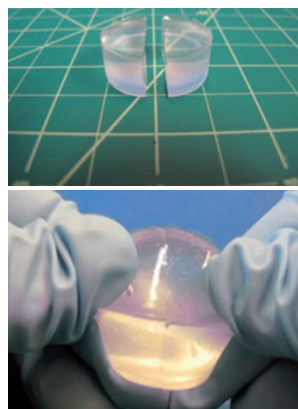


SELF-HEALING MATERIALS

Re-discovered repair

J. Am. Chem. Soc. **134**, 2024–2027 (2012)



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The ability to self-heal is an attractive property in many fields, from packaging to biomedicine, and a great deal of research has recently been devoted to confer it to various materials. Mimicking self-healing biomaterials — such as skin, to mention a familiar example — is one approach. Now, while investigating silicone materials for different purposes, Peiwen Zheng and Thomas McCarthy from the University of

Massachusetts have come across a simple, efficient self-healing mechanism that was apparent from 1950s publications but seems to have since been overlooked.

Zheng and McCarthy partly converted a cyclic octa-methyl-tetra-siloxane species into its dimeric form featuring an ethylene bridge. An anionic (silanolate) polymerization initiator was then added, which catalysed a siloxane equilibration mechanism to form chains. The chains contained ethylene bridges serving as crosslinks, and 'living' reactive silanolate end groups that further reacted with other existing chains. This resulted in the formation of a silicone rubber that can be regarded as a living crosslinked polymer network and exhibits self-healing behaviour.

One such silicone elastomer was cut in two with a razor. It healed so well under mild heating that the repaired sample showed similar cohesive strength and fracture toughness to that of the original silicone. The anionic polymerization, the co-polymerization of the monomeric and dimeric units, and the fact that the reaction is a living process were all described in earlier reports, along with some chemical stress relaxation studies of the silicones' ability to be re-shaped — which suggests the self-healing had been observed at the time. *AP*

ASYMMETRIC CATALYSIS

React then repeat

Angew. Chem. Int. Ed. **51**, 2717–2721 (2012)

Many targets of synthetic chemistry — whether they are potential drugs, natural products or advanced materials — contain multiple contiguous stereocentres. Iterative synthesis aims to introduce one stereocentre at a time by repeating one or more simple synthetic steps. Although this concept is attractive, it can be difficult to put into practice because a stereocentre already present in a substrate can override the inherent selectivity of a catalyst, making it difficult to gain access synthetically to all possible diastereomers. Now, Jin Kyoong Park and Tyler McQuade from Florida State University have described an iterative method of producing both *syn*- and *anti*-1,2-diols.

Park and McQuade's methodology combines an asymmetric allylic boronation (AAB) with a cross-metathesis reaction. Cross-metathesis of an allylic alcohol with *m*-nitrophenyl allyl ether using Hoveyda-Grubbs catalyst gives a new allyl-aryl ether that is the substrate for AAB. In the ensuing AAB reaction mediated by an *N*-heterocycle carbene/copper(I) catalyst, the aryl ether

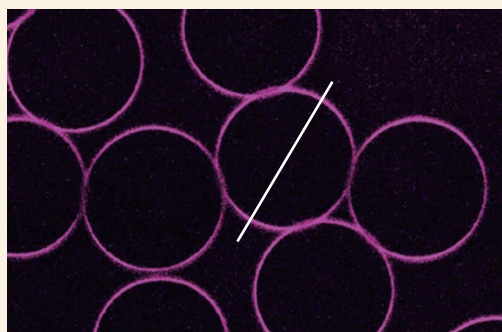
SUPRAMOLECULAR CHEMISTRY

Microfluidics for microcapsules

Science **335**, 690–694 (2012)

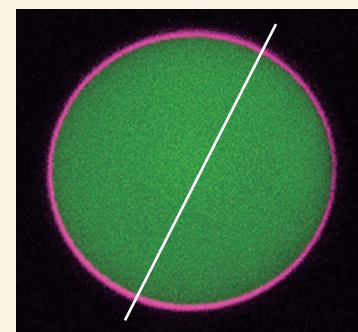
Hollow microcapsules have proved useful for a number of applications because of their ability to encapsulate molecules — or even larger ensembles such as cells — and shelter them from bulk environments. There are a range of different processes that can be used to make synthetic microcapsules, including layer-by-layer deposition onto colloidal templates as well as self-assembly approaches. Each of these techniques has its own drawbacks, and an ideal method would produce relatively monodisperse capsules into which cargo can be loaded efficiently.

Now, a team of researchers at the University of Cambridge led by Oren Scherman and Chris Abell have shown how microfluidic droplets can be used to prepare porous supramolecular microcapsules with a high degree of monodispersity. Their approach takes advantage of the host-guest properties of cucurbit[8]uril (CB[8]) — a toroidal molecule that can accommodate two different aromatic groups inside its



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central cavity. Aqueous solutions of CB[8], gold nanoparticles functionalized with electron-deficient aromatic ligands, and a water-soluble polymer with electron-rich naphthol side chains were prepared. These were then flowed into one arm of a T-junction in a microfluidic device. Oil flowing perpendicularly to the aqueous stream sheared off microdroplets containing the three building blocks, which then assembled into hollow microcapsules as the polymer



chains and nanoparticles are stitched together by the CB[8] hosts.

Both the nanoparticle and polymer components can be tuned to give different properties from the resulting microcapsules. Incorporating a dye into the polymer backbone enabled the shell to be visualized with a confocal microscope (pictured, left) in the same way that a dye-labelled guest trapped inside the capsule was imaged (pictured, right). *SC*