

most organic reagents are not very soluble in it. This property, however, can actually be used to accelerate reaction rates in what are known as 'on water' reactions. These can occur for certain transformations when water-insoluble reactants are vigorously stirred in water to give aqueous emulsions or suspensions. Such reactions are thought to occur at the interface between the immiscible phases, but they are not fully understood. For example, the complicated structure of emulsions makes it difficult to quantify the effects of important reaction parameters such as water surface area and surface-to-volume ratio.

Now, Wilhelm Huck and colleagues at Radboud University Nijmegen and the University of Cambridge, have used a fluidic approach to control the interfacial features of two model 'on water' reactions to better understand and quantify the role played by the water surface. The reaction set-up consisted of a cross-junction fed by tubes containing either water or reagents dissolved in toluene. Monodisperse plugs of toluene and water form at the junction and, by controlling the flow rate of the immiscible phases or changing the diameter of the tubing, Huck and colleagues could control the interfacial surface-to-volume ratio of the reacting plugs. Using this set-up they studied the cycloaddition reaction of quadricyclane with diethyl azodicarboxylate (DEAD), and the ene reaction between β -pinene and DEAD, reactions known from previous studies to exhibit 'on water' behaviour.

Huck and colleagues observed a linear relationship between the percentage conversion of reactants into products (as analysed by NMR spectroscopy) and the interfacial surface area between the plugs, strongly supporting a role for the surface in enhancing the rate. They also calculated a decrease in the activation energy of the reactions when 'on water' in comparison to in toluene, which supports a mechanism involving a hydrogen-bond-stabilized transition state. GA

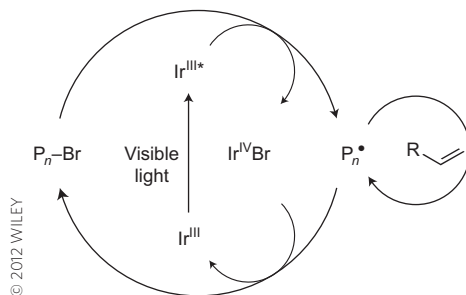
POLYMER CHEMISTRY

Alive with light

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The properties of any given polymeric material are influenced significantly by the molecular weights of the individual polymer chains and also the distribution of those values. Methods that offer very good control over these parameters are therefore prized in polymer synthesis. In particular, controlled living radical polymerization has attracted much attention and acronyms such as ATRP (atom transfer radical

polymerization) and RAFT (reversible addition fragmentation chain transfer polymerization) are now commonplace in the chemical literature. Some relatively recent developments in this area have focused on how to control these reactions with an external stimulus, such as light or an applied electrical current.



Previous attempts to photoregulate living radical polymerization processes have been somewhat limited, either giving rise to poor molecular weight control or only enabling the initiation step — rather than the subsequent chain-growth steps — to be controlled. Now, Brett Fors and Craig Hawker from the University of California, Santa Barbara, have shown that the living radical polymerization of methacrylates can be turned on and off at the flick of a (light) switch by using a commercially available iridium-based photoredox catalyst. The Ir(III) catalyst absorbs visible light to give an excited-state Ir(III)* species that can react with an alkyl bromide initiator to produce an alkyl radical and an Ir(IV)Br complex. The alkyl radical initiates the polymerization of a methacrylate monomer to give a propagating polymer radical, which can then react with the Ir(IV)Br species to give a dormant polymer chain with a bromide end group, at the same time as regenerating the original Ir(III) complex.

In the presence of light, this process (pictured) continues to cycle in this fashion, although the alkyl bromide is no longer a small-molecule initiator but a polymer chain. When the light is turned off, however, the propagation reaction stops almost immediately — importantly, Fors and Hawker show that no chain termination occurs during this resting period. When the light is turned back on an hour later, the polymerization reaction resumes and continues until the light source is removed once more. Further evidence for the living nature of the system is provided through the efficient formation of a diblock copolymer. SC

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey and Anne Pichon.

blogroll

But is it art?

Practical synthetic chemistry shows an artistic side with synthesized doodles, logos and colouring-book molecules.

It's been a busy summer in the blogosphere! Between 'arsenic life' and the newly discovered Higgs boson, science blogs seem more relevant than ever. In all the fuss, though, they may have overlooked some promising chemical artists in their midst.

First up, let's turn our attention to the 2012 London Olympic Games. Chemists at the University of Warwick decided to commemorate the event by synthesizing a new molecular version of the famed Olympic rings. ChemConnector's Antony Williams explains (<http://go.nature.com/oCerSJ>) that a chalkboard 'doodle' evolved into a synthesis of olympicene; the RSC's ChemSpider SyntheticPages later published (<http://go.nature.com/N4OM3p>) the step-by-step details. IBM-Zurich (of pentacene-imaging fame) posted a series of finely resolved atomic images to Flickr (<http://go.nature.com/uPSHll>).

Next we'll talk high fashion. At *Chemistry World*, Phillip Broadwith noted (<http://go.nature.com/VYtBww>) a neat undergraduate synthesis project: making a hydrocarbon to match a clothing label's logo. After just three steps, Plymouth University's Mark Cockerton and Simon Belt had their target...but still no word on whether they've tied up a sponsorship deal with the apparel company in question!

Speaking of synthetic art, we'd be remiss not to wish a happy belated birthday to organic chemist K. C. Nicolaou. Blogger BRSM prepared a special tribute (<http://go.nature.com/jkKft8>) to his penchant for flashy colours and ancient mythology in the figures that adorn his papers and the graphical abstracts that accompany them. A small group of Blogroll's 'usual suspects' — including Adam Azman, Chemjobber and Dr Freddy — re-imagined K.C.'s classic molecules with new artistic twists. Perhaps these entries will finally prompt publication of that chemical colouring book (<http://go.nature.com/dWIUMI>).

Written by See Arr Oh, who blogs at <http://justlikecooking.blogspot.com>