

AUSTRALIAN JOURNAL OF CHEMISTRY

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RESEARCH FRONT: Microwave-Assisted Organic and Polymer Synthesis

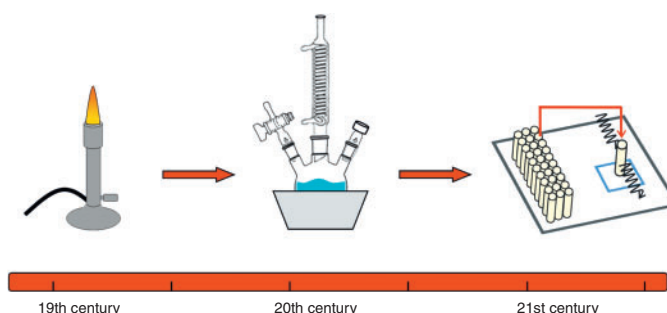
Essay

Microwave-Assisted Organic and Polymer Chemistry

Richard Hoogenboom,
Ulrich S. Schubert

Aust. J. Chem. **2009**, 62, 181–183

The use of microwave-irradiation has evolved from a research topic on its own to a standard laboratory tool in recent years. The present essay introduces the Research Front on *Microwave-assisted organic and polymer chemistry* that is included in the current issue of Australian Journal of Chemistry.



Reviews

Microwave-Assisted Ruthenium-Catalyzed Reactions

François Nicks, Yannick Borguet,
Sébastien Delfosse, Dario Bicchielli,
Lionel Delaude, Xavier Sauvage,
Albert Demonceau

Aust. J. Chem. **2009**, 62, 184–207.

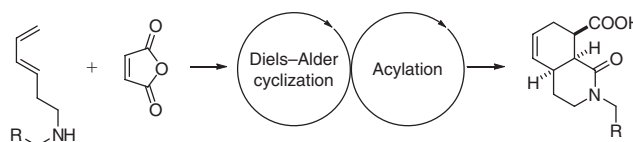
Microwaves make the difference: ever-increasing attention is being paid to microwave-accelerated, transition metal-catalyzed homogeneous catalysis. In particular, significant advances in this field have recently been made with ruthenium-based catalysts. Examples to be presented in this review include olefin metathesis, [2 + 2 + 2] cyclootrimerization reactions, cycloisomerizations, 1,3-dipolar cycloadditions, atom transfer radical reactions, transfer hydrogenation reactions, and H/D exchange reactions. The effect of microwave irradiation on these reactions will be discussed and compared with conventional heating.

Microwave-Assisted Tandem Processes for the Synthesis of N-Heterocycles

Mohammed Abid, Béla Török,
Xudong Huang

Aust. J. Chem. **2009**, 62, 208–222.

Electric arc furnace dust is a widely produced waste material from the steel-making industry. This paper shows a novel process that can take a complex mixture of heavy metals and separate them into a valuable source of important raw materials. The process uses environmentally compatible solvents for the extraction and separation.



Rapid Communications

Solubilization and Functionalization of Cellulose Assisted by Microwave Irradiation

Mona Semsarilar, Sébastien Perrier

Aust. J. Chem. **2009**, 62, 223–226.

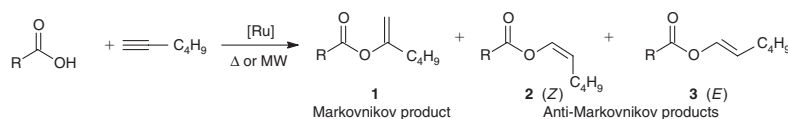
Monomodal microwave irradiation is shown to promote faster and easier dissolution of cellulose, when compared with the use of multimodal microwave irradiation, or conventional heating. Furthermore, we show that monomodal microwave irradiation can be used for the one-pot modification of cellulose, and we illustrate the concept with lauroyl chloride.

Microwave-Assisted Synthesis of Vinyl Esters through Ruthenium-Catalyzed Addition of Carboxylic Acids to Alkynes

François Nicks, Lionel Libert,
Lionel Delaude,
Albert Demonceau

Aust. J. Chem. **2009**, 62, 227–231.

The selective synthesis of enol esters by a rapid and efficient method via the microwave-accelerated addition of carboxylic acids to terminal alkynes is described. Readily available $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ complex is employed as catalyst without the need of bases, and reactions are complete in 20 min.

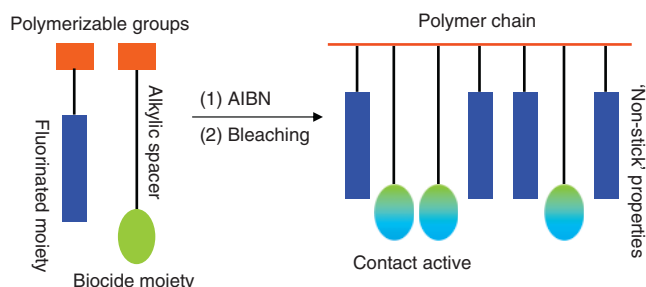


Microwave-Assisted Synthesis of a New Hydantoin Monomer for Antibacterial Polymeric Materials

Mauro Iannelli, Fabio Bergamelli,
Giancarlo Galli

Aust. J. Chem. **2009**, 62, 232–235.

The synthesis of polymers with advanced surface properties remains of interest in macromolecular chemistry. Microwave irradiation is used to synthesize an acrylic monomer with renewable biocidal activity. Copolymerization with a fluorinated acrylate is performed to obtain polymeric materials with both non-stick and antimicrobial properties. Biological tests confirm the efficiency of this approach showing high cellular mortality after short contact time.



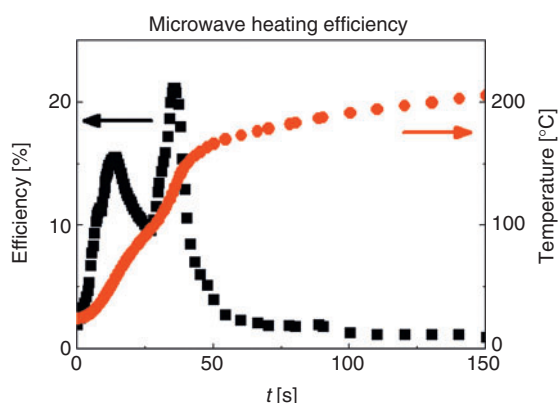
Full Papers

Microwave-Assisted Chemistry: a Closer Look at Heating Efficiency

Richard Hoogenboom,
Tom F. A. Wilms, Tina Erdmenger,
Ulrich S. Schubert

Aust. J. Chem. **2009**, 62, 236–243.

The use of microwave irradiation in organic and polymer chemistry is often claimed to be an efficient method. Here, we discuss the efficiency of microwave heating using various solvents, volumes and microwave reactors. It is demonstrated that microwave irradiation is not an efficient heating method, although microwave synthesis might be more efficient than conventional methods when higher yields and shorter reaction times can be achieved.



Can Molecular Sieves be Used as Water Scavengers in Microwave Chemistry?

Mostafa Baghbanzadeh,
C. Oliver Kappe

Aust. J. Chem. **2009**, 62, 244–249.

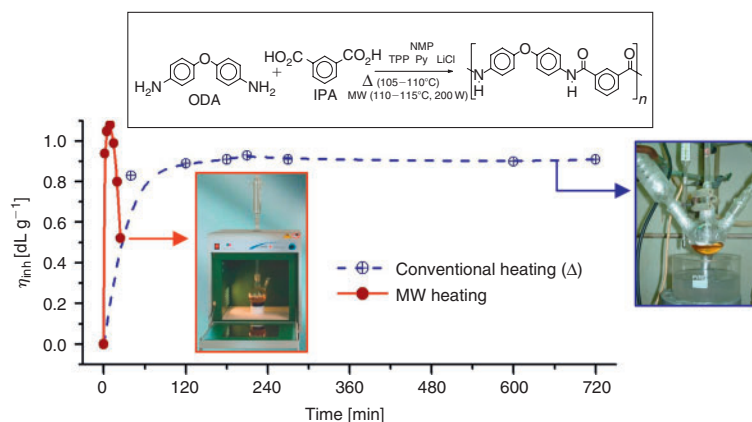
A question that surprisingly has not yet been addressed! Although scientists have used molecular sieves as water scavengers in microwave-assisted synthetic transformations for several years, the question if the sieves are really effective under these conditions has not been answered. Kinetic studies show that owing to the elevated temperatures generally experienced in microwave-heated transformations, molecular sieves are not effective as water scavengers and therefore should not be used.

Microwave-Induced Synthesis of Aromatic Polyamides by the Phosphorylation Reaction

Paula Carretero, Ricardo Sandin,
Regis Mercier, Angel E. Lozano,
Jose G. de la Campa,
Javier de Abajo

Aust. J. Chem. **2009**, 62, 250–253.

An improvement of the method to prepare aromatic polyamides is reported. Here they are synthesized directly from diacids by using the phosphorylation polycondensation, in some few minutes, by use of microwave irradiation. The experimental variables can be easily controlled to obtain high molecular weights, and there are additional advantages concerning energy saving.

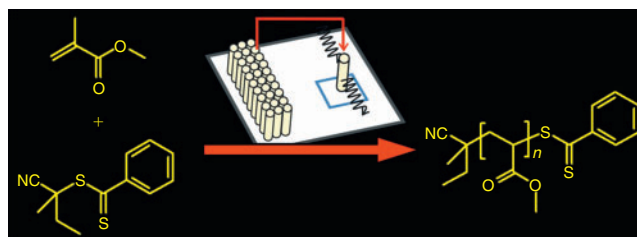


High Temperature Initiator-Free RAFT Polymerization of Methyl Methacrylate in a Microwave Reactor

Renzo M. Paulus, C. Remzi Becer,
Richard Hoogenboom,
Ulrich S. Schubert

Aust. J. Chem. **2009**, 62, 254–259.

Microwave irradiation can be used to safely explore high-temperature conditions that might accelerate organic and polymer synthesis. Here, we report high temperature reversible addition–fragmentation chain transfer (RAFT) polymerization of methyl methacrylate under microwave irradiation leading to an initiator-free controlled polymerization procedure. This simplified RAFT protocol might represent an important step to further widen the scope of RAFT polymerizations, for example towards industrial use.



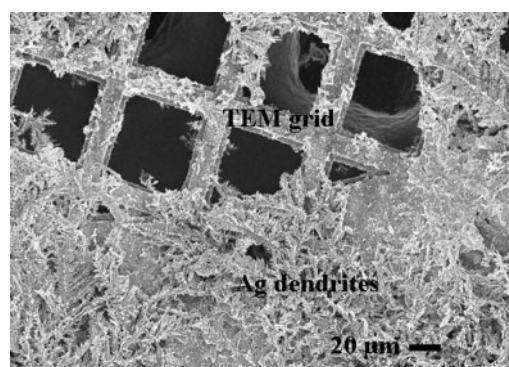
Short Communication

Silver Trees: Chemistry on a TEM Grid

Mallikarjuna N. Nadagouda,
Rajender S. Varma

Aust. J. Chem. **2009**, 62, 260–264.

Spectacular shining silver trees were generated spontaneously on the copper–carbon substrate of a transmission electron microscopy (TEM) grid without the need of any added capping or reducing agent. SEM (scanning electron microscopy) and TEM are routinely used techniques for characterization of nanomaterials. These results demonstrate a facile, aqueous, room-temperature green synthesis of a range of noble metal nano- and meso-structures that have widespread technological potential while at the same time underscoring the need for caution while interpreting TEM data in the absence of confirmatory SEM or other related imaging data.



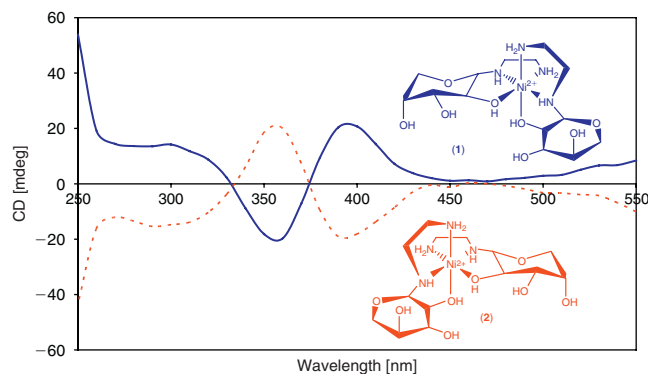
Full Papers

N-Glycoside Complexes of Nickel(II); Probing Carbohydrate–Transition Metal Interactions

Dale Jones, Marcelis van Holst,
Shigenobu Yano, Tomoaki Tanase,
Janice Aldrich-Wright

Aust. J. Chem. **2009**, 62, 265–268.

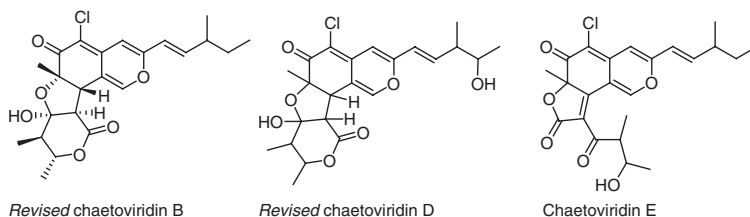
Nickel(II) complexes prepared from D- and L-arabinose (D-ara and L-ara) and 1,2-diaminoethane (en), $[\text{Ni}(\text{en-D-ara})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{en-L-ara})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ **2** (where en-D-ara is 1-((2-aminoethyl)amino)-1-deoxy-D-arabinose) were synthesized and characterized by absorption spectroscopy, circular dichroism, and X-ray crystallography.

**Identification of Chaetoviridin E from a Cultured Microfungus, *Chaetomium* sp. and Structural Reassignment of Chaetoviridins B and D**

Sally R. Kingsland,
Russell A. Barrow

Aust. J. Chem. **2009**, 62, 269–274.

The diverse natural product chemistry elicited from a laboratory cultured fungus, *Chaetomium* sp. is described. Compounds representing multiple biosynthetic pathways were determined, including the known compounds xanthoquinodin A1, cochliodinol, and aureonitol in addition to chaetoviridins. The description of a new compound, chaetoviridin E and the structure reassignment of chaetoviridins B and D is proposed.

**Interconversion of Nitrenes, Carbenes, and Nitrile Ylides by Ring Expansion, Ring Opening, Ring Contraction, and Ring Closure: 3-Quinolynitrene, 2-Quinoxalylcarbene, and 3-Quinolylcarbene**

David Kvaskoff, Ullrich Mitschke,
Chris Addicott, Justin Finnerty,
Pawel Bednarek, Curt Wentrup

Aust. J. Chem. **2009**, 62, 275–286.

3-Quinolynitrene, 4-quinazolylcarbene, and 3-quinolylcarbene were characterized by matrix electron spin resonance, UV, and IR spectroscopy. Matrix photolysis of 3-quinolynitrene causes ring opening to a nitrile ylide, which on further photolysis isomerizes to (2-isocyanophenyl)ketenimine, also obtained on photolysis of 4-quinazolylcarbene. Flash vacuum thermolysis (FVT) of both the nitrene and the carbene affords 3-cyanoindole in high yield, thereby indicating that 3-quinolynitrene and 4-quinazolylcarbene enter the same energy surface. 3-Quinolylcarbene reacts with N_2 and CO and cyclizes to 5-aza-2,3-benzobicyclo[4.1.0]hepta-2,4,7-triene on matrix photolysis, whereas FVT yields a mixture of 2- and 3-cyanoindenes via a carbene–carbene–nitrene rearrangement.

