# Hidden in plain sight: chemically recyclable polyacetals to deliver useful thermoplastics

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## Summary

In a recent issue in Science, high molecular weight polyacetals prepared by Coates and co-workers resolve many standing issues associated with polymers designed for chemical recycling to monomer. These materials simultaneously display tensile strengths similar to commodity polyolefins, high thermal stability and efficiently depolymerize with a strong acid catalyst.

## Preview

The scale of the global plastic waste problem is staggering. Since commercial production started in the mid twentieth century, humankind has collectively consumed and then disposed three quarters of all the polymer resins ever produced. Specifically, the cumulative amount of postconsumer plastic waste ever generated is estimated to have reached almost 7,000 million metric tons by 2017, the majority of which has been dumped in landfills or permeated into the environment.[1] This data highlights two conflicting historical trends: the growing technological dependence on plastic products and the dire inattention to the ecological impact driven by discarded plastics. The balance is clearly unsustainable, particularly if polymer production and end-of-life disposal continues the same upward trend.[2] In response, the surge to find sustainable and more circular alternatives throughout the entire value chain has never been greater. Mechanical recycling (or downcycling) continues to be the go-to method to recirculate waste primarily from single-use packaging materials. However, the low penetration of this market (representing 18% of the global plastic waste management in 2017)[1] emphasizes the challenges faced by reused feedstocks, which can hardly compete in cost or physical performance with virgin plastics.[3]

Chemical recycling, which involves the breakdown of chemical bonds in the polymer chain, entail an attractive approach to extract value from postconsumer plastic waste and could mitigate the problems associated with waste accumulation.[4] For instance, valorization (or upcycling) seeks to generate small molecules and oligomers for applications that differ from those envisioned in the original plastic.[5] On the other hand, chemical recycling to monomer (CRM) generates back monomers that can be reutilized in the manufacture of virgin polymers with virtually no differences in appearance and properties. Plastic materials with low energetic barriers for depolymerization are well suited to provide such high value-added chemicals in good selectivity and cost efficiently. In turn, these thermodynamic and kinetic conditions are met by polymers with accessible ceiling temperatures ($T_c$); that is, those whose polymerization reaction reach an equilibrium between monomer consumption and regeneration at moderate temperatures. This enables depolymerization using mild conditions, often triggered by the use of an appropriate catalyst. Polymers obtained by ring-opening polymerization (ROP) of moderately strained cyclic monomers fall into this category, since the net thermodynamic gain or loss of the forward and backward reactions hovers near zero. However, systems well suited for CRM face many big challenges, mainly achieving high monomer conversions under mild conditions and producing polymers with adequate thermal stability.

Inspiration to develop new sustainable monomer and polymer platforms not only requires pursuing convenient polymerization and depolymerization conditions. Additionally, the materials' attributes should aim to contest, if not surpass, those of the most common plastics if they expect to compete and eventually replace them. Since polyolefins, particularly polyethylene (PE) and polypropylene (PP), are the largest share of commodity plastics in use and discarded today, they are an incredibly valuable target for replacement. However, matching their chemical and thermal inertness and remarkable mechanical performance, while addressing viable depolymerization routes, represent a high stake to climb for polymer chemists.

Heteroatom-containing polymers, such as polyesters, polycarbonates, and polyamides have been positioned at the forefront of these efforts due to vast array of available chemical reactivities to form and break their main-chain linkages as well as their good physical properties.[6] Indeed, recent advances have shown how oxygenated polymers are close to delivering polyolefin-like materials while showcasing ingenious depolymerization routes.[7,8] Still, important considerations remain unsolved, particularly the adoption of low-cost raw materials as well as the potential adaptation and scalability to current industrial processes.

In a recent issue in Science, a team lead by Prof. G. W. Coates reveals that polyacetals, a well-known class of plastics that includes commercial polyoxomethylene, may be in fact capable to answer these long-standing issues.[9] Introducing a newly developed equilibrium process to transform cyclic acetals into high molecular weight polymers, the authors have untapped the overlooked potential of these materials to challenge the performance of most commonly used PE and PP thermoplastics (Figure 1). It turns out, pure enough polyacetals also display high thermal stability (degradation occurs above 335 °C) while their CRM can still be triggered on demand. Importantly, the monomer starting materials (formaldehyde and various diols) are commercially available, cheap, and can even be traced to bio-based sources, paving the way to economically and sustainably viable new plastics.

Cationic ring-opening polymerization (CROP) of 1,3-dioxolane (DXL), a five-membered ring acetal, has traditionally struggled to reliably produce high molecular weight poly(1,3-dioxolane) (PDXL). The oxophilicity of Lewis acid catalysts and the high reactivity of the propagating carbocation chain ends results in sluggish polymerization rates and unwanted termination pathways, respectively. Exposing the exceptional material properties hidden at much higher molecular weights, where ductility and toughness are displayed, required new specialized methods. Acknowledging that the recombination of exposed oxonium and oxocarbenium species hindered desirable CROP control, the authors hypothesized that a selective catalyst and initiator system that promotes reversible-deactivation CROP (RD-CROP) would promote longer lived chain-ends. The key breakthrough was accomplished by tweaking the dormant halomethyl ether species. These neutral chain-ends exchange with active cationic species during the course of the polymerization providing fast yet controlled chain growth.

Indeed, the authors discovered that a carefully selected combination of Lewis acid metal halide catalyst ($InBr_3$), initiator (bromomethyl methyl ether, MOMBr), and proton trap (2,6-di-*tert*-butyl pyridine) achieved high conversions of DXL (> 80%) to PDXL at room temperature. With suppression of unwanted monomer activation pathways, RD-CROP demonstrated living characteristics, including good control of molecular weight based on DXL conversion and successful chain extension following sequential monomer additions. This polymerization was well amenable to other 7- and 8-membered cyclic acetals, as well as a bi-cyclic analogue, achieving impressive number average molecular weights ($M_n$) between 101,000 and 234,000 g $mol^{-1}$ in a matter of minutes. At these unprecedentedly high molecular weight regimes, the tensile strength (33.3–40.4 MPa) and elongation at break (640–720%) of PDXL rival those of isotactic polypropylene and high-density polyethylene. Such thermoplastics, which are no longer weak and brittle, can then be moulded into various shapes that resemble useful packaging applications.

The sub-ambient $T_c$ of 13 °C ($[DXL]_0$ = 4.0 M) remarkably contrast with the good resistance to thermal degradation of isolated PDXL (> 330 °C), indicating that the uncatalyzed depolymerization is kinetically prevented. Once the polymer is formulated or mixed with catalytic amounts of Brønsted acid, almost all (98%) of the polymer can be transformed back to monomer by simple distillation at 140 °C under ambient pressure. This circular recovery of monomer is almost ideal, as it does not require specialized infrastructure or high energy inputs, it can be coupled with mixtures of discarded plastics containing various additives, and the resulting pure DXL monomer can be effectively reutilized to produce new high molecular weight PDXL.

Yet, a few challenges need addressing for this technology to jump to large scale adoption. First, elevating the melting transition ($T_m$ = 58 °C) and water resistance of these polyacetals will open up an important range of applications that require good durability when exposed to harsher operating conditions. Other features such as gas permeability and UV resistance will equally determine their possible consumer functionalities. Second, greener and lower cost catalysts that could still retain such exceptional RD-CROP activities will make this technology much more desirable. Lastly, understanding the composition and toxicity of any hydrolysable products will be of uttermost importance to trace their biological impact if PDXL or other similar polyacetals were to find its way into water ecosystems.

In the end, our current plastic waste crisis demands an overhaul of the system that brought us to this unsustainable state. Exceling at technical functions without considering any external harms is insufficient to respond to these changes. Instead, desirable performances in the future, guided in the context of a circular economy, must take into account sustainability as a defining factor.[10] Addressing the fate of plastic materials after becoming waste will be a critical part of this new design process, and polymers that undergo CRM constitute an important piece of this puzzle. In this ever-exciting quest, re-examining well-known polymers with modern lenses, as Coates and co-workers have demonstrated with these newly revisited polyacetals, will deliver gratifying surprises.

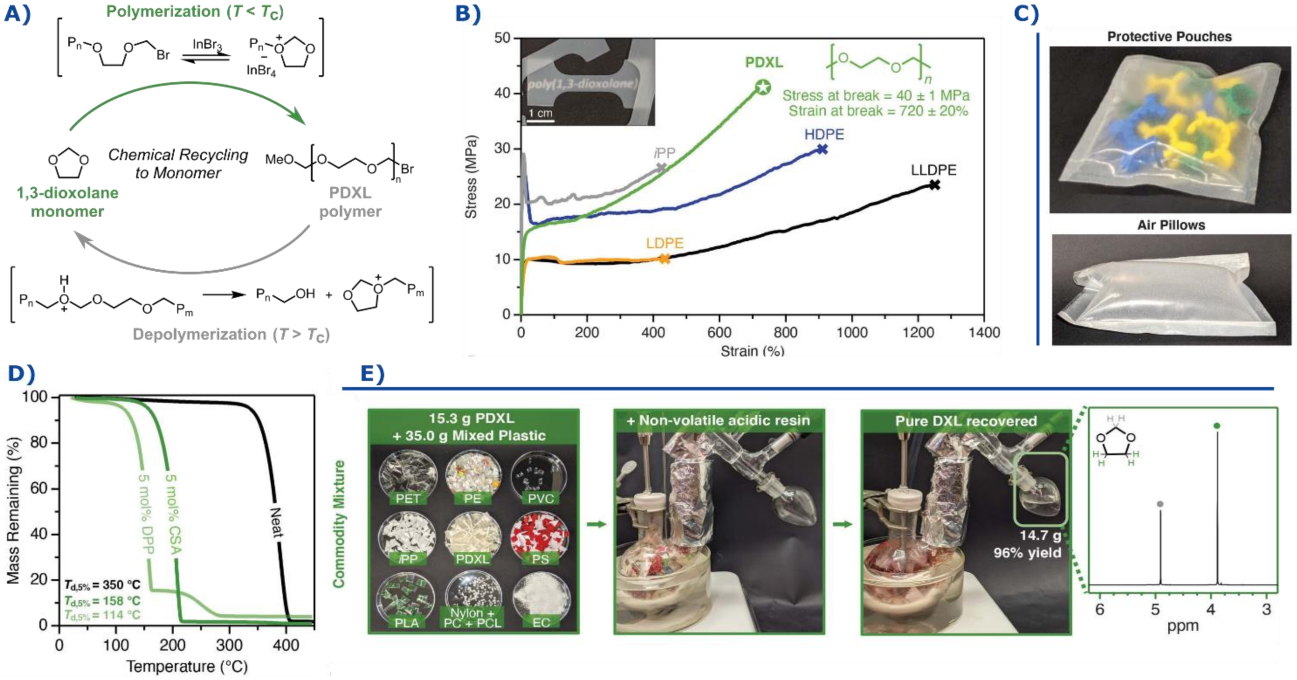

**Figure 1. Preparation, physical properties and recycling of poly(1,3-dioxolane).**

(A) RD-CROP of DXL and depolymerization of PDXL. (B) Stress-strain curves of PDXL and common polyolefins. (C) PDXL prototypes by melt-processing. (D) Acid-catalyzed thermal degradation of PDXL. (E) Chemical recycling to monomer of PDXL from a mixture of commodity plastics. Figure adapted from Abel et al.[9] Reprinted with permission from AAAS.

## Declaration of Interest

Charlotte K. Williams is founder and Chief Scientific Officer of Econic Technologies.

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