Sustainable chemistry

Closing the loop on recycling bioplastics

High-performance plastic made from plant oils is chemically recyclable by design

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Plastics are invaluable materials, but they use up petroleum resources and persist in the environment. A high-performance plastic derived from renewable oils has been designed at the molecular level to be truly recyclable. See p.XXX

Stark images of plastic mounting up in landfills and oceans has prompted a reconsideration of its use. Not only do plastics consume depleting crude-oil resources, but most are not effectively recycled and are environmental pollutants. There are many types of plastic, but all contain polymers. Solving the plastics problem will require many different approaches, but fundamentally their polymer chemistry must be redesigned to improve their sustainability.[1] Key targets are to diversify the raw materials used to make plastics beyond only fossil fuels; to conserve the embedded energy and valuable resources in their structures; to fully maintain their useful properties through multiple recycling loops; and to design plastics whose molecular structure can be completely disassembled when necessary.[2–4] On page XXX, Häuβler *et al*.[5] report a plastic that has the potential to meet all of these criteria.

High-density polyethylene (HDPE) is a widely used plastic, featuring long straight chains of polyethylene — a polymer consisting of repeated CH_2 units. When crystallized, HDPE has excellent properties for diverse applications, including as electrical insulators, pipes and detergent bottles. HDPE is regularly recycled mechanically by melting and reprocessing (Fig. 1a).[6] Nonetheless, current plastic waste management is ineffective, with less than 10% of all plastics, and only about 30% of HDPE bottles, in the USA truly being recovered from mixed plastic waste streams and recycled.[7] Mechanical recycling can also yield inferior materials after each recycling loop and, in the case of HDPE, it can be challenging to control the crystallinity of the recycled products.[8,9]

An alternative to mechanical recycling is chemical recycling, in which long-chain polymers are deconstructed after use to produce the same molecular building blocks (monomers) that were originally used to make them. The advantage of this approach is that these monomers can be re-polymerized repeatedly to produce materials that have the same high performances and properties. Unfortunately, such a strategy is ineffective for polyethylene because a lot of energy is required to break its carbon–carbon bonds. The strength of these bonds also explains the environmental persistence of polyethylene and its recalcitrance to enzymes.

Häuβler *et al*. now report plastics that have many of the key properties of HDPE, but are also designed for complete closed-loop recycling.[5] The authors developed efficient, high yielding (>95%) chemistry for transforming oils derived from plants or microalgae into polymers that contain a small fraction of regularly placed carbonate or ester linkages in every polymer chain (Fig. 1b). Well-established 'solvolysis' reactions with water or common alcohols can then be used to completely break up all of the polymer chains, enabling almost full recovery (96%) of the monomers and closed-loop recycling. The authors report that isolation of the monomers from the solvolysis reactions is straightforward, and that the monomers can be successfully re-polymerized to produce materials that retain the properties of the original plastic.

The key advance of this work is that it simultaneously solves many longstanding and difficult challenges that have dogged the field of sustainable polymers. Researchers from the same group as Häuβler *et al*. have pioneered, over several decades, the chemistry now used to transform natural oils into useful monomers.[10] The authors use highly efficient catalysis (80-90% yield) to selectively install chemical groups at ends of the monomers; these groups form the basis of the desired 'break points' in the polymers. The monomers are then polymerized using well-established methods. The authors find that, by using a particular co-monomer (diethyl carbonate) in the polymerization reaction, the resulting polymer has a high molecular mass. This is essential for making a plastic that matches the thermal, mechanical and processing properties of HDPE.

Häuβler and colleagues demonstrate that the new plastic can be processed using common industrial techniques such as injection moulding and 3D printing, as well as to include colorants or carbon fibres (which are widely used as additives to strengthen polymers). They also show that solvolysis of the new plastic occurs selectively when it is mixed with conventional plastics such as commercial poly(ethylene terephthalate) (PET), which is widely used in drinks bottles and is also a candidate for chemical recycling by solvolysis. This proof-of-concept result hints that selective recycling of the new plastic might be possible in the future.

Although the findings hold great promise, it is important to recognize that this is still early-stage, fundamental research. Polymer-to-polymer recycling has been demonstrated for only 20 grams of the new material, and much work will be required to translate this into industrial-scale processes and products. Major engineering challenges remain to be solved in other parts of polymer's life cycle, including finding ways to produce the biomass-derived monomers effectively and the development of large-scale processes for making, forming and recycling the plastic.

Furthermore, economic considerations overshadow these endeavours. Industrially used plastics, such as HDPE, are produced on the multi-million tonne scale, and usually sell for 1–3 US dollars per kilogram (ref. 11). It would be unreasonable to expect a new plastic to be cost-competitive immediately, but such price issues have destroyed many emerging technologies in the past.

Questions also need to be answered about how well the new plastic integrates with existing waste-management systems — if it is to replace HDPE, it must be shown to be compatible with all the methods for separating waste plastics presently used across multiple facilities and geographies. Unlike most current recycling strategies, the type of chemical recycling reported by Häuβler *et al*. requires a chemical plant. Encouragingly, however, the reported chemistries seem well-suited for use with known industrial methods. Moreover, the reported system seems consistent with European legislation that requires manufacturers to take responsibility for the plastics used in their products after consumer use, removing potential barriers to its adoption, at least in that part of the world.

Häuβler and colleagues' work is exciting and inspiring, because it is extremely challenging to come up with plastics that can be derived from renewable resources, have outstanding properties, are compatible with large-scale manufacturing and processing techniques and are fully recyclable — few materials meet all criteria. The authors' work is an excellent example of how scientific innovation can solve all the facets of a problem, rather than just individual components. The next step must be to build on the life-cycle assessments presented in the current work, to provide even greater improvements in sustainability. More broadly, society must also demand that manufacturers provide equivalent life-cycle assessments and evaluations of all the environmental impacts of currently used plastics to ensure delivery of truly beneficial alternatives.

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C.W. declares a CFI

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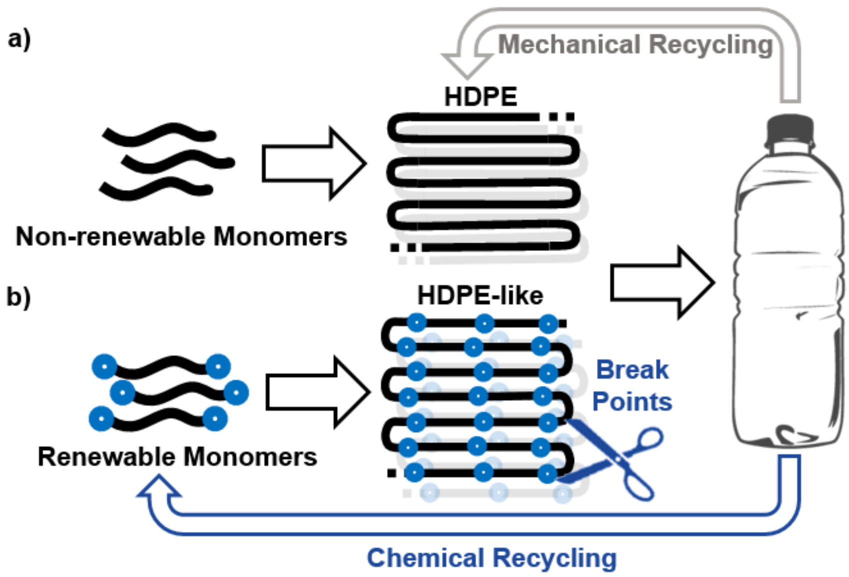

Figure 1| Redesigning high-density polyethylene (HDPE). a, Commercial HDPE is a widely used plastic that consists of a chemically inert polymer, formed from non-renewable petroleum-based monomers. Although it can be recycled mechanically (by melting and reprocessing), this can lead to a reduction of the material's performance. **b**, Häuβler et al.[5] report a plastic that has comparable properties to HDPE and which is formed from renewable plant- or microalgae-derived monomers. The monomers have chemical groups at each end that form 'break points' in the resulting polymer chains. These break points allow the polymer to be chemically recycled back to its monomers, which can then be used to re-make the plastic. The properties of the plastic do not degrade after each recycling loop.