

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

SPECIAL ISSUE: 30th Australasian Polymer Symposium

Essay

Vibrant Macromolecular Science at the 30th Australasian Polymer Symposium

Christopher Barner-Kowollik

Aust. J. Chem. **2009**, 62, 749–750.

The 30th Australasian Polymer Symposium was held in December of last year. The present special ‘polymer’ issue of the *Australian Journal of Chemistry* contains a compilation of papers from the keynote and invited speakers, showing the depth and vibrancy of the science presented at the meeting.

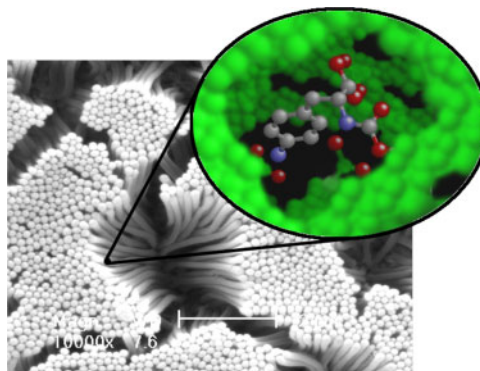
Reviews

Molecularly Imprinted Polymers and Controlled/Living Radical Polymerization

Marc Bompart, Karsten Haupt

Aust. J. Chem. **2009**, 62, 751–761.

Molecularly imprinted polymers are tailor-made biomimetic receptors obtained by polymerization with molecular templates. To solve general problems associated with these materials, in particular their morphological and binding site heterogeneity, controlled/living radical polymerization methods are increasingly used for their synthesis. This also facilitates their generation as nanomaterials, nanocomposites and thin films.



Polymer/Carbon Nanotube Composites

*Caroline McClory, Seow Jecg Chin,
Tony McNally*

Aust. J. Chem. **2009**, 62, 762–785.

The extraordinary electrical, mechanical, and thermal properties of carbon nanotubes (CNTs) make them ideal candidates as functional additives for polymers. This article reviews the synthesis, composite preparation, surface functionalization, characterization, and properties of polymer/CNT composites. Polymer/CNT composites will find widespread application in technologies as diverse as sensors, actuators, tissue engineering, drug delivery, and electromagnetic interference shielding.

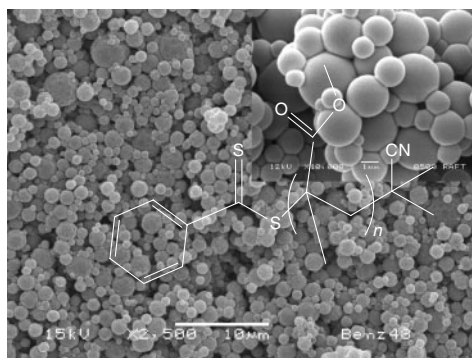
Highlight

**Controlled Dispersion
Polymerization in Supercritical
Carbon Dioxide**

Kristofer J. Thurecht,
Steven M. Howdle

Aust. J. Chem. **2009**, 62, 786–789.

This short report describes progress in heterogeneous polymerizations in supercritical carbon dioxide with a particular focus upon recent developments in the application of RAFT dispersion techniques to prepare microparticles of block copolymers using this novel solvent system.



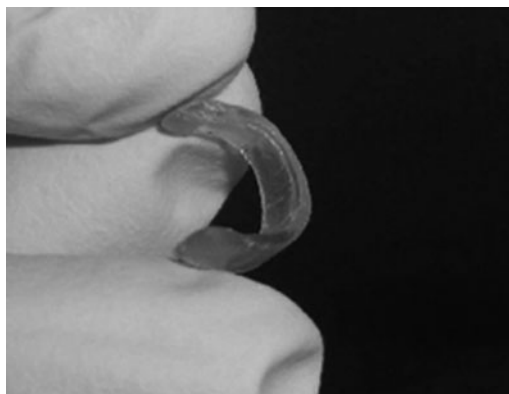
Rapid Communications

**Thermally Responsive Elastomeric
Supramolecular Polymers
Featuring Flexible Aliphatic
Hydrogen-Bonding End-Groups**

Philip Woodward, Daniel Hermida
Merino, Ian W. Hamley, Andrew T. Slark,
Wayne Hayes

Aust. J. Chem. **2009**, 62, 790–793.

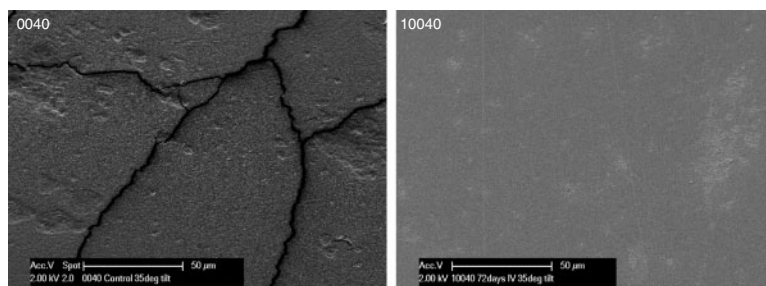
The present paper details the synthesis, characterization, and preliminary physical analyses of a series of polyisobutylene derivatives featuring urethane and urea end-groups that enable supramolecular network formation to occur via hydrogen bonding – these materials exhibit interesting thermoreversible and elastomeric properties.


**Polydimethylsiloxane-Based
Polyurethanes: Phase-Separated
Morphology and In Vitro
Oxidative Biostability**

Taeyi Choi, Jadwiga Weksler,
Ajay Padsalgikar, Rebeca Hernández,
James Runt

Aust. J. Chem. **2009**, 62, 794–798.

Three series of segmented polyurethane block copolymers were synthesized and investigated. Copolymers synthesized with the PDMS-based macrodiols consist of three microphases: a PDMS phase, hard domains, and a mixed phase of ethers and some dissolved hard segments. Degrees of phase separation were characterized, and the morphology was found to be closely related to the in vitro oxidative biostability.



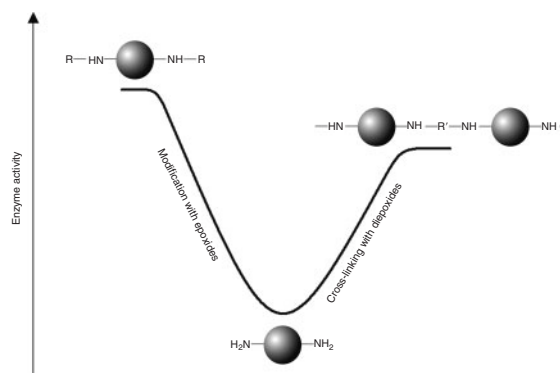
Full Papers

Over-Stabilization of Chemically Modified and Cross-Linked *Candida antarctica* Lipase B Using Various Epoxides and Diepoxides

Nemanja Miletić, Katja Loos

Aust. J. Chem. **2009**, 62, 799–805.

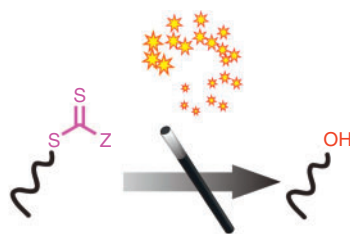
Natural enzymes have excellent features (activity, selectivity, specificity) that, however, can be rarely used as industrial catalysts owing to very fast denaturation in organic media. An important route to improve enzyme performance in non-natural environments is to modify or cross-link them with various reagents. Here, the authors report on the modification of *Candida antarctica* lipase B with various epoxides and its cross-linking with various diepoxides, resulting in an increase of enzyme activity and thermal stability.



A Novel One-Pot Procedure for the Fast and Efficient Conversion of RAFT Polymers into Hydroxy-Functional Polymers

Till Gruendling, Mathias Dietrich, Christopher Barner-Kowollik

Aust. J. Chem. **2009**, 62, 806–812.



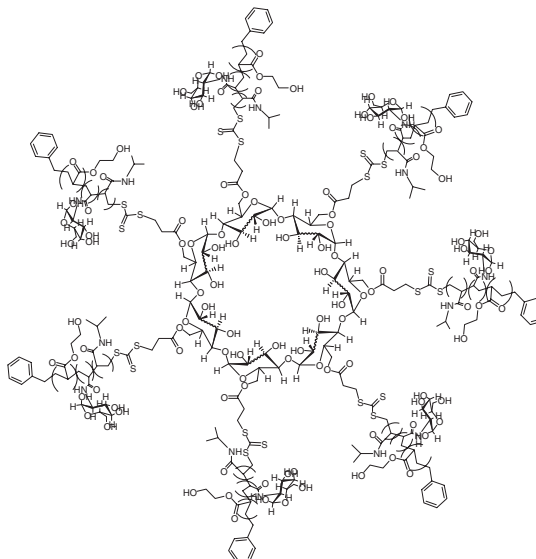
A novel straightforward and highly efficient method for the conversion of polymers capped by thiocarbonylthio groups, prepared by the RAFT process, into hydroxy-terminated polymers is reported. The new backbone-linked hydroxy group facilitates chemical end-group conversions and conjugation reactions with prepared RAFT polymers, and alleviates problems with the rather limited ability of the dithioester-end-group to undergo non-radical transformations.

Spherical Glycopolymers Architectures using RAFT: From Stars with a β -Cyclodextrin Core to Thermoresponsive Core-Shell Particles

Ling Zhang, Martina H. Stenzel

Aust. J. Chem. **2009**, 62, 813–822.

Seven-arm star glycopolymers with a β -cyclodextrin core have been successfully prepared using RAFT polymerization using the core-first technique. The arm-first technique was employed using block copolymer arms based on *N*-acryloyl glucose and poly(*N*-isopropyl acrylamide). The block copolymers were self-assembled into micelles followed by core-crosslinking with hexan-1,6-diol diacrylate to give unimolecular micelles with thermoresponsive properties.

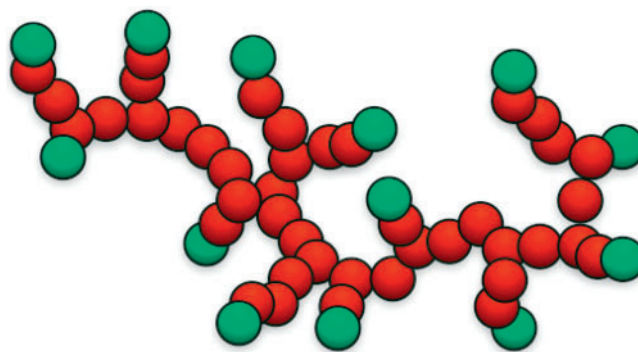


Where are the End-Groups in a Hyperbranched Polymer?

Dominik Konkolewicz

Aust. J. Chem. **2009**, 62, 823–829.

Hyperbranched polymers have potential applications such as drug delivery, and they have many end-groups that could be functionalized to give catalytic activity to the polymer. This paper considers the end-group location, and it shows that certain synthetic strategies lead to the majority of end-groups being at the surface of the polymer. This is important for applications such as those where the end-group is used to support a catalyst because having the majority of the end-groups at the surface should give fewer inaccessible end-groups and catalysts.

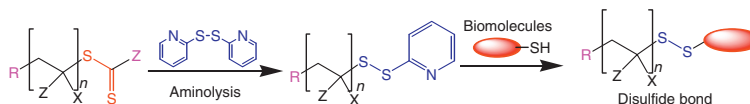


RAFT Polymer End-Group Modification and Chain Coupling/Conjugation Via Disulfide Bonds

Cyrille Boyer, Jingquan Liu,
Volga Bulmus, Thomas P. Davis

Aust. J. Chem. **2009**, 62, 830–847.

The conversion of trithiocarbonate or dithioester end-groups into a pyridyl disulfide (PDS) functionality by aminolysis in the presence of 2,2'-dithiodipyridine and simultaneous thiol specific reactions gives rise to the (bio) functionalization of a RAFT polymer. The generation of PDS functional polymers preserves the thiol reactivity for subsequent reaction with other thiol compounds, at room temperature, under mild conditions.

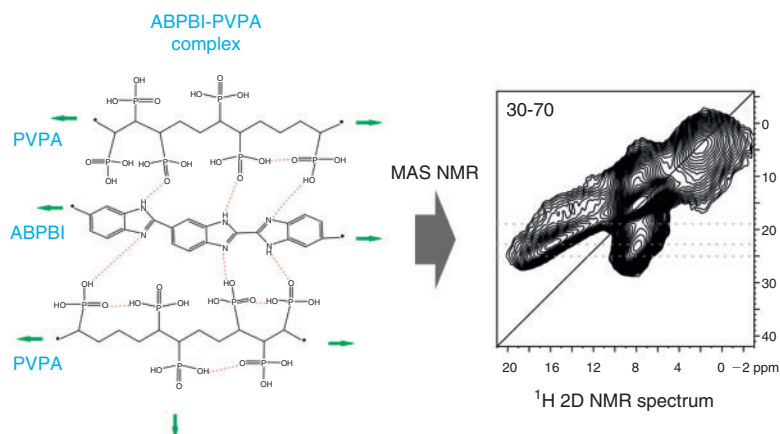


Anhydrous Poly(2,5-benzimidazole)–Poly(vinylphosphonic Acid) Acid–Base Polymer Blends: a Detailed Solid-State NMR Investigation

Ümit Akbey, Robert Graf, Peter
P. Chu, Hans Wolfgang Spiess

Aust. J. Chem. **2009**, 62, 848–856.

Complexes of acidic and basic polymers form complex hydrogen-bond networks, which can form the basis of proton-conducting materials. Advanced two-dimensional proton NMR spectroscopy can unravel the structure and dynamics of the hydrogen bonds. This information is crucial for the design of advanced materials for applications in fuel cells.

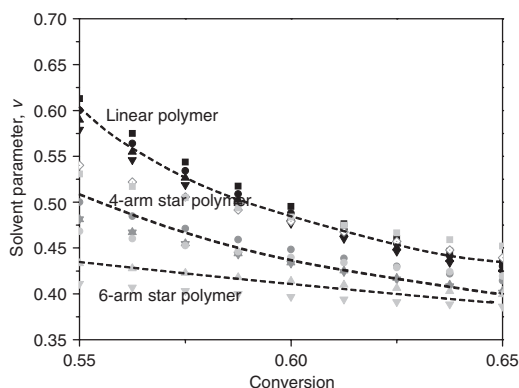


Termination in Semi-Dilute and Concentrated Polymer Solutions

Geoffrey Johnston-Hall,
Michael J. Monteiro

Aust. J. Chem. **2009**, 62, 857–864.

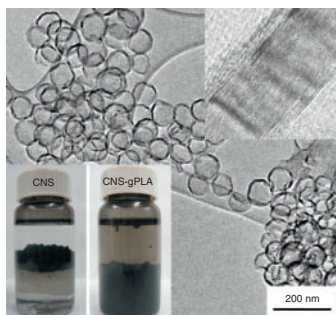
We have examined one of the oldest and arguably most difficult problems in radical polymerization kinetics, the physical mechanism controlling diffusion-controlled bimolecular termination in semi-dilute and concentrated polymer solutions. Therefore, in this study we have used the RAFT-CLD-T method to accurately evaluate the evolution of the conversion and chain length-dependent termination rate coefficient, $k_t^{i,i}(x)$, for linear polystyrene radicals in semi-dilute and concentrated solution regimes for solutions of linear, four-arm star and six-arm star polystyrene. For semi-dilute solutions, we found that theoretical predictions based on the blob model were in good agreement with the experimentally observed evolution of $k_t^{i,i}(x)$. In concentrated solutions, for chains larger than a critical chain length, i_c , chain entanglement was found to dominate termination and was increasingly significant in star polymer solutions.



Supramolecular BioNanocomposites: Grafting of Biobased Polylactide to Carbon Nanoparticle Surfaces

Margaret J. Sobkowicz,
John R. Dorgan, Keith W. Gneshin,
Andrew M. Herring, J. Thomas McKinnon

Aust. J. Chem. **2009**, 62, 865–870.



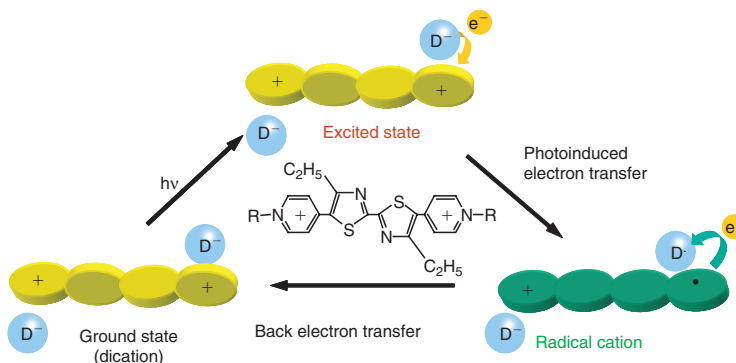
Polymer nanocomposites containing carbon nanostructures find many applications ranging from biomedical devices to optoelectronics and photovoltaics. Here, renewable biopolymer polylactide is grafted from the surfaces of two different carbon nanostructures. Successful functionalization enables tailoring of interactions between the nanoparticles and surrounding media.

Synthesis and Photophysical Properties of a Photoelectrochromic Polymer Containing the bis(2-(4-Pyridiniumyl)thiazole) Chromophore

Toshihiko Nagamura, Yasuhiro Sota

Aust. J. Chem. **2009**, 62, 871–876.

Tetraphenylborate salts of a newly synthesized polymer containing the chromophore bis(2-(4-pyridiniumyl)thiazole) showed absorption spectral changes in the visible to near-infrared region accompanying a colour change from yellow to green on steady photoirradiation. Steady or transient absorption changes were achieved due to a photoinduced electron-transfer reaction between bis(2-(4-pyridiniumyl)thiazole) and counter anions.

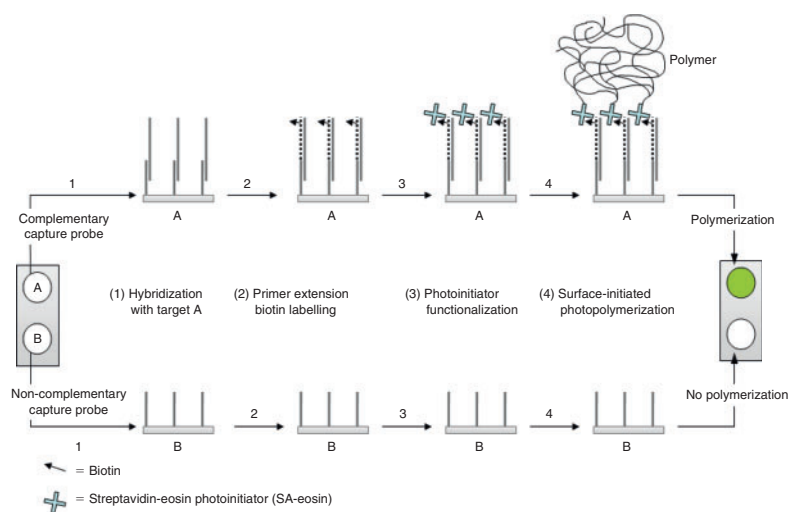


Characterization of the Assaying Methods in Polymerization-Based Amplification of Surface Biomarkers

Leah M. Johnson, Heather J. Avens,
Ryan R. Hansen, Holly L. Sewell,
Christopher N. Bowman

Aust. J. Chem. **2009**, 62, 877–884.

Polymerization-based amplification (PBA) provides visual, sensitive, and cost-effective detection of biological interactions by combining radical chain polymerization with surface bio-recognition events. PBA was employed to characterize the dynamic polymer film heights on microarrays that result from DNA hybridization of *KRAS* proto-oncogene biomarkers with 20 nm films at the 500 pM DNA detection limit.

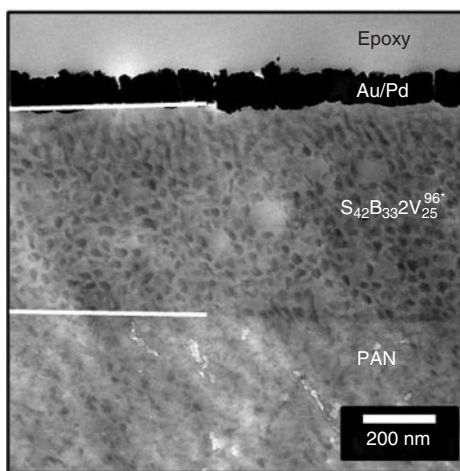


New Insights into the Control of Self-Assembly of Block Copolymer Membranes

Daniel Fierro, Kristian Buhr,
Clarissa Abetz, Adriana Boschetti-
de-Fierro, Volker Abetz

Aust. J. Chem. **2009**, 62, 885–890.

The morphological properties of a 3-miktoarm star terpolymer on a support layer are reported. Different orientations of the microdomains can be obtained by directly casting the star terpolymer solution on the support, depending on the prior treatment of the support layer and the casting conditions.

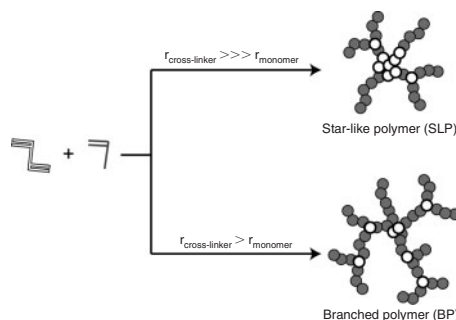


PMMA Star-Like Polymers via One-Pot Conventional Free-Radical Copolymerization

Tor Kit Goh, Anton Blencowe,
Jing Fung Tan, Kristopher D. Coventry,
Feng Qian, Tatchkul Tachasirinugune,
Greg G. Qiao

Aust. J. Chem. **2009**, 62, 891–898.

Star polymers are architecturally unique macromolecules and are interesting candidates for a variety of commercial applications. Simplification of the synthetic strategy is therefore highly desirable. A one-pot conventional free-radical copolymerization strategy for poly(methyl methacrylate) (PMMA) star-like copolymers is presented; formulation domain diagrams, the polymer formation mechanism and rheological behavior were established.



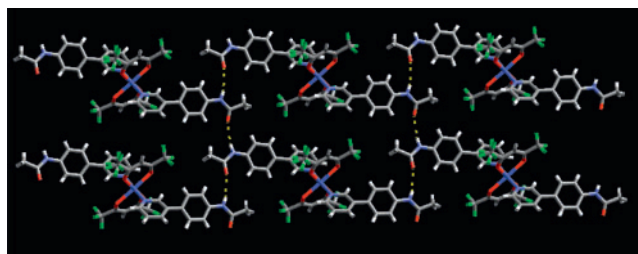
Full Papers

Versatile Ligands for the Construction of Layered Metal-Containing Networks

Christer B. Aakeröy, Izhar Hussain,
Safiyah Forbes, John Desper

Aust. J. Chem. **2009**, 62, 899–908.

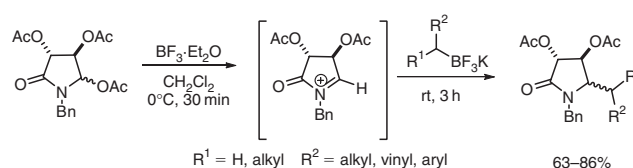
The strength and directionality of hydrogen bonds can offer supramolecular pathways towards the directed assembly of metal-containing networks of precise metrics and topology. The acetamido moiety is shown to be robust enough to organize relatively large complex metal ions into extended networks using self-complementary N–H···O=C hydrogen bonds and these synthons may also be utilized for the construction of 3-D architectures with accessible cavities with controllable size and shape.

Stereoselective Nucleophilic Addition of Potassium Alkyltrifluoroborates to Cyclic *N*-Acyliminium Ions: a Simple and Mild Approach to Chiral 5-Alkyl-pyrrolidin-2-ones

Adriano S. Vieira, Fernando
P. Ferreira, Alexandre S. Guarezemini,
Helio A. Stefani

Aust. J. Chem. **2009**, 62, 909–916.

Functionalized *N*-heterocycles are efficiently formed by the reaction of potassium alkyltrifluoroborates with *N*-acyliminium ion precursors that have been activated by Lewis acid promoters. The steric bulk of the nucleophile is found to affect the diastereoselectivity of the products. Such a method may be useful for the synthesis of indolizidine ring systems important to many useful alkaloids.

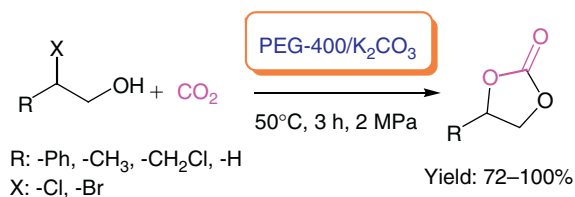


Poly(ethylene glycol): an Alternative Solvent for the Synthesis of Cyclic Carbonate from Vicinal Halohydrin and Carbon Dioxide

Jing-Lun Wang, Liang-Nian He,
Xiao-Yong Dou, Fang Wu

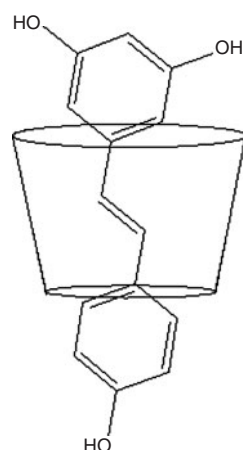
Aust. J. Chem. **2009**, 62, 917–920.

Poly(ethylene glycol) proved to be an efficient reaction medium for the reaction of vicinal halohydrins with CO₂ to synthesize cyclic carbonates. This process may have potential application in the industrial production of cyclic carbonates because of its simplicity, cost benefits, readily available starting materials, and mild reaction conditions.

UV Light Stability of α -Cyclodextrin/Resveratrol Host–Guest Complexes and Isomer Stability at Varying pH

Kerrilee E. Allan, Claire E. Lenehan,
Amanda V. Ellis

Aust. J. Chem. **2009**, 62, 921–926.



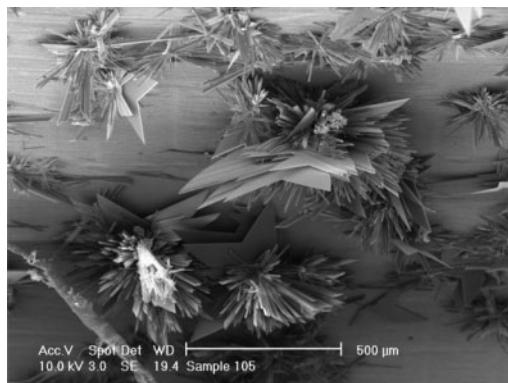
Found predominantly in grape skin, *trans*-resveratrol is believed to be a bioactive material with major health benefits. *trans*-Resveratrol is highly unstable in UV light and isomerizes to the *cis* form. The formation of a *trans*-resveratrol/ α -CD IC in pH 8.0 phosphate-borate-SDS buffer greatly enhances its UV stability.

Effects of Organic Additives on Calcium Sulfate Scaling in Pipes

Tung A. Hoang, H. Ming Ang,
Andrew L. Rohl

Aust. J. Chem. **2009**, 62, 927–933.

Small amounts of inorganic or organic compounds can have dramatic effects on crystal growth and morphology. The influence of nine carboxylic and phosphonic additives on the formation of calcium sulfate scale is investigated. The chemical structure, and not the complexation ability, appears to be more important in blocking the active sites on the crystal surface.

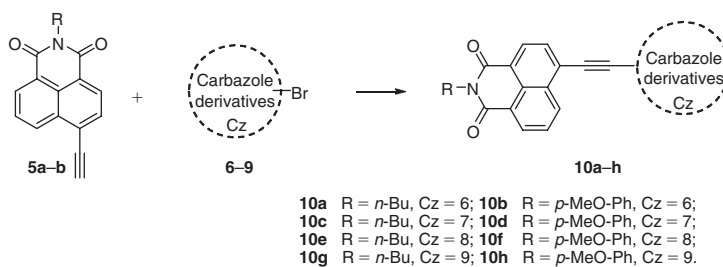


Synthesis and Properties of Novel ‘Ethyne-Linked’ Compounds Containing Carbazole and 1,8-Naphthalimide Groups

Yu Liu, Hai-Ying Wang, Gang Chen,
Xiao-Ping Xu, Shun-Jun Ji

Aust. J. Chem. **2009**, 62, 934–940.

A series of novel ‘ethyne-linked’ compounds containing carbazole and 1,8-naphthalimide groups have been synthesized by Pd/Cu-catalyzed Sonogashira reaction. As we expected, the results indicated that these compounds could improve the charge-transport ability and fluorescent quantum yield by introducing the electron-transporting emitting moieties naphthalimide and alkyne-group to carbazole moieties.

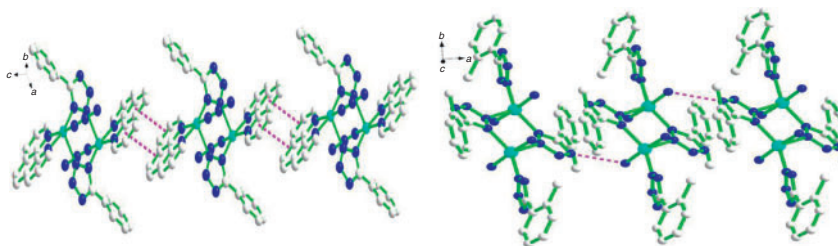


Two Dinuclear Cu^{II}–Tetrazolate Complexes: Syntheses, Structures, and Magnetic Properties

Wei-Chao Song, Jian-Rong Li,
E. Carolina Sañudo, Jia Liu,
Xian-He Bu

Aust. J. Chem. **2009**, 62, 941–946.

Two tetrazolyl bridged dinuclear Cu^{II} complexes, [Cu(L¹)(N₃)(phen)]₂ (**1**) and [Cu(L²)₂(NH₃)₂]₂ (**2**), have been synthesized and characterized. Variable temperature magnetic susceptibility data indicate a weak ferromagnetic coupling between the Cu^{II} ions in **1** and weak antiferromagnetic coupling between the Cu^{II} ions in **2**, possibly owing to the different coordination geometries of the Cu^{II} ions in the two complexes.



Corrigendum

Synthesis of Epoxides Catalyzed by a Halide-Free Reaction-Controlled Phase-Transfer Catalytic System: [(CH₃(CH₂)₁₇)₂N(CH₃)₂]₃[PW₄O₃₂]/H₂O₂/Dioxan/Olefin

Yong Ding, Baochun Ma, Dejie Tong,
Hui Han, Wei Zhao

Aust. J. Chem. **2009**, 62, 947.