

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

RESEARCH FRONT: RAFT Polymerization

Foreword

The Emergence of RAFT Polymerization

Graeme Moad

Aust. J. Chem. **2006**, *59*, 661–662.

Radical polymerization has, in under a decade, emerged to become the foremost tool to create complex yet well-defined macromolecules. This issue's Research Front explores the RAFT process, ranging over studies of its mechanism and a view towards future applications and advances.

Reviews

The Genesis of the Reversible Radical Addition–Fragmentation– Transfer of Thiocarbonylthio Derivatives from the Barton–McCombie Deoxygenation: A Brief Account and Some Mechanistic Observations

Samir Z. Zard

Aust. J. Chem. **2006**, *59*, 663–668.

The story of the serendipitous discovery of a powerful new carbon–carbon bond forming method is briefly related. The process hinges on a subtle degenerative reversible radical addition–fragmentation mechanism and provides a solution to the longstanding problem of intermolecular radical additions to non-activated olefins. Iteration of the process in the case of polymerizable olefins leads to block polymers with well-defined architectures through what has become known as the RAFT and MADIX technologies.

Living Radical Polymerization by the RAFT Process—A First Update

*Graeme Moad, Ezio Rizzardo,
San H. Thang*

Aust. J. Chem. **2006**, *59*, 669–692.

RAFT polymerization remains one of the most versatile techniques for producing polymers with well-defined architectures. Research in this field has accelerated, demanding a comprehensive review published last year needs an equally comprehensive update.

Controlled Radical Polymerization in Aqueous Dispersed Media

*Maud Save, Yohann Guilleaumeuf,
Robert G. Gilbert*

Aust. J. Chem. **2006**, *59*, 693–711.

Until a decade ago, free radical polymerization, widely used to make a vast range of products, was regarded as a mature industry. Then a revolution came along: controlled radical polymerization, which has the potential to let chemists be molecular watchmakers who could put any group anywhere in a polymer chain. To be made industrially useful, this had to be implemented in emulsion systems (or in aqueous disperse media, to be more general), which is used to make paints, adhesives and a host of other polymers on the multi-tonne scale in an environmentally friendly way. However, simply adding an agent for controlled radical polymerization to a conventional emulsion polymerization led to a mess—loss of the 'watchmaker' control and coagulation, as the worst offences. This problem has been overcome over the last few years by examining the synthetic process from a mechanistic point of view, and large-scale production using these techniques is in the pipeline.

Current Chemistry

Ab Initio Kinetic Modelling in Radical Polymerization: A Paradigm Shift in Reaction Kinetic Analysis

*Michelle L. Coote,
Christopher Barner-Kowollik*

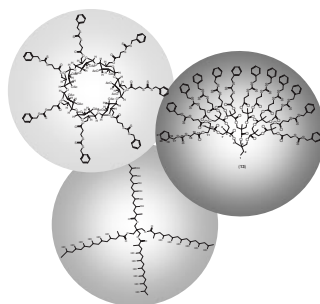
Aust. J. Chem. **2006**, *59*, 712–718.

The study of the kinetics and mechanism of (living) free-radical polymerization is a highly complex exercise. Herein we propose to reverse the conventional approach to kinetic data analysis, which typically consists of measuring kinetic data and a subsequent fit of the data to a model scenario. The present approach makes use of high-level ab initio quantum chemical calculations to arrive at elemental rate parameters, which are subsequently employed in a kinetic model whose output is then compared with the measured kinetic data.

Synthesis of Star Polymers using RAFT Polymerization: What is Possible?

*Christopher Barner-Kowollik,
Thomas P. Davis, Martina H. Stenzel*

Aust. J. Chem. **2006**, *59*, 719–727.



RAFT polymerization is a versatile tool to synthesize star polymers using a variety of monomers including functional monomers as well as vinyl acetate and vinyl pyrrolidone. Several approaches are presented and the two core-first techniques (R- and Z-group) are discussed in detail.

Communications

RAFT-Mediated Emulsion Polymerization of Styrene using a Non-Ionic Surfactant

*Carl N. Urbani, Hang N. Nguyen,
Michael J. Monteiro*

Aust. J. Chem. **2006**, *59*, 728–732.

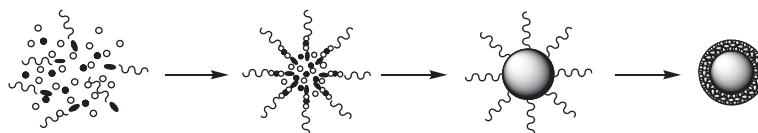
Nanoscale latexes prepared using living radical polymerization methods often meet in failure. Addition of a surfactant, so polymerization occurs within micelles, does improve matters. Ideal living behavior and low polydispersity for styrene polymerization in the miniemulsion system occurs for targets of below M_n 9000; above this limit superswelling of the micelle affects the nucleation rate and interferes with living polymerization.

One-Pot Synthetic Strategy to Core Cross-Linked Micelles with pH-Sensitive Cross-Linked Cores and Temperature-Sensitive Shells through RAFT Polymerization

Li-Ping Yang, Cai-Yuan Pan

Aust. J. Chem. **2006**, *59*, 733–736.

Polymeric functional micelles display unique properties and have potential applications in catalysis and the biological and biomedical fields. The synthesis of water-soluble micelles from double hydrophilic block copolymers is challenging, and micelles with a pH-sensitive poly(acrylic acid) core and temperature-sensitive poly(*N*-isopropylacrylamide) shell have been achieved by a one-pot synthetic strategy.



RAFT Graft Polymerization of 2-(Dimethylaminoethyl) Methacrylate onto Cellulose Fiber

*Debashish Roy, James T. Guthrie,
Sébastien Perrier*

Aust. J. Chem. **2006**, *59*, 737–741.

The high level of control that RAFT polymerization imparts is utilized here to graft poly(2-(dimethylamino)ethyl methacrylate) from cellulose. The graft ratio increases with monomer conversion, polymerization time, and degree of polymerization. Using a free chain transfer agent also increases the grafting ratio and limits homopolymer formation.

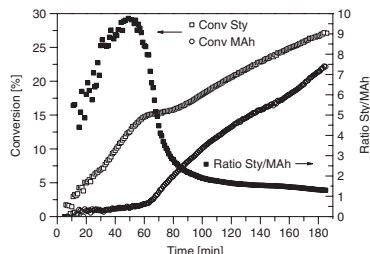
Full Papers

Investigation into the Initialization Behaviour of RAFT-Mediated Styrene–Maleic Anhydride Copolymerizations

Eric T. A. van den Dungen,
Jacques Rinqest, Nadine O. Pretorius,
Jean M. McKenzie, James B. McLeary,
Ron D. Sanderson, Bert Klumperman

Aust. J. Chem. **2006**, 59, 742–748.

Highly selective reactions are observed during the early stages of the RAFT-mediated copolymerization of styrene and maleic anhydride. Almost exclusive addition of the cumyl radical to maleic anhydride and of the 2-cyanoprop-2-yl radical to styrene takes place. The results indicate that the addition of a primary radical to the first monomer unit is rate determining during the initialization process.

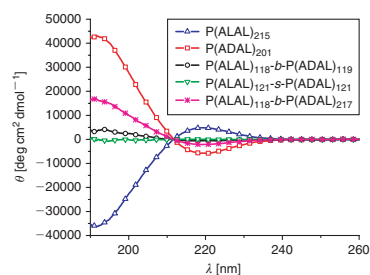


Chiroptical Properties of Homopolymers and Block Copolymers Synthesized from the Enantiomeric Monomers *N*-Acryloyl-L-Alanine and *N*-Acryloyl-D-Alanine Using Aqueous RAFT Polymerization

Brad S. Lokitz, Jonathan E. Stempka,
Adam W. York, Yuting Li,
Hitesh K. Goel, G. Reid Bishop,
Charles L. McCormick

Aust. J. Chem. **2006**, 59, 749–754.

A controlled free radical polymerization technique (RAFT) has been utilized for the first time to produce optically active homopolymers and block copolymers from pure D- and L-amino acid based monomers. The circular dichroism spectra reflect mirror image behavior of the respective D- and L-homopolymers and enhanced chiroptical activity as compared to their low molecular weight analogues. The enhanced activity and the ability to prepare ‘tunable’ chiroptic blocks with precise compositions suggest a number of potential applications in tunable optics, chiral separations, asymmetric catalysis, and biopharmaceutics.

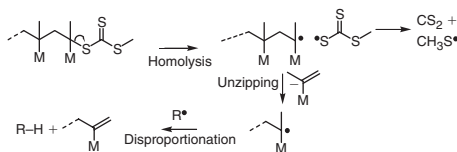


Thermolysis of RAFT-Synthesized Poly(Methyl Methacrylate)

Bill Chong, Graeme Moad,
Ezio Rizzardo, Melissa Skidmore,
San H. Thang

Aust. J. Chem. **2006**, 59, 755–762.

Elimination of the coloured thiocarbonylthio group from polymers prepared using RAFT methods is easily and cleanly effected by thermolysis. Mechanistic studies show two pathways, depending on the RAFT agent used.



Synthesis of Carboxylic Acid and Ester Mid-Functionalized Polymers using RAFT Polymerization and ATRP

Nino Malic, Richard A. Evans

Aust. J. Chem. **2006**, 59, 763–771.

Polymers with a single central point of carboxylic acid or ester functionality were prepared by living radical polymerization methods. The RAFT agents and ATRP initiators employed for their synthesis were prepared by a convenient, water-based procedure. The ability to couple functional molecules to the middle of polymers would provide better protection or interaction of the functional molecule with the polymer than conventional end attachment.

