# AUSTRALIAN JOURNAL OF CHEMICAL SCIENCE

# SPECIAL ISSUE: Polymer Chemistry - From Fundamentals to Applications

#### Foreword

From Fundamentals to Applications: Living Polymer Science at the 29th Australasian Polymer Symposium

Christopher Barner-Kowollik

Aust. J. Chem. 2007, 60, 697-698.

#### Reviews

## Recent Advances in Star Polymer Design: Degradability and the Potential for Drug Delivery

James T. Wiltshire, Greg G. Qiao

Aust. J. Chem. 2007, 60, 699-705.



The 29th Australasian Polymer Symposium was held in February 2007 in Hobart. The current special issue of the *Australian Journal of Chemistry* is a compilation of contributions from selected keynote lectures.

class of material, particularly in the areas of degradability and functionalization, are highlighted with a focus on their potential application in the biomedical field as drug delivery devices.  $(\bigcap_{ROP} \bigcap_{n} O ) \longrightarrow_{ROP} O \longrightarrow_{Hydrolysis} Monomer$ 

macromolecule because of their unique three-dimensional architecture and

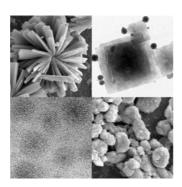
subsequent properties. Several recent developments in the synthesis of this

Core cross-linked star polymers represent an interesting class of

# Self-Association and Crystallization of Amylose

Alain Buléon, Gabrielle Véronèse, Jean-Luc Putaux

Aust. J. Chem. 2007, 60, 706-718.



Starch is the main source of calories in diets and a major source of plant material for non-food purposes. Crystalline assemblies formed in vitro by self-association of amylose, the linear  $\alpha$ -glucan of starch, are described. Knowledge of the structure and physical behaviour of the products is important to optimize their properties and to understand starch biosynthesis.

# Electrospinning of Nanofibres: Towards New Techniques, Functions, and Applications

Roland Dersch, Martin Graeser, Andreas Greiner, Joachim H. Wendorff

Aust. J. Chem. 2007, 60, 719–728.



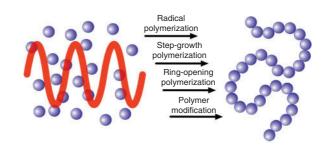
Nanofibres with diameters down to a few nanometer can be produced from synthetic and natural polymers, metals, and ceramics by electrospinning. Modification of the electrospinning process yields nanofibres with complex architectures and specific functions. These offer applications in textiles, filters, microelectronics, sensors, and catalysis, but also in tissue engineering, wound healing, or drug delivery.

#### Recent Advances in Microwave-Assisted Polymer Synthesis

Sebastian Sinnwell, Helmut Ritter

Aust. J. Chem. 2007, 60, 729–743.

The use of microwave irradiation has become a well established method in polymer synthesis. The advantages, which include a strong reduction in reaction time, and greener and sustainable chemistry, have facilitated improvements in reaction processing for nearly all types of polymerization reactions. This review summarizes the recent developments in this field with special emphasis on radical, step-growth, and ring-opening polymerizations, and polymer modifications.



#### **Full Papers**

Radical Ring-Opening Polymerization of Phosphorus Heterocycles: Computational Design of Suitable Phosphetane Monomers

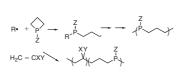
Michelle L. Coote, Jennifer L. Hodgson, Elizabeth H. Krenske, Mansoor Namazian, S. Bruce Wild

Aust. J. Chem. 2007, 60, 744-753.

#### Further Effects of Chain-Length-Dependent Reactivities on Radical Polymerization Kinetics

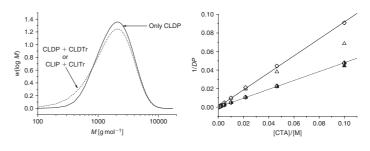
Johan P. A. Heuts, Gregory T. Russell, Gregory B. Smith

Aust. J. Chem. 2007, 60, 754–764.



Radical ring opening polymerization of phosphetanes is a new computationally designed route to polyphosphines. Highlevel *ab initio* calculations have been used to identify monomers with suitable reactivities for copolymerization with alkenes, and to illustrate stereocontrol with chiral monomers. The results should allow the incorporation of phosphorus atoms into the backbones of polyalkenes to improve polarity or metal ion binding characteristics.

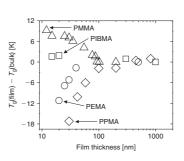
The chain-length dependence of individual rate coefficients in radical polymerization has been ignored for many decades, but in particular with the increasing interest in the synthesis of shorter polymers, this simplification is often not applicable anymore. In the current paper, we investigate further the effects of chain-length-dependent termination, propagation and transfer rate coefficients on the observed kinetics and resulting molecular weight distribution, and especially in the case of chain-length-dependent chain transfer, we uncover some striking and unexpected effects. Experimental confirmation of the ventured predictions now awaits.



# Effects of Nanoscale Confinement and Interfaces on the Glass Transition Temperatures of a Series of Poly(n-methacrylate) Films

Rodney D. Priestley, Manish K. Mundra, Nina J. Barnett, Linda J. Broadbelt, John M. Torkelson

Aust. J. Chem. 2007, 60, 765-771.



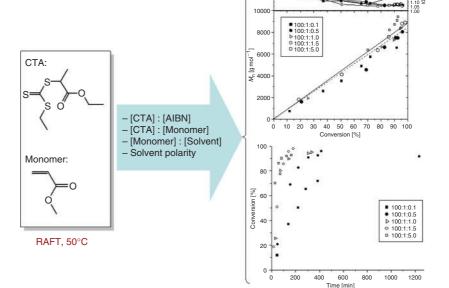
With nanoscale confinement, the glass transition temperature of polymer films can deviate substantially from the bulk behaviour. We show how slight variations to the side groups of poly(n-methacrylate) films supported on silica can greatly impact the effect of nanoscale confinement on the glass transition temperature. In addition, using a unique fluorescence/multilayer technique, we show that interfacial effects are responsible for the observed deviations of the glass transition temperature with confinement.

#### Investigation of the Experimental Factors Affecting the Trithiocarbonate-Mediated RAFT Polymerization of Methyl Acrylate

Murray R. Wood, David J. Duncalf, Paul Findlay, Steven P. Rannard, Sébastien Perrier

Aust. J. Chem. 2007, 60, 772-778.

This study investigates the effect of experimental parameters on the RAFT polymerization of methyl acrylate. This work aims to provide non-experts with optimal reaction conditions for the RAFT polymerization of acrylate derivatives.



## Chain-Length-Dependent Termination in Acrylate Radical Polymerization Studied via Pulsed-Laser-Initiated RAFT Polymerization

Michael Buback, Pascal Hesse, Thomas Junkers, Thomas Theis, Philipp Vana

Aust. J. Chem. 2007, 60, 779–787.

#### The Use of Novel F-RAFT Agents in High Temperature and High Pressure Ethene Polymerization: Can Control be Achieved?

Markus Busch, Marion Roth, Martina H. Stenzel, Thomas P. Davis, Christopher Barner-Kowollik

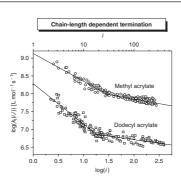
Aust. J. Chem. 2007, 60, 788-793.

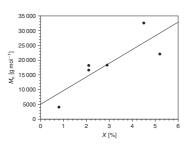
#### Focus

#### **Flexible Honeycomb Films**

Luke A. Connal

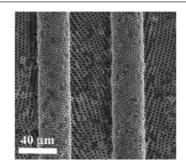
Aust. J. Chem. 2007, 60, 794.





Chain length dependent termination rate coefficients,  $k_t(i,i)$ , for methyl acrylate and dodecyl acrylate were determined using the single pulse pulsed-laser polymerization near-infrared reversible additionfragmentation chain transfer (SP-PLP-NIR-RAFT) technique. *Composite model* behaviour was verified for both monomers. The parameters describing the chain-length dependence of  $k_t$  were found to be governed by chain flexibility.

RAFT polymerization plays a major role in macromolecular science. However, never before has this polymerization technique been applied to test its applicability towards high pressure ethene polymerizations. The current work elucidates first experiments in this field, demonstrating that some degree of control may indeed be achieved.



Recent developments utilizing the breath figure (BF) technique are highlighted. Porous, honeycomb-like films have been successfully coated onto a range of nonplanar substrates, for example, transmission electron microscopy grids (as shown), particulate surfaces, and extremely rough metallic surfaces. These advances significantly broaden the scope of the BF technique.