RAFT polymerization under microwave irradiation: Towards mechanistic understanding

Yusuke Sugihara,1 Mona Semsarilar,2 Sébastien Perrier,2 Per B. Zetterlund 1*

1 Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia
2 Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, NSW 2006, Australia

Microwave irradiation has been used in a number of polymerization systems as an alternative to thermal heating, sometimes resulting in higher monomer to polymer conversions and higher rates of polymerization. The use of microwave irradiation in controlled/living radical polymerization has led to mixed results, with rate acceleration and good molecular weight control observed in some cases. In the case of RAFT polymerization, a marked increase in the polymerization rate without loss of control/livingness has been reported for various monomers. There is very limited mechanistic understanding of these processes, and the present work is aimed at redressing this deficiency using both theoretical and experimental approaches.

Previously published experimental data for the RAFT system cyanoisopropyl dithiobenzoate (CPDB)/styrene1 have been compared with results from modeling and simulations performed using PREDICI software. Quantitative analysis of the experimental polymerization rate revealed that the total accumulated number of terminated radicals (assuming classical kinetics) exceeds the total number of radicals generated (via AIBN decomposition and spontaneous initiation of styrene), and the high radical concentration inferred from the polymerization rate is not consistent with controlled/living behaviour. Three models were tested: (i) an elevation in temperature caused by microwave irradiation, (ii) microwave-enhanced propagation \( k_p \) and addition to RAFT moiety \( k_{\text{add}} \), and (iii) microwave-induced radical generation from monomer. Model (ii) gives the best agreement with experimental data. It has been speculated that microwave irradiation may lead to radical generation via monomer decomposition.2 This theory has been investigated experimentally by carrying out polymerizations under microwave irradiation in the presence of a suitable radical trap.

![Figure 1](image1.png)

**Figure. 1.** Conversion vs time plots for RAFT polymerization of styrene using CPDB and AIBN under microwave irradiation (○), and various simulations as indicated.

![Figure 2](image2.png)

**Figure. 2.** \( M_n \) vs conversion for RAFT polymerization of styrene using CPDB and AIBN under microwave irradiation (○), and various simulations as indicated.

---

1 S. L. Brown, C. M. Rayner, S. Graham, A. Cooper, S. Rannard, S. Perrier, *Chem. Comm.*, 2007, 2145

---

**Yusuke Sugihara**
Ph.D. student
Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia
Phone: +61 2 9385 5577; Fax: +61 2 9385 5966
E-mail: y.sugihara@student.unsw.edu.au

Personal History

- 2005: B.Sc. Kobe University, Japan
- 2005-2007: M.Sc. Kobe University, Japan
- 2010-: Ph.D. student at UNSW

Research interests: kinetics of polymerization, polymer dispersions, MW irradiation