POLYMER CHEMISTRY

Polymer design for the circular economy

Addition of keto groups to polyethylene helps it degrade while maintaining its properties

By **Margaret J. Sobkowicz**

The field of polymer science and engineering has produced elegant chemical structures and highly functional economical materials during the past century. However, society still faces fundamental challenges recycling even the simplest polymer, polyethylene (PE). The advent of Ziegler-Natta and metallocene catalysts (*1*) has enabled synthesis of PEs with targeted branching structures, spurring their use in an ever-increasing range of applications, including broad adoption in single-use packaging. By comparison, approaches to recover the ethylene monomer or otherwise recycle PE have not kept pace. On page 604 of this issue, Baur *et al.* (*2*) describe a catalytic approach to redesigning PE to facilitate its inclusion in the circular economy by maintaining its properties but making it easier to degrade to monomers.

In 2016, 242 million tonnes of plastic waste were generated worldwide (*3*), and this number continues to rise annually. In theory, polymers could be easily remelted and reformed into new objects, but the recycling rate has stagnated at only 9% of all plastics produced globally (*4*), or only 14% of plastic packaging (*5*). This low recycling rate not only represents an inefficiency in manufacturing and loss of material value but also results in unintended leakage to the environment (*6*) and damage to ecosystems (*7*).

At the heart of the struggle is that separations, purifications, and subsequent thermomechanical processing cannot completely restore recycled plastics to their original quality, and the recovered material ends up in lower-value products. Advanced recycling approaches focus on recovering purified chemicals for repolymerization or use in other chemical applications, such as fuels and solvents (see the figure). Processes that are more energy intensive—such as pyrolysis, gasification, and biochemical digestion—can create higher-value product. Hybrid (*8*) and solvent-based (*9*) processes are also attracting interest. Catalysts can target specific bonds for cleavage and lower the energy threshold for polymer deconstruction.

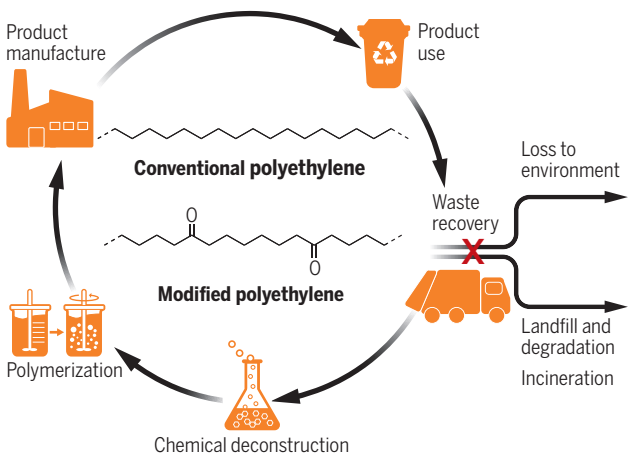
The zero-waste hierarchy (*10*) suggests that the most preferred option for solving the plastics waste problem is to rethink or redesign the polymer itself. Compostable plastics such as poly(lactic acid) could fill this role with appropriate infrastructure (*11*), but their properties are much different than those of the fossil fuel–derived materials to which industry is accustomed. "Oxo-degradable" materials, which contain 1 to 2 wt % of transition metal complexes that promote free-radical chain scission (*12*), may reduce accumulation of visible recalcitrant waste but do not advance recovery and reuse and could inhibit greater adoption of current mechanical recycling and composting infrastructures (*13*).

Baur *et al.* describe a class of nickel-phosphinophenolato catalysts that favor random incorporation of oxygenated carbonyl groups into high–molecular weight PE, rendering it more susceptible to oxidative and enzymatic deconstruction. Notably, they controlled the degree of substitution of keto groups in a nonalternating fashion along the carbon backbone, distinct from other attempts to incorporate such oxygen functionality in the past. These ketone-modified PEs have thermal and mechanical properties comparable to those of conventional PE of similar molecular weight, which is critical if they are to be used as drop-in replacements for existing materials. This approach may give these materials a competitive advantage, considering the existing challenges that have hindered adoption of new biodegradable plastics. The study demonstrates that exposure to ultraviolet light results in photodegradability similar to that of the additive-modified PEs previously described.

This promising approach to polymer redesign should be incorporated into the toolbox of strategies to achieve a circular economy for plastics. Moving forward, the field must develop approaches for processing these materials into packaging structures and work toward controlled depolymerization to recover valuable feedstocks. As with the oxo-degradable additive approach, the degradation products should not be dispersed into the environment unless they are proven safe to ecosystems. More work is needed to establish the time- and environment-dependent breakdown of modified PE to optimize both its in-use properties and end-use recycling methodologies. ■

Circular polymer design

Polyethylene recycling by converting to monomers and chemicals is made easier by Baur *et al.*, who incorporated ketone groups into the backbone chain.



Department of Plastics Engineering, University of Massachusetts Lowell, 1 University Avenue, Lowell, MA, 01854, USA. Email: margaret_sobkowiczkline@uml.edu

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