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RESEARCH FRONT: Click Chemistry

Essay

Bringing Efficiency to Materials Synthesis: The Philosophy of Click Chemistry

Craig J. Hawker, Valery V. Fokin,
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Aust. J. Chem. **2007**, *60*, 381–383.

Click chemistry not only allows particular new materials to be prepared, it opens up whole new avenues for materials in general to be prepared more efficiently. It also allows existing materials classes to be prepared with unprecedented efficiency and versatility opening up an array of new structures. This issue's Research Front addresses many of the key features of click chemistry and presents some of the myriad synthetic possibilities.

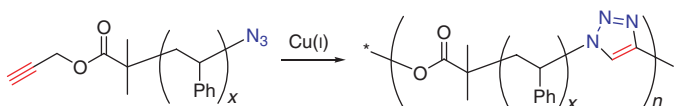
Review

The Rise of Azide–Alkyne 1,3-Dipolar ‘Click’ Cycloaddition and its Application to Polymer Science and Surface Modification

Richard A. Evans

Aust. J. Chem. **2007**, *60*, 384–395.

The copper(I) mediated ‘click’ azide–alkyne cycloaddition reaction has generated intense interest in the brief time since its first report in 2002. Polymer scientists have rapidly appropriated the methodology for polymer synthesis, functionalization, and modification as evidenced by at least 40–50 papers since 2004. This review will provide an overview of the azide–alkyne cycloaddition reaction, its application to polymer science, and possible future directions.

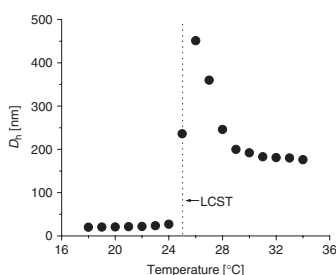


Rapid Communications

Hyperbranched Polymers via RAFT Copolymerization of an Acryloyl Trithiocarbonate

Andrew P. Vogt, Sudershan R. Gondi,
Brent S. Sumerlin

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Engineering macromolecular materials with precisely controlled 3D morphologies is a primary concern of nanomaterial design. This paper reports the controlled synthesis of hyperbranched polymers, prepared using a method based on a branching agent obtained by copper-catalyzed azide–alkyne ‘click chemistry’. The polymers so constructed reversibly change their solution conformation and/or solubility in response to temperature.

Multisegmented Block Copolymers by ‘Click’ Coupling of Polymers Prepared by ATRP

Patricia L. Golas, Nicolay V. Tsarevsky,
Brent S. Sumerlin, Lynn M. Walker,
Krzysztof Matyjaszewski

Aust. J. Chem. **2007**, *60*, 400–404.

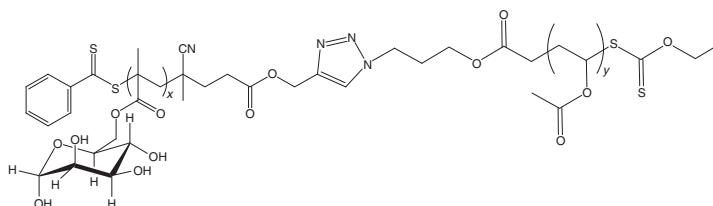
The combination of controlled radical polymerization techniques with highly efficient functionalization methods has substantially enhanced the accessible range of polymeric architectures and materials. This manuscript reports the use of atom transfer radical polymerization together with click chemistry to easily prepare multisegmented block copolymers, which exhibit unique glass transition and mechanical behaviours. The inherent robustness of this technique can potentially allow for the preparation of a wide range of novel multisegmented materials.

RAFT Chemistry and Huisgen 1,3-Dipolar Cycloaddition: A Route to Block Copolymers of Vinyl Acetate and 6-*O*-Methacryloyl Mannose?

S. R. Simon Ting, Anthony M. Granville, Damien Quémener, Thomas P. Davis, Martina H. Stenzel, Christopher Barner-Kowollik

Aust. J. Chem. **2007**, *60*, 405–409.

The combination of RAFT chemistry and Huisgen 1,3-dipolar cycloaddition ('click' chemistry) allows for the synthesis of poly(6-*O*-methacryloyl mannose)-*block*-poly(vinyl acetate), which is otherwise not easily accessible via conventional RAFT chemistry. The self-assembly of the slightly amphiphilic block copolymer was investigated and a rod-sphere transition was observed.

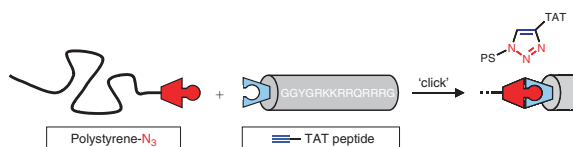


'Click' Bioconjugation of a Well-Defined Synthetic Polymer and a Protein Transduction Domain

Jean-François Lutz, Hans G. Börner, Katja Weichenhan

Aust. J. Chem. **2007**, *60*, 410–413.

Polymer–peptide bioconjugates are appealing structures, which combine the properties of synthetic and biological materials. However, their construction requires selective chemical tools since polypeptides are generally highly functional macromolecules. Herein, a facile pathway based on Sharpless 'click' chemistry was investigated for linking a model synthetic polymer and a 14-mer oligopeptide, which mimics the transduction domain of the TAT protein.

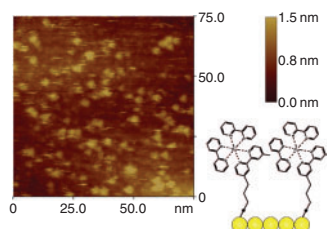


Full Papers

Synthesis and Surface Assembly of Ruthenium Bipyridine Complexes

Veronica Marin, Daan Wouters, Stephanie Hoepfner, Elisabeth Holder, Ulrich S. Schubert

Aust. J. Chem. **2007**, *60*, 414–419.



Ruthenium bipyridine complexes are widely studied compounds that have a breadth of applications, e.g., for solar cells and light emitting devices. The synthesis of thiol and disulfide-functionalized bipyridines and a study of their self-assembly behaviour on gold is reported. STM is used to reveal the monolayered organization of the ligands, as well as the bipyridine complexes.

Oxidation of Aromatic Alkynes with Nitrate Radicals (NO₃·): An Experimental and Computational Study on a Synthetically Highly Versatile Radical

Uta Wille, Jilliarne Andropof

Aust. J. Chem. **2007**, *60*, 420–428.

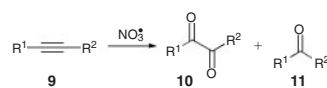
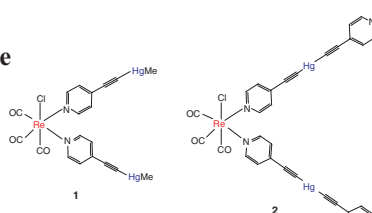


Photo- and electrochemically generated nitrate radicals react with aromatic alkynes **9** to give 1,2-diketones **10** and chain-shortened ketones **11** in a new type of self-terminating radical oxygenation. Experimental and computational studies provided insight into the reaction mechanism. This work reveals a novel method to generate carbene intermediates through γ -fragmentation in vinyl radicals.

Exploring the Coordination Chemistry of Some Organometallic Mercury Derivatives of 4-Ethynylpyridine

Li Liu, Cheuk-Lam Ho, Wai-Yeung Wong

Aust. J. Chem. **2007**, *60*, 429–434.



Mercury(II) derivatives of 4-ethynylpyridine are useful synthons to afford mixed-metal alkynyl complexes. Two new heterotri-nuclear rhenium(I)–mercury(II) complexes **1** and **2** were synthesized by the self assembly of Re(CO)₅Cl with (4-pyridylethynyl)-methylmercury and bis(4-pyridylethynyl)-mercury, respectively. The spectroscopic and photophysical properties of both compounds were investigated.

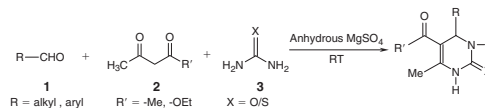
Short Communications

Anhydrous Magnesium Sulfate Mediated Solvent-Free Synthesis of Dihydropyrimidin-2(1H)-ones at Ambient Temperature

D. M. Pore, U. V. Desai, T. S. Thopate, P. P. Wadgaonkar

Aust. J. Chem. **2007**, *60*, 435–438.

The synthesis of Biginelli compounds, using inexpensive inorganic salts at ambient temperature and under solvent-free conditions, remains of interest in organic synthesis. Anhydrous magnesium sulfate, combining both a mild Lewis acidity and dehydrating properties, has been utilized for the synthesis of such compounds. This approach is broadly applicable, avoids organic solvents, and uses common reagents with a simple work-up procedure.

**Effect of Redundant Chain Packing on the Uptake of Calcium Phosphate in Poly(2-Hydroxyethyl Methacrylate) Hydrogels**

Traian V. Chirila, Anita J. Hill, David T. Richens

Aust. J. Chem. **2007**, *60*, 439–443.

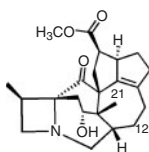
Spontaneous calcification is a major cause transparency loss in ocular devices made of synthetic hydrogels (e.g., contact lenses). A method to reduce or prevent the deposition of these calcium phosphate phases, based on the reduction of the free volume between poly(2-hydroxyethyl methacrylate) polymer chains, a hydrogel extensively used in ocular applications, by formation of interpenetrating polymer networks is reported.

Focus

Density Functional Theory as a Tool in Structure Evaluation

Nicholas Aberle

Aust. J. Chem. **2007**, *60*, 444.



The use of molecular modelling to assist in structure evaluation has become increasingly popular as access to powerful computers has become more widespread. Density functional theory has emerged as a leading approach to predict a range of properties. Specifically, it has been used recently to calculate solution conformations, NMR parameters, and absolute stereochemistries of natural products.