

The Emergence of RAFT Polymerization

Graeme Moad^A

^A CSIRO Molecular and Health Technologies, Bag 10, Clayton South VIC 3169, Australia.
Email: graeme.moad@csiro.au

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Radical polymerization is one of the most widely used processes for the commercial production of high molecular weight polymers.^[1] The last ten years has seen the emergence of effective techniques for implementing radical polymerization characteristics associated with living polymerization. Thus we have a set of tools that allow unprecedented control over the process and the polymer product while retaining much of the versatility of conventional radical polymerization. Radical polymerization with reversible addition–fragmentation chain transfer (RAFT) is foremost among these tools.

Original Discovery

Prior to its first publication in 1998, RAFT polymerization with use of thiocarbonylthio compounds (dithioesters, trithiocarbonates, xanthates, and dithiocarbamates) saw parallel development in the laboratories of CSIRO in Australia^[2] and in the laboratories of Rhodia (then Rhone Poulenc) in France. The stages in evolution of RAFT polymerization at CSIRO were briefly described in a previous review published in the *Australian Journal of Chemistry* in mid-2005.^[3] In this Research Front Zard^[4] provides brief review describing the organic chemistry of xanthates that forms one aspect of the prehistory of RAFT polymerization and some of the thought processes which lead to the development of MADIX (Macromolecular Design by Interchange of Xanthates—RAFT with xanthates) at Rhodia. Zard^[4] also provides a personal view on some of the mechanistic dilemmas given further mention below.

Recent Rapid Growth in RAFT Usage

The eighteen months since we submitted our 2005 review^[3] has seen a major growth in the literature on RAFT

polymerization with the publication of over 200 papers. These developments demanded an update review^[5] and the publication of this Research Front. Save et al.^[6] provide a review of recent developments of radical polymerization in dispersed media (emulsion polymerization, miniemulsion polymerization, and suspension polymerization) using three forms of controlled radical polymerization (RAFT, nitroxide mediated polymerization (NMP), or atom transfer radical polymerization (ATRP)).

Is it Living?

According to the IUPAC recommendation,^[7–9] radical polymerizations which show the characteristics of a living process (the majority of chains retain the ability to grow in the presence of monomer), in that they inevitably involve a finite amount of termination by radical–radical reactions, should not be called ‘living polymerizations’, which require the total absence of events leading to chain death (termination, irreversible chain transfer). They also should not be generically called ‘controlled polymerizations’ without clear indication of the form of control involved since there are many forms of controlled polymerization which show no living characteristics.

Questions of Kinetics

The basic mechanism for RAFT polymerization proposed in 1998 is generally not questioned. However there remains significant controversy on aspects of the kinetics of the process and what side reactions might accompany RAFT.^[10] The use of theoretical methods and, in particular, ab initio calculations to predict kinetic parameters associated with RAFT polymerization may provide a way of resolving the dilemma.^[11] Studies of initialization (conversion of the initial



Graeme Moad obtained his B.Sc.(Hons1) in 1974 and Ph.D. in 1977 from the University of Adelaide in the field of organic free radical chemistry. Between 1977 and 1979 he undertook postdoctoral research at Pennsylvania State University in the field of biological organic chemistry. He joined CSIRO as a research scientist in 1979 and is currently a chief research scientist. Dr Moad is coauthor of the book ‘The Chemistry of Free Radical Polymerization’ which appeared as a second edition in 2006. His research interests lie in the fields of polymer design and synthesis (free radical polymerization, reactive extrusion), polymerization kinetics and mechanism, and most recently polymer nanocomposites.

RAFT agent) are also providing crucial information. In this Research Front van den Dungen et al.^[12] report on initial-ization of RAFT copolymerization of styrene with maleic anhydride.

Whitewater RAFTing

Studies of polymerization in dispersed media (whitewater RAFTing) make up a significant part of the recent literature on RAFT polymerization.^[5,6] Urban et al.^[13] report on the emulsion polymerization of styrene with a nonionic surfactant.

Creating Complex Architectures

One of the recognized benefits of living radical polymerization is the ability to synthesise complex, yet well defined, polymer architectures such as blocks, stars, combs, and grafts/brushes. RAFT polymerization has advantages over other methods in this context because of its compatibility with a wide range of monomers and reaction conditions and many examples have been reported.^[3] In this Research Front Lokitz et al.^[14] examine the synthesis and properties of homopolymers and block copolymers of the optically active acrylamides, *N*-acryloyl-D-alanine and *N*-acryloyl-L-alanine, produced by RAFT polymerization in aqueous solution. Barner-Kowolik et al.^[15] provide a review of the work of the CAMD group at the University of New South Wales in the area of star polymer synthesis. Yang and Pan^[16] describe the synthesis of star microgels with poly(*N*-isopropyl acrylamide) arms and a poly[(acrylic acid)-*co*-(ethylene glycol dimethacrylate)] core by the arm-first method. Malic and Evans^[17] describe the use of ATRP or RAFT to prepare well defined polymers with a single mid chain functional group (in this case carboxyl) for potential elaboration to three-arm star or mid-chain conjugate. Roy et al.^[18] demonstrate grafting of poly(2-(dimethylamino)ethyl methacrylate) onto cellulose.

In some circumstances it is desirable to cleave the thiocarbonylthio groups from RAFT synthesized polymers. Chong et al.^[19] report on the thermolysis of RAFT-synthesized poly(methyl methacrylate) and show that the mechanism of the process and the suitability of thermolysis as a means of end group removal depend strongly on the particular polymer and the RAFT agent used in its synthesis.

The Future: Revolutionizing Polymer Industry?

The publication rate on RAFT polymerization continues to increase. While there remains substantial scope for increasing our understanding of the process, a change in focus from the study of the scope and mechanism of RAFT polymerization towards applications of the process is clearly evident. We can also note that the first RAFT patent^[20] now appears seventh in the list of most cited patent families for 2005 in chemistry and related science just published by Chemical Abstracts Service's Science Spotlight.^[21] RAFT polymerization, in

providing a tool to manipulate molecular architecture of polymers, means that it is no longer a formidable task to apply radical polymerization to the synthesis of blocks, stars or other polymers of complex architecture. RAFT polymerization is being employed to facilitate the current revolution in those areas of materials science grouped under the nanotechnology umbrella and we can anticipate that new materials with the potential to further revolutionize polymer industry will continue to appear.

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