

# Chain-Length Dependence in Living Polymerizations: Physical Manifestation and Monte Carlo Simulation of RAFT in Emulsion Polymerization

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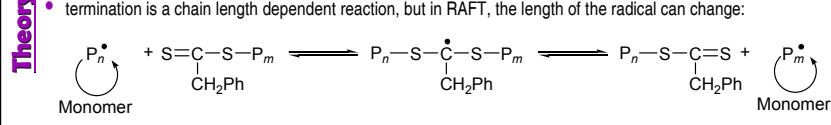
## Introduction

- ### Objectives
- how does RAFT alter emulsion polymerization mechanisms (e.g. particle growth, radical entry, radical exit)?
  - can traditional emulsion polymerization tools (e.g. zero-one kinetics,  $\gamma$ -relaxations) be used on RAFT/emulsion systems?

- ### Motivations & Background
- RAFT offers ways to create block and star polymers easily; emulsion polymerization allows fast polymerization rates and high molecular weights
  - previous studies with [RAFT] = 16 mM have reported difficulties/unusual behavior [1]:
    - low conversion  $\bar{n}$  is less than non-RAFT system
    - an increase in  $\bar{n}$  is evident throughout the experiment
    - an inhibition period that decreases with increasing [initiator], but is not observed in the equivalent bulk system.

- ### Outline of Poster
- theory: development of a Monte Carlo model
  - numerical experiments: how RAFT agents affect the kinetics
  - discussion: chain length dependent kinetics and RAFT systems

## Theory of Chain-Length Dependent Reactions



## Monte Carlo Simulations

- evolution equations intractable (distribution of radical lengths and dormant chain lengths): try Monte Carlo
- consider a particle with a pre-existing radical (and  $10^2$  to  $10^5$  dormant chains)
- dormant chains length,  $X_0$ , same as pre-existing radical
- use a random number  $U_1 \in [0, 1]$  to choose which event occurred:
  - termination:  $P(P_1' + P_2') = \frac{k_t^j [N_A V_s]}{\Delta_i}$
  - propagation:  $P(P_1' + M) = \frac{k_p^j [M]}{\Delta_i}$
  - transfer to dormant chain:  $P(P_1' + D_k) = \frac{k_{tr,D} [D_k]}{\Delta_i}$
- and increment the time of the molecules involved [2]:  $\tau = -\frac{\ln(U_2)}{\Delta_i}$
- lifetime of radical (in terms of number of propagation steps) calculated

## Results

### A. Effect of Dormant Chain Length ( $X_0$ )

- with short dormant chains, system is **highly** zero-one
  - all radicals are on short chains
  - length of radical only grows at rate  $k_p[M]/([RAFT]N_A V_s)$  instead of  $k_p[M]$
  - radicals **always** on short chains
- with longer dormant chains, system is **not** zero-one
  - most radicals are on long chains

### B. Effect of [RAFT]

- no **direct** effect for high-activity and low-activity RAFT agents
  - high-activity RAFT agent will **always** cause transfer regardless of [RAFT]
  - low-activity RAFT agent (e.g. xanthates) will **never** cause transfer before termination takes place, regardless of [RAFT]
- indirect** effect for high-activity RAFT agents:
  - higher [RAFT] makes short chains last longer into reaction:  $X_d = \frac{X_0[M]_0}{[RAFT]}$

### C. Length of Terminating Chains

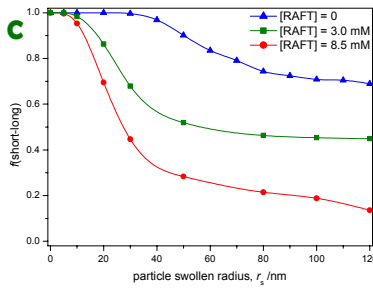
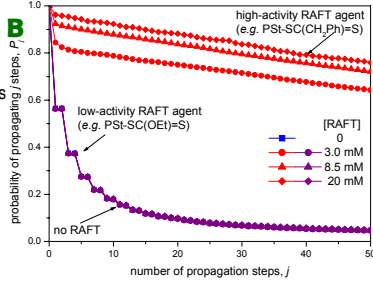
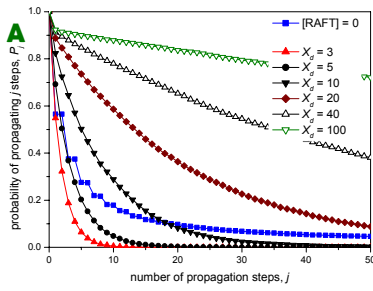
- length of chains involved in termination reaction gives idea of influence of short-long and long-long reactions
- entry brings in short chain (with all other chains being long); chain transfer occurs rapidly, leaving a short dormant chain
- for  $r_s = 50$  nm,  $X_0 = 100$ , [RAFT] = 8.5 mM:
  - 28% of termination reactions short-long
  - only 0.037% of dormant chain population is short
  - lots of polymer made (see Fig. A above) so not just entering species that is terminating

### Short Dormant Chains

- radical length changes slowly (more slowly than in the absence of RAFT)
- termination is always short-short

### Long Dormant Chains

- radical moves from short chain to long chain by transfer to dormant species
- either long-long termination or transfer back to the short dormant chain is **required** for termination



## Particle Growth Kinetics

- zero-one kinetics may be appropriate for the initial stages of the experiment but are unlikely to be applicable thereafter
- pseudo-bulk kinetics may be appropriate at later stages
- neither zero-one nor pseudo-bulk kinetics are necessarily applicable
- rapidly changing CLD-rate coefficients make using (or obtaining) values for  $\langle k_p \rangle$  inappropriate

## Experimental Comparison

- at low conversions, short-short termination dominates, so lifetime of radicals in two-radical particles is reduced
- as conversion increases, the dormant chain length increases and particles may support more than one radical, giving an acceleration in rate
- amphiphatic, oligomeric RAFT agent  $(AA)_x-(BA)_y-S-C(Z)=S$  shown to be good for styrene by Ferguson *et al.* [5] behaves like longer dormant chain (5 to 10 units long)

## Implications for Experimental Design

- longer-chain dormant species lead to an increased lifetime for the radicals – use of an oligomeric RAFT-adduct is an advantage
- [RAFT] has no **direct** effect on the lifetime of the radicals in the particles
- [RAFT] has an **indirect** effect by prolonging retardation caused by short chains

## RAFT Simulation

- Monte Carlo models provide significant insights into the importance of the different processes (propagation, transfer to dormant and termination)
- CLD kinetics *must* be considered

## Acknowledgements

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## Notes

- ### System Details
- styrene, 50 °C,  $S_2O_8^{2-}$  initiator,  $r_s = 50$  nm, [RAFT] = 3 – 20 mM, diffusion model from [3,4]
  - high-activity, benzyl-activated RAFT agent

- ### Symbols
- |        |                                |            |                              |
|--------|--------------------------------|------------|------------------------------|
| $CLD$  | chain length dependent         | $k_t^j$    | CLD termination rate coeff.  |
| $P_1'$ | propagating radical length $i$ | $k_p$      | propagation rate coeff       |
| $D_k$  | dormant chain length $k$       | $k_{tr,D}$ | rate coeff. for $P_1' + D_k$ |
| $V_s$  | swollen volume of particle     | $X_d$      | length of dormant chain      |
| $r_s$  | swollen radius of particle     | $x$        | conversion                   |

## References

- Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417.
- Fichthorn, K. A.; Weinberg, W. H. *J. Chem. Phys.* **1991**, *95*, 1090.
- Scheren, P. A. G. M.; Russell, G. T.; Sangster, D. F.; Gilbert, R. G.; German, A. L. *Macromolecules* **1995**, *28*, 3637.
- Griffiths, M. C.; Strauch, J.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 7835.
- Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawke, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243.