Degradable plastics

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# A new CAMMP-ing ground for polymers

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A polymerization strategy – termed CAMMP – combines two types of olefin metathesis monomers to produce degradable copolymers without sacrificing the mechanical properties of the equivalent homopolymer.

Synthetic elastomers, thermosets, and thermoplastics are lightweight and robust materials used in wide-ranging applications in our everyday lives. As a result, these materials are produced on a large scale worldwide. It is estimated that since 2015, 6,300 metric tons of plastic waste have been produced, with only 9% recycled, while most of the waste (79%) has accumulated in landfill sites or the environment[1]. This plastic waste problem makes it paramount that research efforts investigate new strategies for recycling or degrading plastics, or search for alternative end-of-life treatments for plastic waste. Current mechanical recycling strategies are often not economically viable, owing to a depreciation in value of the plastic and the loss of useful mechanical properties upon recycling[2]. Some examples of alternatives to mechanical recycling include polymers with enhanced (bio)degradability, the upcycling of polymers to higher value products, or the reversal of their synthesis in a process termed 'chemical recycling to monomer'[3–5].

Now, writing in *Nature Synthesis*, Si and Chen report a metathesis polymerization strategy for the random incorporation of degradable functional groups into the macromolecular backbone of a variety of polyolefin-based thermosets and thermoplastics[6]. These weak links are easily cleavable covalent bonds and are incorporated to make the

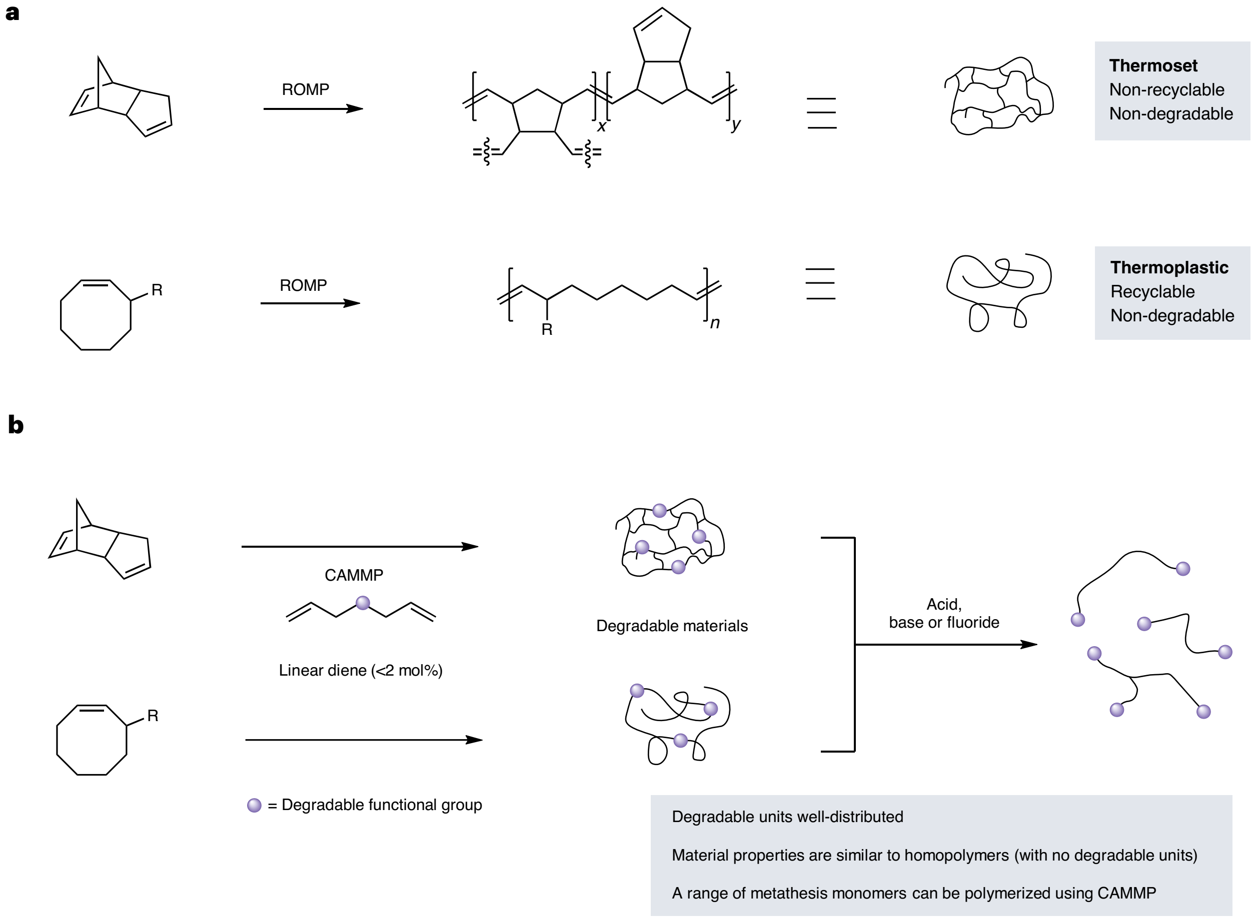

**Fig. 1 | Cyclic–acyclic monomers metathesis polymerization (CAMMP) to incorporate degradable segments within traditionally persistent polyolefins. a**, Traditional ROMP methods using only strained cyclic olefins to produce thermosets and thermoplastics. **b**, The CAMMP strategy, incorporating <2 mol% of linear diene which contains a degradable functionality within it (purple circle). The incorporation of these degradable moieties within the polymer produces degradable polyolefins similar to those produced in **a**.

materials susceptible to various degradation strategies. Moreover, as a consequence of the low proportion of degradable groups compared with the linear backbone of the polymer, these materials maintain the desired salient properties traditionally employed for polyolefin materials, but with an alternative way for end-of-life treatment to reduce persistent plastic waste.

Olefin metathesis polymerization is a powerful route to synthesize hydrocarbon-rich elastomers, thermosets and thermoplastics. As a result of the excellent functional-group tolerance of commercially available ruthenium (Grubbs-type) metathesis catalysts, a wide range of functionality can be incorporated into the polymers. The two main approaches are ring-opening metathesis polymerization (ROMP) (Fig. 1a) and acyclic diene metathesis (ADMET) polymerization. Although ROMP and ADMET both connect monomeric olefins into macromolecular chains, the two approaches have different polymerization mechanisms: ADMET is a step-growth polymerization of linear dienes, whilst ROMP is a chain-growth polymerization of strained cycloolefins.

In 2002, Grubbs and co-workers introduced a unique combination of ADMET and ROMP using highly reactive linear diacrylate-based comonomers along with a cycloolefin, such as *cis*-cyclooctene, respectively[7]. This combination was termed 'ring-opening-insertion-metathesis polymerization' (ROIMP), and could be used to produce alternating copolymers derived from each type of monomer[7]. Since that time, investigations to exploit copolymerization strategies using these two metathesis propagation methods have been underexplored. Now, this polymerization strategy developed by Si and Chen brings the combination of such strategies back into focus[6].

In the method reported by Si and Chen, very low quantities (<2 mol%) of a commercially available or easily accessible linear triene or diene comonomer are seeded into the feedstock of traditional ROMP monomers. These ROMP monomers typically produce thermosets (when using dicyclopentadiene) or thermoplastics (when using *cis*-cyclooctenes). The key feature of the linear diene and triene monomers used in the reactions is the inclusion of functional groups that are susceptible to degradation, thereby enabling the degradation of the resultant polymer. For example, the use of silyl ether functional groups, such as those previously employed by the Johnson group[8], enables thermoset degradation through the use of hydrofluoric acid or tetrabutylammonium fluoride. In another example, inspired by the work of Mecking and co-workers[9], semi-crystalline segments of polyethylene can be doped with degradable ester or carbonate groups, which are also degraded using fluoride treatment.

Si and Chen coin this hybrid metathesis polymerization strategy as 'cyclic–acyclic monomers metathesis polymerization' (CAMMP), and present a variety of degradable linear trienes or dienes in combination with traditional ROMP monomers to produce both thermosets and thermoplastics (Fig. 1b). Owing to the very low proportion of diene or triene monomer required for enhanced degradability, the mechanical and thermal properties of these copolymers are similar to the properties of non-degradable homopolymers made from the ROMP monomer. Therefore, degradability is gained without the loss of the useful properties of the polyolefin material. Furthermore, investigation of the by-products formed after degradation of the polymers indicates that the linear diene monomer components are well-distributed within the macromolecular structures, enabling a more uniform degradation.

Si and Chen have devised a simple yet versatile method to synthesize degradable polyolefins. Strategies moving forward will benefit from a more in-depth understanding of the synergy between the ROMP and ADMET propagation, and how the active Ru-alkylidene chain end negotiates between the two, which is likely to be sensitive to the monomers, conditions and stoichiometries used. For some of the linear dienes chosen, ring-closing metathesis, may also be a competitive pathway, which would produce low-strain cyclic comonomers, in situ, amenable to carry forward ROMP propagation. Actively propagating Ru-alkylidene species are highly reactive to terminal olefins and hence, these species are scrupulously purified away from the monomer feedstocks when better control is needed[10]. By deliberately adding such species, investigations of this interplay of reactivities and conditions could uncover new insights to gain better control over the molar mass and dispersity of the polymers produced by CAMMP, opening the door to a variety of controlled yet degradable architectures. Alternative degradation chemistries, particularly those that move away from fluoride or hydrofluoric acid, are also welcomed. Nevertheless, this study is an exciting step towards a divergent number of potentially competitive plastics with improved degradability.

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## Competing interests

The authors declare no competing interests.