C. J.

POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia–San Sebastian, Spain

POLYKEY, Centro Jose Mari Korta, Avenida de Tolosa, 72, 20018 Donostia–San Sebastian

E-mail: coralie.jehanno@polykey.eu

ORCID: 0000-0003-3180-2834

H. S.

POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia–San Sebastian, Spain

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E-mail: haritz.sardon@ehu.eus

ORCID: 0000-0002-6268-0916

A. J. M.

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109-1055, USA
E-mail: ajmcneil@umich.edu

ORCID: 0000-0003-4591-3308

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Macromolecular science has advanced alongside society, as evidenced by the broad use of polymers in materials and technologies integral to modern living. However, the global use of synthetic polymers has come with a high cost to the environment. Approximately 99% of plastics are synthesized from non-renewable sources, increasing our dependence on fossil resources. Additionally, pollution from plastics manufacturing processes increases our carbon footprint. Now, mismanaged plastic waste has become a significant pollutant. It is estimated that only <9% of the over 6.3 billion metric tons of plastic waste generated since the 1950s has been recycled.[1] Most of this waste currently resides in landfills or has leaked into oceans and other natural habitats. Once leaked into the environment, plastic waste rarely fully degrades, but instead erodes into detrimental microplastics and nanoplastics. This pollution problem results from the "take-make-dispose" linear production model, yielding a plastic economy that is unsustainable from both an atom economy and global health perspective.

A polymer or a material can be considered sustainable by optimizing the different steps of its life cycle, including raw material sourcing, polymerization process, use stage, and end-of-life fate. Collectively, this special issue includes topics spanning the entire polymer life cycle, with individual contributions focusing on one-to-two life-cycle steps at a time for a particular polymer class. Examples from each step of the life cycle include: decoupling monomers from petroleum sources

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(replacing with bio-sources, renewable feedstocks, or plastic waste), following green chemical principles during polymer synthesis (e.g., avoiding solvents, using efficient catalysis, or reducing the energy employed), improving the lifetime of plastics through self-healing, evaluating the end-of-life fate of materials through degradation studies, and enabling a circular plastics economy by designing recyclable or reprocessable materials.

For decades, the driving force for material synthesis has been optimization of production cost and quality of the polymer product. This approach has resulted in the linear production and consumption plastics economy. This situation needs to change by considering the sustainability of both the feedstock and the technology employed for obtaining the material. Renewable resources, including bio-sources and plastic waste, offer an alternative to petroleum feedstocks. The polymerization reactions should aim for mildness, limiting the carbon footprint, the residues associated with the reaction, and the quantities of water, solvents, and chemicals employed.

An example illustrating both aspects is the article of Khaled O. Sebakhy, Francesco Picchioni, and co-workers, employing a bio-sourced lactone to replace conventional methyl methacrylate, using a green solvent (article 2200045). The α-methylene-γ-butyrolactone is a derivative of itaconic acid, a naturally occurring molecule industrially obtained from fermentation. The authors demonstrate that the controlled RAFT polymerization of this exocyclic monomer in supercritical CO_2 leads to polymers with high glass transition temperatures and high solvent resistance. This example shows that it is possible to obtain functional materials while considering a sustainable pathway. Another example of green synthesis is reported by Sylvain Coste and co-workers (article 2100833), who explore non-isocyanate polyurethanes (NIPUs) as an alternative to conventional polyurethane. Specifically, the aminolysis of 5-membered dicyclic carbonates and dithiocarbonates enables high reactivity while the release of CO_2 during synthesis is avoided by adding a blowing-agent. The net result is more sustainable polyurethanes. Different types of chemistry need to be explored to obtain more sustainable polymers, as highlighted in the review article of Anna Liguori and Minna Hakkarainen on imine-based covalent adaptable networks (article 2100816). Here, the lifetime of the material itself is considered a crucial parameter for sustainability. In this article, different types of bio-based

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components including vanillin-, syringaldehyde-, lignin- or carbohydrate-based structures are reviewed for their transformation into recyclable thermosets. The synthesis and curing methods employed are analyzed as well as the final properties of the materials obtained. Junping Zheng, Ruofei Hu, and co-workers (article 2200234) used polymer waste as a feedstock by repurposing chewing-gum residue into a reversibly cross-linked gel. This gel displayed self-healing and mechanical properties suitable for application in biomechanical sensors.

A major need in polymer sustainability is materials that advance the circular economy. These circular materials are designed to enable complete recycling, keeping the matter in the production chain. Circularity can be achieved through chemical recycling, whereby thermoplastic polymers are converted back into monomers. This special issue includes papers that report on both the fundamental chemistry underlying bond breaking/forming reactions involved in chemical recycling and the engineering constraints needed to bring circular materials into applications. Eugene Y.-X. Chen, Haritz Sardon, and co-workers (article 2200008) investigate a structure–property relationship on a known circular thermoplastic derived from a biobased trans-hexahydrophthalide monomer. The authors revealed the impact of stereochemistry on the thermal, mechanical, and transport properties of this polymer, providing critical information needed to extrapolate this material into packaging applications. Although traditional thermosets are non-recyclable, new recyclable thermosets are being developed. These thermosets (also known as covalent adaptable networks) can be readily reprocessed through reversible-covalent bonds. A review article from Ranjita K. Bose and co-workers (article 2200023) details the latest developments in understanding the Diels–Alder reaction in thermoreversible click reactions that enable recycling. In related work, Songqi Ma and co-workers (article 2100777) develop a recyclable thermoset by combining associative Diels–Alder and dissociative Schiff-base adducts in their network design. These articles showcase the latest advancements in new materials designed for complete recyclability, representing the efforts polymer scientists are taking to realize a circular plastics economy.

Finally, the end-of-life management of polymers should be considered. The literature lacks detailed studies on the mechanisms for degrading a macromolecular chain, either through biodegradation or recycling technologies. Such pragmatic studies can be found in this special issue. For example, the biodegradation of poly(acrylic acid) (PAA) was performed by Stephanie M. Barbon, Matthew C. D.

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Carter, and co-workers to establish a correlation between the chain length and the bacterial mineralization of the polymer (article 2100773). The authors propose an updated analysis for low molecular weight PAA in which they correlate polymerization degrees (DP) with biodegradation through both in-house mini respirometer and an industrial Organization for Economic Cooperation and Development (OECD) standard test. This study is critical for selecting the appropriate length of PAA to use in applications where the product can easily leak into the environment (e.g., cosmetics and cleaning products). Another polymer end-of-life aspect to consider is the recycling technology employed. Margaret J. Sobkowicz and co-workers evaluate how the pre-treatment given to the plastic wastes influences the efficiency of enzymatic recycling of poly(ethylene terephthalate) (PET) (article2100929). Pre-treatment of PET is required to enzymatically depolymerize PET at relatively low temperature (60–80 ºC) in a reasonable time frame. The authors demonstrated that increasing the specific surface area (SSA) through melt-processing of the PET wastes produces more reactive sites for the enzymes to bind to, thereby, increasing the overall depolymerization rate. However, this technique can also lead to increased crystallinity (at the micro- and nano-scale) which attenuates enzymatic depolymerization rates. A balance needs to be found between these two parameters (SSA and crystallinity) for reaching an optimized depolymerization reaction. The functionalization of common polymers is another strategy for affording more recyclable or degradable materials, which is reviewed by Quentin Carboué, Sami Fadlallah, and co-workers (article 2200254). The functionalization (direct, or post-polymerization) of the main classes of polymers such as polyesters, polyurethanes, polyacetals, vinyl-based or phosphorous-containing polymers are considered. Functionalization can lead to specific degradation conditions for the resulting materials, although most degradation studies are lacking in both accuracy and uniformity. The entire carbon loop of plastics should be considered while choosing to use or dispose of a material. This topic as it relates to end-of-life treatments of plastic is reviewed from a carbon footprint perspective by Schirmeister and Mülhaupt (article 2200247). The article describes advantages, drawbacks, and suggestions for "closing the loop" of the plastic industry. Critical research areas are highlighted, including: mechanical recycling, biobased plastics, biodegradable plastics, molecular recycling, and carbon capture. The authors encourage employing appropriate tools (metrics in general, LCA in particular) for evaluating best practices for optimizing the carbon loop of a plastic per each specific product, application, and location.

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The collection of articles in this special issue all aim to improve the sustainability of the plastics economy. As this research field progresses, care should be taken to avert common assumptions related to sustainability. For example, using a bio-based feedstock may not be greener than a petroleum-based feedstock, or a polymer designed for recycling may not be better for the environment than a polymer already in use. The future of polymer sustainability research will require accessible metrics to ascertain if a new material or process is truly more sustainable than a predecessor. Existing quantitative tools include calculating e-factors to estimate the "greenness" of a chemical process or performing a life cycle assessment (LCA) to gauge the total environmental impact of a material or process. Although comprehensive LCAs are typically performed in later development stages because they are data-intensive, simplified LCAs can be designed in earlier development stages to compare the sustainability of one system to another in a specific context. Routine tools need to be established for bench scientists to ensure that new polymers or related processes are indeed sustainable.

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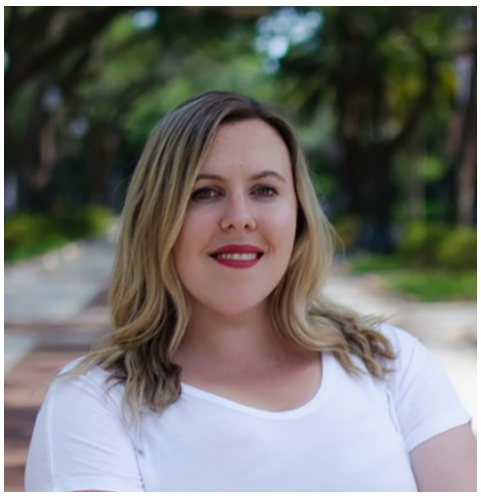
Author Biographies



Danielle E. Fagnani is a post-doctoral researcher in the Department of Chemistry at the University of Michigan. Her current research interests include polymer sustainability, chemical recycling of plastic waste, and electrosynthesis. Prior to Michigan, she received her B.S. in chemistry from Drexel University and her Ph.D. in organic chemistry from the University of Florida.

Coralie Jehanno, after an M.Sc. in chemistry and physics in Bordeaux (France), obtained her Ph.D. with a thesis focusing on the depolymerization of polymers in 2019. She performed both experimental and computational investigations on this topic between the University of the Basque Country (Spain), the University of Warwick (UK), and the IBM Research Center (USA). Coralie is currently a postdoctoral researcher at the POLYMAT institute where she is focusing on recycling methodologies for plastics. She is also co-founder and scientific director of the start-up POLYKEY, created in 2020.

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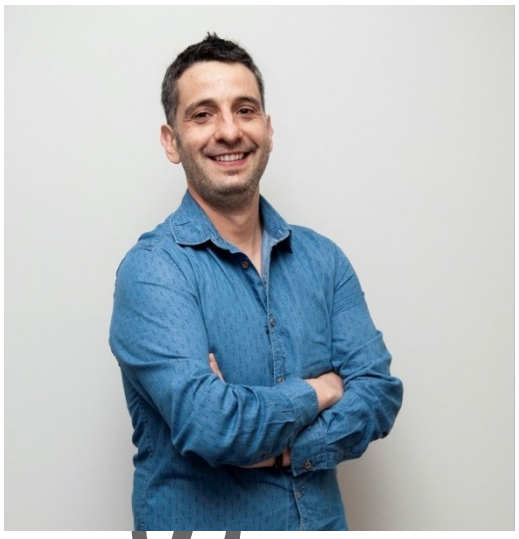
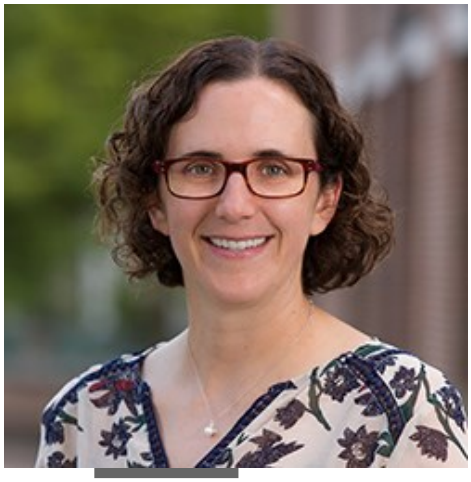


Haritz Sardon has been an associate professor at the University of Basque Country since 2022. He graduated from the University of Basque Country in 2011 with honors before joining the group of Dr. Hedrick at IBM Almaden Research Center as a postdoc in 2012. His overall research aims to prepare new functional polymeric materials using sustainable polymerization processes. Specifically, his investigations involve the use of green polymerization processes such as monomers from plastic recycling, reagents from renewable sources, or the use of less hazardous organocatalysts.



Anne J. McNeil is the Carol A. Fierke Collegiate Professor of Chemistry and Macromolecular Science and Engineering at the University of Michigan. Her research interests include chemical recycling of plastic waste, degradable polymer synthesis, methods for capturing microplastics, and identifying new materials for redox flow batteries. Prior to Michigan, she received her B.S. in chemistry from the College of William and Mary, her Ph.D. from Cornell University, and was a L'Oreal Postdoctoral Fellow at MIT.

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