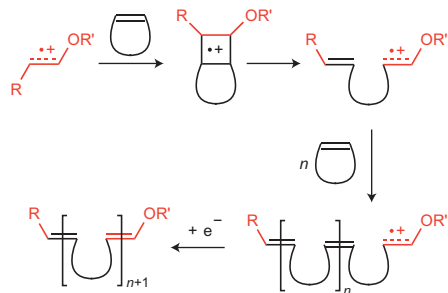


POLYMER SYNTHESIS

Photoredox ROMP

J. Am. Chem. Soc. <http://dx.doi.org/10.1021/ja512073m> (2015)



With applications in biomedical engineering, photovoltaics and drug delivery, ring-opening metathesis polymerization (ROMP) has quickly become a standard technique for polymer synthesis. The reaction is tolerant of multiple functional groups and its 'living' nature produces polymers with low dispersity. Many transition-metal catalysts have been developed for ROMP, but now Andrew Boydston and co-workers from the

University of Washington have described a metal-free version of the reaction.

Though the use of metal catalysts for these reactions has already been successful, even very small amounts of metal byproducts can be problematic if, for example, the polymers are to be applied in a biological setting. Boydston and co-workers set out to develop a ROMP method initiated by the one-electron oxidation of a vinyl ether. They envisaged that the reaction would proceed through a [2+2] cycloaddition to form a cyclobutyl radical cation and that the use of a suitable cyclic alkene monomer could allow a ring opening to compete with reduction and lead to propagation. Early experiments focussed on the polymerization of norbornene in the presence of a variety of simple vinyl ethers with the reaction initiated by bulk electrolysis. The results were promising — producing polymers with an average molecular weight of 11.8 kDa and a dispersity of 2.2 — but only in low yield. The researchers attributed this to the low solubility of the polymer in the nitromethane solvent required for electrolysis and the heterogeneous nature of the initial oxidation; they thus turned to photoredox catalysis.

Blue light irradiation of a 100:1 mixture of norbornene monomer and vinyl ether initiator, in the presence of a pyrylium photoredox mediator, produced a polymer with properties very similar to those made using the more traditional ruthenium catalysis. The change in molecular weight of the polymer during the reaction, however, did not follow the same trend as for a ruthenium-catalysed process. This was attributed to the reaction possibly featuring reversible termination events — an observation that could be exploited in a spatiotemporally controlled polymerization. SD

ASYMMETRIC EPOXIDATIONS

Challenging substrates

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201410557> (2015)

Asymmetric epoxidation is a popular process, largely due to the utility of chiral epoxides as synthetic intermediates or products in their own right. However, despite the fact that methods abound for this type of reaction — including metal-catalysed and organocatalytic processes — some substrates are inherently

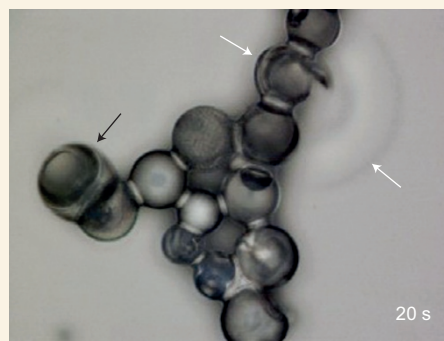
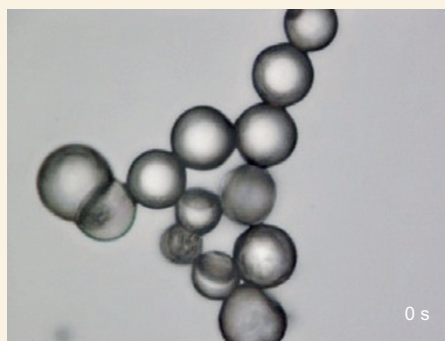
STIMULI-RESPONSIVE MATERIALS

Bursting bubbles

Angew. Chem. Int. Ed. <http://dx.doi.org/10.1002/anie.201410778> (2015)

Encapsulation and triggered release of drugs or other small molecules is one method to ensure that said molecules are delivered at the correct time, location and in the right amounts. Generally, these strategies involve bespoke syntheses of capsules or containers that have responsive functionalities embedded in them — when applying the relevant environmental trigger, the capsules degrade and release their cargo. Now, Andreas Herrmann, Damien Berthier and colleagues from Firmenich, a perfumery and flavour chemical company, have adopted a different, yet complementary, approach to small molecule release.

Instead of tailoring the capsule with photoresponsive functionalities, they used 'off-the-shelf' non-responsive polyurea-based hollow microcapsules. These microcapsules simply burst if an overpressure of gas is built up inside. To achieve this, the team modified their intended cargo — volatile fragrance molecules containing ketones or aldehydes — to contain a 2-oxoacetate functionality. Visible light degrades 2-oxoacetates creating ketones and aldehydes, and also



releasing a molar equivalent of CO or CO₂. Since the microcapsules are gas permeable to a certain degree, some optimization of the precise 'profragrant' 2-oxoacetate species was required, in order to ensure that degradation (and thus generation of overpressure) was much faster than the diffusion of the gas out of the microcapsule. They found that the thickness of the capsule wall in comparison to the amount of gas contained within was also an important parameter to control.

Using optical microscopy, they observed gas bubbles forming inside the

microcapsules (black arrow), as well as a 'burst release' of the cargo (white arrow) on rupture. Because 2-oxoacetates degrade into two separate aldehyde- or ketone-containing molecules, potentially two different fragrance molecules can be released at once. Additionally, spectator fragrance molecules can also be co-encapsulated, either with a non-functional oxoacetate that serves as the gas source only, or with a profragrant oxoacetate that both supplies the overpressure and releases additional fragrant aldehydes or ketones. CH