

wide range of complex macromolecular architectures can be made in many different ways. Most polymerization processes start when all of the reagents are added, and finish when quenched; typically there is little that can be done to affect the course of the reaction while it is actually happening. The ability to control polymerization with an external stimulus is an appealing feature, particularly if it could be achieved with light — an input that is easy to regulate. Photo-controlled initiation of polymer growth is quite common; however, finer control in a reversible ‘on/off’ manner has only recently been achieved in some radical-based systems.

Ring-opening polymerization (ROP) reactions have not, as yet, received much attention when it comes to the possibility of their external control. One type of organocatalyst used in ROP reactions are *N*-heterocyclic carbenes (NHCs). Now, Christopher Bielawski and Bethany Neilson at the University of Texas, Austin, have found that UV light can be used to control the activity of a dithienylethene-substituted NHC catalyst through the light-driven interconversion between its annular and ring-opened isomers. Only the ring-opened form of the NHC catalyses the ROP of lactones to form poly(esters), hence it can be used as the basis of a light-controlled organocatalytic polymerization system. Negligible chain propagation was observed when a mixture of initiator, lactone monomer and NHC was irradiated with UV light — conditions under which the NHC remained in its ring-closed form. In contrast, fast polymerization was observed when the reaction was exposed to visible light.

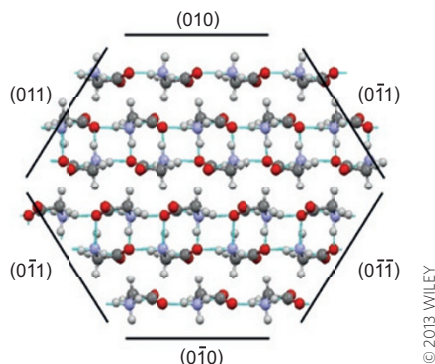
The proposed mechanism for the on/off switching involves deactivation of the carbenoid centre by formation of an NHC–alcohol adduct, which is favoured when the NHC is in its cyclic state. Visible light results in cycloreversion, the active catalytic site is regenerated and the polymerization continues. Successful photo-controlled copolymerization of two different lactones was also demonstrated, suggesting that this method could be used to make more complex (co)polymer architectures in the future. *CH*

#### PYROELECTRICITY

### Surface effects

*Angew. Chem. Int. Ed.* <http://dx.doi.org/10.1002/anie.201301836> (2013)

Some crystalline materials generate an external electric current in response to a temperature change — a ‘pyroelectric’ effect. This can be exploited in temperature sensors, such as for alarm devices, because body heat from a distance creates



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a sufficient voltage. The phenomenon arises from spontaneous polarization: as molecules move slightly within the lattice, changes in their dipole moments lead to the creation of two oppositely charged faces and a voltage across the material. This effect, determined by a crystal's symmetry, occurs for the ten crystal classes that are non-centrosymmetric polar (that is, those having a dipole in their unit cell).

Meir Lahav, Igor Lubomirsky and co-workers at the Weizmann Institute of Science have now observed pyroelectricity in nonpolar, centrosymmetric crystals of amino acids. The researchers grew crystals of  $\alpha$ -glycine on a glass substrate, in an aqueous solution and in the presence of *L*-alanine, whose occlusion prevents crystal twinning that could lead to artefacts. Crystals of different morphologies, with different faces exposed at the interface with the aqueous solution, were prepared. All of them exhibited a pyroelectric effect at their {010} faces, despite the crystals' centrosymmetric lattice.

The characteristics of the current — direction and time dependence — showed that the pyroelectric effect did not arise from the bulk crystal or from the glass substrate, but from the presence of a thin polar layer near the surface. Characterization at different temperatures provides evidence that the pyroelectricity arises from thin polar films of hydrated  $\alpha$ -glycine. Although water molecules are also adsorbed at other faces, they can only adopt a suitable polar configuration near the {010} surfaces. This is in good agreement with the fact that the surface pyroelectricity disappeared on heating the crystals above 80 °C, which coincides with the removal of the adsorbed water molecules. Similar surface pyroelectricity was observed at specific faces of other nonpolar crystals of amino acids, *L*- and *D*-alanine, showing that the limitations arising from a crystal's symmetry can be circumvented. *AP*

Written by Ruth Doherty, Claire Hansell and Anne Pichon.

## blogroll

### Digital discourse

Chemists chat, share snippets of research, and try to out-draw each other during #RealTimeChem week.

Are you connected? The rise of smartphones and social networks is blurring the line between conference and lab, allowing chemists to share and discuss their discoveries in real time. In April, students, postdocs, industrial chemists and professors were in full presentation mode, sharing their research struggles and triumphs in #RealTimeChem week. Doctor Galactic curated the @RealTimeChem twitter feed and picked his favourite tweets each day (<http://go.nature.com/jLogck>). Meanwhile, JessTheChemist kept tabs on the blog posts, providing a quick summary for each (<http://go.nature.com/5Ay78G>). All told, around 700 people took part, and Mark Borkum built the interactions into a beautiful illustration (<http://go.nature.com/9Jzjar>).

As the week progressed, contributions ranged from Andrew Bissette's serious take on classic research papers (<http://go.nature.com/SpgJn2>) to Vittorio Saggiomo's light-hearted music video (<http://go.nature.com/zftF9u>), with several ancillary hashtags gaining popularity. On Thursday, JessTheChemist threw down the gauntlet, challenging her fellow chemists to tweet their hand-drawn structures under #FreeHandRings (<http://go.nature.com/HBlvDH>). From simple six-membered rings came ever more elaborate structures, until See Arr Oh squashed the competition with a beautifully crafted maitotoxin (<http://go.nature.com/KgmyvQ>).

No two hand-drawn structures are alike, as shown in an earlier post on the Baran group blog, Open Flask (<http://go.nature.com/QEpski>). Polling the lab, Dane Holte discovered that not only did his labmates have a preferred double-bond arrangement (the two Kekulé variants were far more popular than the inner-ring Thiele model), but that drawing the hexagon was quite contentious. The most popular line order was used by only 5/25 chemists, with eleven other options receiving at least one vote.

Written by Brandon Findlay, who blogs at <http://chemtips.wordpress.com>