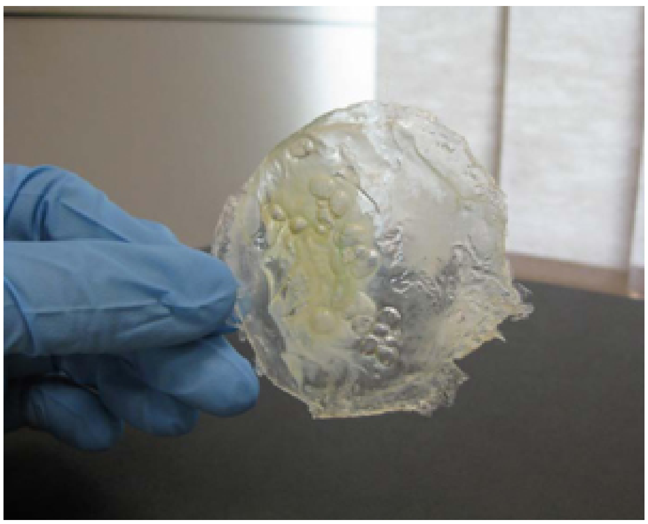
Polymer chemistry: A pinch of copper proves invaluable

November 21 2012



Acrylic acid-based polymers and co-polymers (pictured) can now be synthesized using free radical chemistry, thanks to new ligand–initiator type molecules. Credit: 2012 A*STAR Institute of Chemical and Engineering Sciences

Production of biocompatible and super-absorbent materials may become easier, thanks to Anbanandam Parthiban and co-workers at the A*STAR Institute of Chemical and Engineering Sciences. Using a modification to the high-precision technique known as atom transfer radical polymerization (ATRP), which links molecules into long chains, the researchers have developed new compounds that can directly polymerize acidic vinyl monomers, such as acrylic acid. Acrylic acid polymers are water-absorbing materials widely used in diapers and as emulsifying agents for pharmaceuticals and cosmetics.

Previous attempts to use ATRP with polar vinyl monomers, including acrylic acid, were unsuccessful, a failure that some chemists attributed to catalyst 'poisoning' by carboxylic acids. Parthiban and his team's compounds resolve this problem by binding to the catalyst while simultaneously initiating the radical polymerization process. This process prevents poisoning and dramatically reduces metallic waste.

Despite ATRP's inability to directly produce acrylic acid polymers, it is used in laboratories worldwide: it allows researchers to assemble complex polymers in a step-by-step fashion that gives enormous control over product architectures. The key is using a catalyst that can readily switch between two oxidation states, such as a copper salt, explains Parthiban. The copper catalyst first interacts with an ATRP initiator molecule to activate organic free radicals and an oxidized metal complex. The free radicals then quickly polymerize target monomers, while the metal complex undergoes equilibrium with a dormant, lower oxidation state. With appropriate reaction conditions, chemists can then restart polymerization with new monomers.

Parthiban and co-workers addressed ATRP's limitation by developing 'unimolecular ligand–initiator systems' (ULIS), a series of branched molecules containing multiple binding sites for copper atoms, as well as halogens for activating free radical species. In this approach, the ULIS molecules become part of the polymer chain during the active–dormant cycles instead of remaining isolated. The researchers envisaged that this interconnection would suppress the acidic side-reactions that lead to catalyst poisoning.

Experiments by the researchers proved their theories correct: they could efficiently polymerize acrylic acid and other vinyl monomers using ULIS-promoted ATRP (see image). Surprisingly, they found that these reactions could be achieved using less than 100 parts-per-million concentrations of copper catalyst, a quantity comparable to residues left in conventional ATRP purified polymers.

Parthiban notes that although the ULIS ligands are part of the polymer chain and might be expected to produce high amounts of metal waste, the homogenous nature of intramolecular-based free radical polymerization allows less metal to be used—an important consequence for sustainable chemistry efforts.

More information: Jana, S., Parthiban, A. & Choo, F. M. Unimolecular ligand–initiator dual functional systems (ULIS) for low copper ATRP of vinyl monomers including acrylic/methacrylic acids. *Chemical Communications* 48, 4256–4258 (2012). dx.doi.org/10.1039/c2cc16663a

Provided by Agency for Science, Technology and Research (A*STAR), Singapore

Citation: Polymer chemistry: A pinch of copper proves invaluable (2012, November 21) retrieved 10 April 2024 from https://phys.org/news/2012-11-polymer-chemistry-copper-invaluable.html