Materials made from organic polymers represent a significant part of nearly every consumer product offered today. The advent of plastics as a commodity material has triggered major advances in medicine and food preservation as well as improvement of energy efficiency in cars and aircraft through weight reduction. Although plastics have in many ways revolutionized the way we live, they have also had a massive impact on our environment. Despite the near ubiquity of recycling bins in our homes and workplaces, much of our plastic waste ends up in landfills, or worse, dispersed in the environment, wreaking havoc in our ecosystem. Much of this situation can be attributed to the irresponsible use and management of plastic waste. However, many types of plastics cannot be easily reused or recycled, even in the hands of the most conscientious consumers. In recent years, there have been considerable efforts put toward the production of polymers that can be made from green or renewable sources as well as those that can degrade into benign byproducts or even their constituent monomers. However, for many applications, there simply are no suitable “green” replacement plastics. In cases where these materials cannot be easily recycled, the plastics are either “down-cycled”, meaning that they are reprocessed for use in other applications as lower value materials, or simply discarded into landfills or other waste streams. In their latest work published in this issue of ACS Central Science, Dichtel, Ellison, and co-workers show how simple chemistry can be used to give new life to previously unrecyclable plastics by harnessing the power of dynamic covalent chemistry. They created a method that activates covalent cross-links in polyurethane (PU) foams to break and reform rapidly during the recycling process, allowing polymers to be melted and reshaped into new products (Figure 1). The fate of these plastics is often determined by their molecular structure and composition. Thermoplastic polymer chains have a linear molecular structure, meaning that they are:

**Figure 1.** Dynamic covalent chemistry has the power to convert previously unrecyclable polymers into new high value products that can be used in new applications.

They created a method that activates covalent cross-links in polyurethane foams to break and reform rapidly during the recycling process, allowing polymers to be melted and reshaped into new products.
they can be recycled or reprocessed simply by melting and remolding them into a different shape. Thermoset polymers have a cross-linked network-type molecular structure that gives them enhanced mechanical properties as well as improved resistance to thermal and chemical degradation. However, these same properties make them particularly troublesome to recycle as thermoset polymers cannot be melted and reshaped.

Polyurethane (PU) thermoset foams are durable materials that have found many applications in our everyday life, ranging from furniture to automotive seat padding. However, the covalently cross-linked molecular structure of PU foams makes them exceptionally difficult to recycle despite their relatively high value as a material. Mechanical grinding methods have been used to downcycle PU foams into fillers to improve adhesive compounds, but chemical recycling of PU foams into high value materials remains a challenge.

PU thermosets are typically synthesized through the reaction of isocyanates and monomers containing alcohol groups, resulting in the formation of urethane groups. The wide range of mechanical properties of PUs is a result of the diverse structural availability of both alcohol and isocyanate monomers. The desirable mechanical properties of PU thermoset plastics come from a combination of the “hard” domains formed by urethane groups that are capable of hydrogen bonding and provide stiffness and toughness, and “soft” domains that come from aliphatic monomers and provide flexibility to the material. Several strategies to make remoldable PUs have been previously reported. These typically involve incorporating conventional dynamic covalent bonds into the PU backbone or cross-links. The major limitation to these approaches involves the cost of the materials themselves in that they are much more expensive to produce when compared with their nonrecyclable counterparts.

The key innovation in the work by the Dichtel and Ellison groups is the conversion of the conventionally produced PU thermosets into covalently adaptable networks. The key innovation in the work by the Dichtel and Ellison groups is the conversion of the conventionally produced PU thermosets into covalently adaptable networks. To accomplish this feat, the team facilitated urethane bond exchange in PU foams by incorporating a catalyst, dibutyltin dilaurate (DBTDL), through solvent swelling. DBTDL can trigger the carbamate exchange, but only at higher temperatures (Figure 2). This means that the PU thermosets retain their desired mechanical properties at room temperature, but become processable at higher temperatures. To reprocess the foams, Dichtel, Ellison and co-workers used twin-screw extrusion to produce new PU thermoset shapes, such as films, with mechanical properties that compare to PU films that have not undergone this process. This two-step recycling strategy was then extended to a commercially available sample of PU foam sourced from furniture padding. Despite the fact that this sample still contained a variety of additives incorporated during the production process, it could still be formed into polymer films with properties comparable to unprocessed PU elastomers.

This dynamic chemical approach could impact other areas of polymer production and processing as well. The authors point out that this work could have implications in additive manufacturing. Indeed, dynamic covalent chemistry has already proven to be a powerful tool for improving the mechanical properties of objects made by 3D printing—a process.
where a polymer’s ability to be thermally reshaped can be paramount. This new method may provide a pathway to introduce recycled plastics into the additive manufacturing supply stream, as well as expand the library of cross-linked materials available to extrusion-based 3D printers.

There is no doubt that polymers play an important, but simultaneously harmful, role in our lives. We clearly need polymers that can be made from renewable sources that will reduce our carbon footprint and reliance on petrochemicals. In cases where this is not possible, we need to find ways to make our “not-so-green” plastics friendlier to the environment. Dichtel, Ellison, and co-workers have shown how simple, fundamental chemistry can help make this happen.

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Notes
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