

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

RESEARCH FRONT: RAFT Chemistry

Forewords

RAFT Polymerization: Materials of The Future, Science of Today: Radical Polymerization – The Next Stage

Graeme Moad, San H. Thang

Aust. J. Chem. **2009**, *62*, 1379–1381.



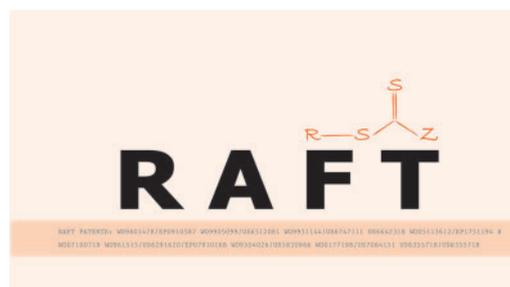
This Research Front explores recent developments in radical polymerization and its application. A particular focus is radical polymerization with reversible–addition fragmentation chain transfer (RAFT). This issue also celebrates the 65th birthday and record of scientific achievement of Dr Ezio Rizzardo (CSIRO Molecular and Health Technologies), a pioneer of reversible deactivation radical polymerization and one of the inventors of the RAFT process.

The RAFT Alliance, a Global Community Promoting Innovation

Kate Dawson

Aust. J. Chem. **2009**, *62*, 1382–1383.

Companies that network with other organizations, including research institutions and their customers, have been shown to have greater success in process and product innovation. The RAFT Alliance has been established specifically to foster knowledge transfer and accelerated learning in the RAFT polymerization technology. This paper discusses the RAFT Alliance and how it can benefit those seeking to innovate and develop networks around this novel technology.

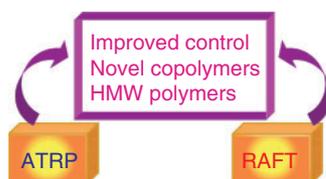


Reviews

Synergistic Interaction Between ATRP and RAFT: Taking the Best of Each World

Yungwan Kwak, Renaud Nicolaj, Krzysztof Matyjaszewski

Aust. J. Chem. **2009**, *62*, 1384–1401.



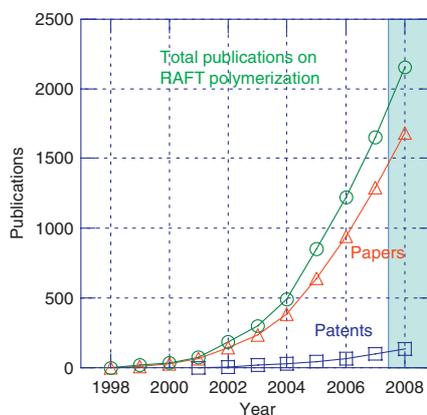
This review covers recent developments on the combination of ATRP and RAFT polymerization to prepare well-defined homo-, block, and high molecular weight (co)polymers, that otherwise could not be prepared directly. The relative reactivity of the R group is discussed, amongst other factors. A one-step chain transfer agent synthesis by ATRP is also discussed.

Living Radical Polymerization by the RAFT Process – A Second Update

Graeme Moad, Ezio Rizzardo,
San H. Thang

Aust. J. Chem. **2009**, *62*, 1402–1472.

This review of RAFT polymerization cites >500 papers that appeared during the period 2006–2009 and covers reagent synthesis and properties, polymerization kinetics and mechanism, polymer syntheses and a diverse range of applications. Significant developments have occurred with respect to RAFT agents, end-group transformation, micro/nanoparticles and modified surfaces, and biopolymer conjugates.

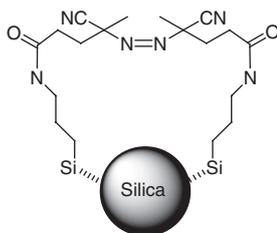


Communications

A Bipedal Silica-Immobilized Azo-Initiator for Surface-Confined Radical Polymerizations

Robert Rotzoll, Philipp Vana

Aust. J. Chem. **2009**, *62*, 1473–1478.



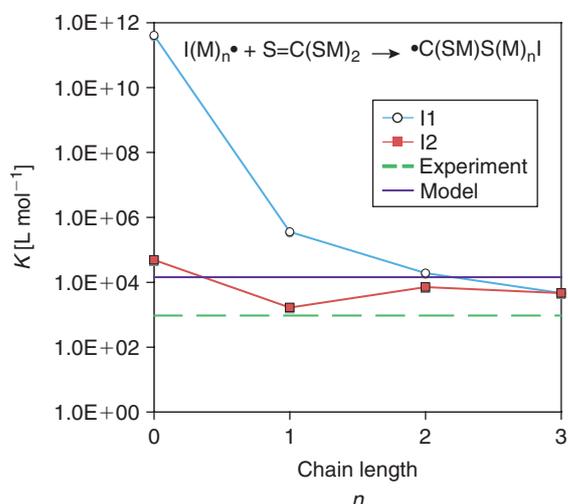
A novel doubly anchored silica-immobilized azo-initiator (ACTA) for the surface-initiated radical polymerization is explored on the example of methyl acrylate (MA) polymerization. While the sole use of ACTA produced grafted pMA of high molecular weight, the polymerization in combination with two different doubly-fixed RAFT agents exhibited well-controlled formation of polymer loops.

How Well Can Theory Predict Addition–Fragmentation Equilibrium Constants in RAFT Polymerization?

Ching Yeh Lin, Michelle L. Coote

Aust. J. Chem. **2009**, *62*, 1479–1483.

Computational quantum chemistry is used to study the addition–fragmentation equilibrium of S-S'-bis(methyl-2-propionate)-trithiocarbonate mediated polymerization of methyl acrylate in toluene at -30°C . The results, which show strong solvent and chain length effects, are in good order of magnitude agreement with recent experimental results for a closely related system.

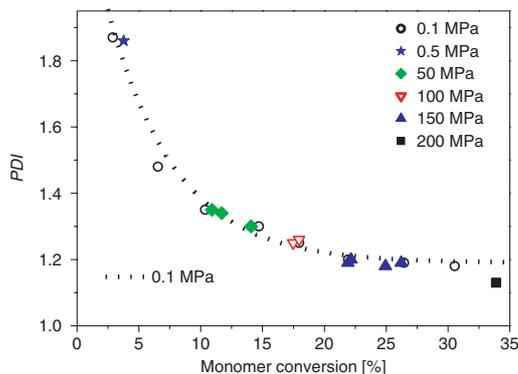


Mechanism of CPDB-Mediated RAFT Polymerization of Methyl Methacrylate: Influence of Pressure and RAFT Agent Concentration

Michael Buback, Wibke Meiser,
Philipp Vana

Aust. J. Chem. **2009**, *62*, 1484–1487.

RAFT polymerizations of methyl methacrylate in bulk at 60°C were performed up to 200 MPa using 2-(2'-cyanopropyl)dithiobenzoate as the RAFT agent. High pressure increases the rate of the well controlled polymerizations, but has no effect on polydispersity. The observed slight retardation is adequately

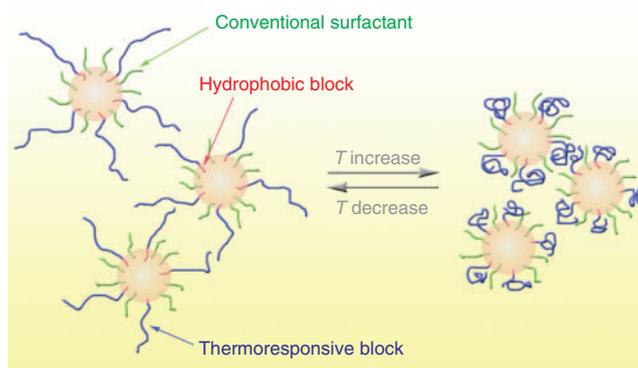


MADIX Thermoresponsive Amphiphilic Block Copolymers as Stimulable Emulsion Stabilizers

Mathias Destarac, Aurélie Papon,
Eric Van Gramberen,
Katerina Karagianni

Aust. J. Chem. **2009**, *62*, 1488–1491.

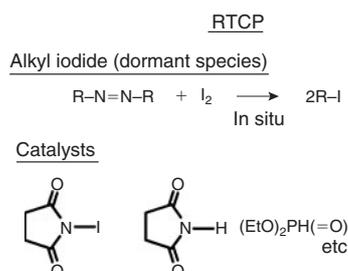
A series of MADIX-derived amphiphilic block copolymers exhibiting lower critical solution temperature behaviour was synthesized and evaluated as silicone oil-in-water emulsion co-stabilizers. It was shown that the cloud point of the block copolymer is mainly controlled by the chemical composition of the *N*-isopropylacrylamide-based hydrophilic block.



Reversible Chain Transfer Catalyzed Polymerization of Methyl Methacrylate with In-Situ Formed Alkyl Iodide Initiator

Atsushi Goto, Koji Nagasawa,
Ayaka Shinjo, Yoshinobu Tsujii,
Takeshi Fukuda

Aust. J. Chem. **2009**, *62*, 1492–1495.



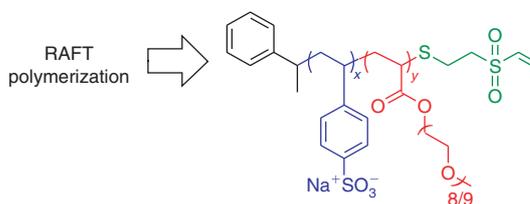
The alkyl iodide in situ formed in the polymerization was successfully used as a low-mass dormant species in the reversible chain transfer catalyzed polymerizations (RTCPs) (living radical polymerizations) with several nitrogen and phosphorus catalysts. This method is robust and would enhance the utility of RTCP.

Synthesis of Michael Acceptor Ionomers of Poly(4-Sulfonated Styrene-co-Poly(ethylene Glycol) Methyl Ether Acrylate)

Steevens N. S. Alconcel, Gregory N.
Grover, Nicholas M. Matsumoto,
Heather D. Maynard

Aust. J. Chem. **2009**, *62*, 1496–1500.

Ionomers containing sodium 4-styrene sulfonate and poly(ethylene glycol) methyl ether acrylate were synthesized by RAFT polymerization in aqueous solution. The chain ends of the resulting well-defined polymers were transformed to the Michael acceptor vinyl sulfone moiety.



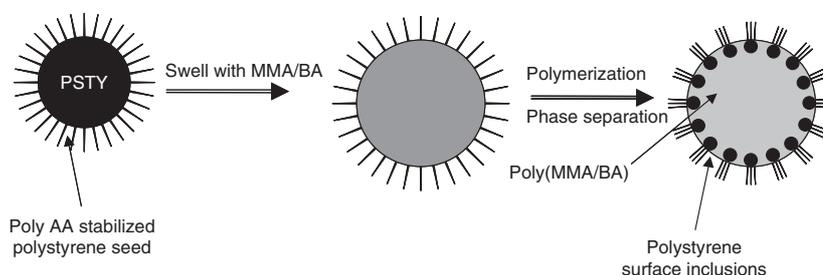
Highlight

Control of Particle Morphology in *Ab Initio* RAFT Mediated Emulsion Polymerization

Ewan Sprong, Hank De Bruyn,
Christopher H. Such,
Brian S. Hawkett

Aust. J. Chem. **2009**, *62*, 1501–1506.

An interesting property of RAFT-controlled emulsion polymerization is that nearly every polymer molecule has, within statistical limits, the same structure and size. In this paper some examples are presented of how this property can be utilized to control particle morphologies.



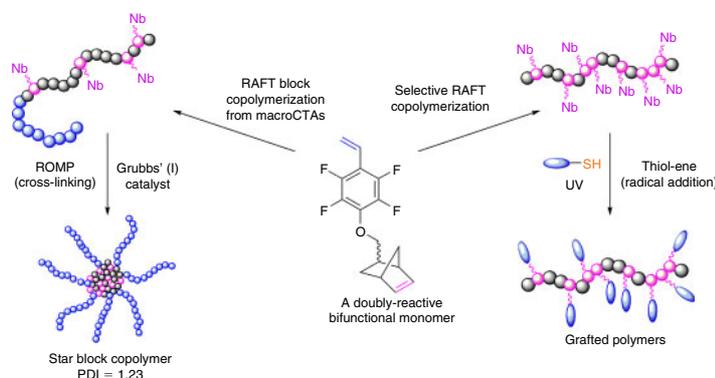
Full Papers

The Power of RAFT for Creating Polymers Having Imbedded Side-Chain Functionalities: Norbornenyl-Functionalized Polymers and their Transformations via ROMP and Thiol-ene Reactions

Jun Ma, Chong Cheng,
Karen L. Wooley

Aust. J. Chem. **2009**, *62*, 1507–1519.

RAFT-based radical polymerization is a powerful tool for the synthesis of well-defined polymers containing imbedded side-chain functionalities. These functional polymers bearing pendant reactive groups have great potential to perform robust, efficient and orthogonal chemistries, which are becoming increasingly important for the construction of sophisticated materials. This paper demonstrates selective RAFT copolymerization of a doubly-reactive bifunctional monomer and the preparation of norbornenyl-functionalized statistical and block copolymers, which were then shown to undergo two different orthogonal types of chemical reactions to afford discrete nanoscale objects and functional derivative structures.

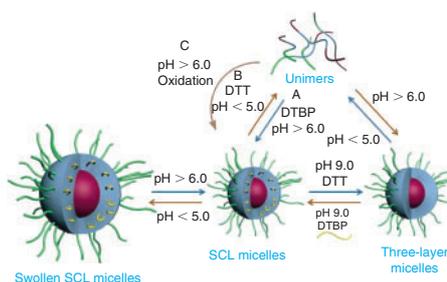


Facile 'One-Pot' Preparation of Reversible, Disulfide-Containing Shell Cross-Linked Micelles from a RAFT-Synthesized, pH-Responsive Triblock Copolymer in Water at Room Temperature

Xuwei Xu, Adam E. Smith,
Charles L. McCormick

Aust. J. Chem. **2009**, *62*, 1520–1527.

Reversible, disulfide-containing, shell cross-linked micelles were prepared using a 'one-pot' method, in which a dithiopropionimide was reacted with primary amine groups of amphiphilic triblock copolymers in their assembled form above pH 6.0. The pH-responsive triblocks were prepared by facile aqueous RAFT polymerization directly in water at 70°C without resorting to protecting group chemistry. The shell cross-linked micelles, which are readily cleaved under reducing conditions, have potential in nanomedicine as carriers for pharmaceutical and diagnostic agents.

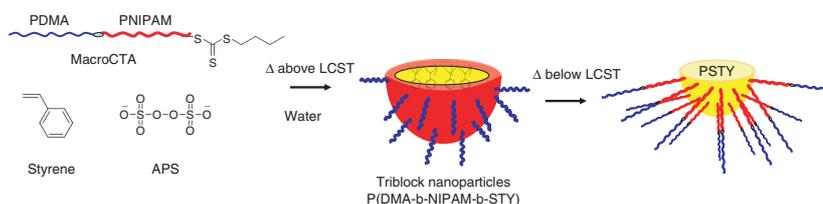


RAFT-Mediated Emulsion Polymerization of Styrene in Water using a Reactive Polymer Nanoreactor

Carl N. Urbani, Michael J. Monteiro

Aust. J. Chem. **2009**, *62*, 1528–1532.

We have demonstrated a nanoreactor methodology to produce polystyrene with narrow molecular weight distributions and control over the final particle size distributions. Our reactive thermoresponsive diblock copolymer nanoreactor is an ideal setting to carry out otherwise difficult RAFT-mediated polymerizations, resulting in surfactant-free nanoparticles that can be tuned to size and MWD.

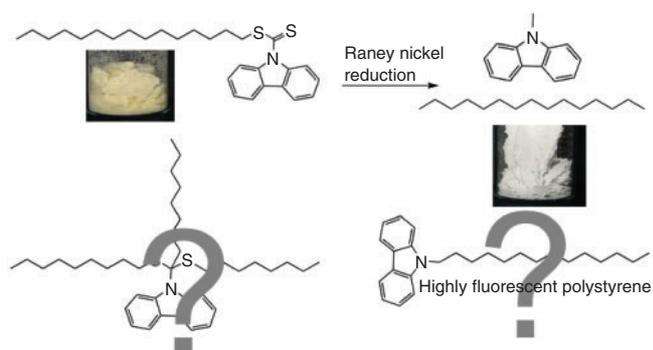


Searching for Stars: Selective Desulfurization and Fluorescence Spectroscopy as New Tools in the Search for Cross Termination Side-products in RAFT Polymerization

Steven L. Brown, Dominik Konkolewicz, Angus Gray-Weale, William B. Motherwell, Sébastien Perrier

Aust. J. Chem. **2009**, *62*, 1533–1536.

Fluorescent spectroscopy was used to determine the occurrence of termination reaction between propagating radicals and intermediate radicals in RAFT polymerization. Results suggest that if termination occurs, they only involve short propagating polymeric chains.



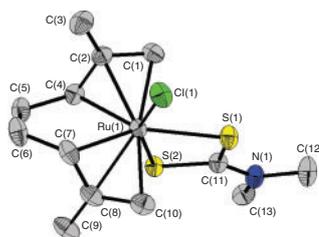
REGULAR PAPERS

Full Papers

Bis(allyl)ruthenium(IV)-initiated S–S and C–S Bond Cleavages in Tetraalkylthiuram Sulfides. Formation and X-ray Crystal Structures of Dithiocarbamate Complexes

Chang Xu, Sumod A. Pullarkat, Lai Yoong Goh

Aust. J. Chem. **2009**, *62*, 1537–1543.

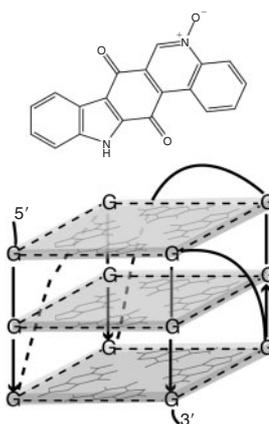


The reaction of $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ with tetraalkylthiuram disulfides $[(\text{R}_2\text{NC}(\text{S})\text{S})_2]$, ($\text{R} = \text{Me}, \text{Pr}$) and monosulfide $[\text{Me}_2\text{NC}(\text{S})_2\text{S}]$ led to the formation of orange solids of $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\eta^2\text{-S}_2\text{CNR}_2)\text{Cl}]$ in high yields. Reaction of the same complex with KPF_6 and monosulfide $[\text{Me}_2\text{NC}(\text{S})_2\text{S}]$ resulted in $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CH}_3\text{CN})](\text{PF}_6)$.

Exploring the Binding of Calothrixin A to the G-Quadruplex from the *c-myc* Oncogene Promotor

Elisabeth A. Owen, Max A. Keniry

Aust. J. Chem. **2009**, *62*, 1544–1549.

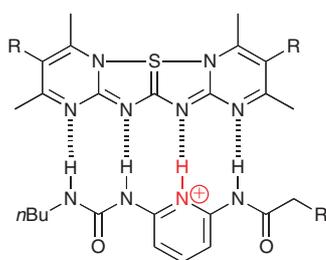


Calothrixin A, a bioactive metabolite from cyanobacteria with anti-cancer activity, has been shown to bind to the DNA quadruplex-forming sequence from the *c-myc* promotor. Quadruplex formation in promoters has been linked to the regulation of gene expression. This work provides a new direction in which to explore the bioactivity of calothrixin A.

The AAAA·DDDD Hydrogen Bond Dimer. Synthesis of a Soluble Sulfurane as AAAA Domain and Generation of a DDDD Counterpart

Jörg Taubitz, Ulrich Lüning

Aust. J. Chem. **2009**, *62*, 1550–1555.

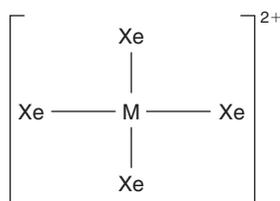


Molecular recognition by multiple hydrogen bonds, as in DNA, can be extended to four hydrogen bonds that consist of donors (D) and acceptors (A). The new pair AAAA·DDDD has been made accessible by protonation of a DDAD hydrogen bonding domain to give a DDDD partner for the AAAA receptor and the heterodimer complex formation investigated.

Theoretical Investigation of Square-Planar MXe_4^{2+} ($M = Cu, Ag, Au$) Cations

PingXia Zhang, YongFang Zhao,
XiuDan Song, GuoHua Zhang,
Yang Wang

Aust. J. Chem. **2009**, *62*, 1556–1560.



Compounds containing noble gas atoms and high-oxidation-state noble metal ions have received a great deal of attention in experiments and theories. Here, we carry out investigations on the square-planar doubly charged MXe_4^{2+} ($M = Cu, Ag, Au$) cations by using molecular orbital methods. It is found that xenon atoms can interact directly with divalent noble metal ions, namely Cu^{2+} , Ag^{2+} , and Au^{2+} , but the square-planar structure is only suitable for Ag^{2+} and Au^{2+} .



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