



# RAFT Techniques in Emulsion Polymerization: Living Character, RAFT Agent Transport and Rate of Polymerization

Stuart W. Prescott,<sup>♦\*▲</sup> Christopher M. Fellows,<sup>♦</sup> Mathew J. Ballard,<sup>\*</sup> Ezio Rizzardo<sup>\*▲</sup> and Robert G. Gilbert<sup>▲</sup>

<sup>♦</sup> Key Centre for Polymer Colloids, School of Chemistry, University of Sydney NSW 2006, Australia

<sup>\*</sup> CSIRO Molecular Science, Private Bag 10, Clayton South VIC 3169, Australia

<sup>▲</sup> Cooperative Research Centre for Polymers, 32 Business Park Drive, Notting Hill VIC 3168, Australia

## Objectives

- to successfully use RAFT techniques in emulsion polymerization systems
- to determine the effect of RAFT techniques on the physical processes involved in emulsion polymerization

## Motivations & Background

- RAFT offers ways to create block and star polymers easily;<sup>1,2</sup> emulsion polymerization allows fast polymerization rates and high molecular weights<sup>3</sup>
- previous studies have reported quite slow rates and high levels of coagulum<sup>4,5</sup>

## Outline of Poster

- introduction:** difficulties in combining RAFT and seeded emulsion polymerization
- experimental:** RAFT agent transport into the latex particles, reaction techniques
- results and discussion:** the effects of RAFT on molecular weights and rates

## 2a. Seed Preparation: RAFT Agent Transport

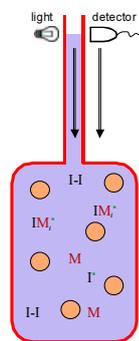
- polystyrene seed latex synthesized
- final latex statistics  
size:  $r_w = 39 \text{ nm}$   $r_w/r_n = 1.18$   
MW:  $M_n = 74700$   $M_w/M_n = 3.3$
- water added (to final dilution for latex)
- acetone added (20% w/w on total water)
- RAFT agent added as crystalline solid
- stirred for 24 to 72 h
- acetone assists RAFT agent transport into latex particles; particles contain RAFT agent
- rotary evaporator used to strip acetone from latex ( $1.5 \times$  mass of acetone removed)
- seed latex topped up with water
- monomer added to mixture with stirring
- particles swell over time, so there are no monomer droplets left
- seed now ready for use in reactions

## 2b. Reaction Techniques

- all reactions performed at 50 °C in a jacketed glass reactor, sodium persulfate initiator, sodium dodecyl sulfate surfactant
- particle sizes from an LS230 sizer (Coulter)
- molecular weights determined using a DRI GPC (Waters) and analyzed using GPC for Windows (Chemware)

## 2c. Dilatometry

- 100 mL reaction vessel overfilled into capillary and change in height of meniscus monitored by computer (diagram on right)
- polymer is more dense than monomer so meniscus height gives reaction progress



## 2d. Sampled Reactions

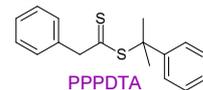
- 10 mL samples taken at intervals throughout experiment, short-stopped using hydroquinone (10 ppm)
- particle size, conversion (by gravimetry) and molecular weight distribution determined for each sample

## 4. Conclusions

- RAFT agents may be successfully incorporated into a seed for emulsion polymerization without an adverse effect on latex stability
- living character in emulsion polymerization systems has been achieved, showing molecular weight control and reduction in molecular weight polydispersity
- rate of polymerization slowed to 30 – 50% of rate in control experiments
- significant inhibition period seen, but may be overcome by using more initiator (but this may compromise living character of final polymer)
- further work with analogous RAFT agents and additional dilatometry experiments (e.g.  $\gamma$ -relaxation) required to fully understand reduction in rate and inhibition period

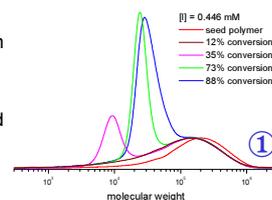
## 1. Introduction: Reversible Addition-Fragmentation Chain Transfer (RAFT)

- a number of questions are yet to be answered for RAFT techniques in emulsion polymerization systems:
  - how does the RAFT agent get into the particles? how long does this take?
  - how will the RAFT agent effect aqueous phase processes (initiation and entry)?
  - what sort of RAFT agent will give satisfactory results (water soluble or not)?
  - can the compartmentalization of radicals in emulsion polymerization be used to improve polymerization rates compared to RAFT in solution or bulk?
- classical emulsion polymerization of styrene is well-studied; good choice of monomer for this study
- RAFT agent chosen for study:  
2-phenylprop-2-ylphenyldithioacetate (PPPDTA)



## 3a. Evolution of Molecular Weight Distributions

- MWD shows broad peak from seed polymer and sharp peak from new (RAFT) polymer at various initiator concentrations (① [ $I$ ] = 0.446 and ② [ $I$ ] = 1.39 mM)
- GPC signal subtraction (based on mass of polymer present) used to find  $M_n$  and  $M_w$  for each sample
- polydispersity of samples ( $M_w/M_n$ ) between 1.2 and 1.4
- peak due to new polymer seen to move to higher molecular weight at higher conversion;  $M_n$  seen to be linearly dependant on conversion (③)



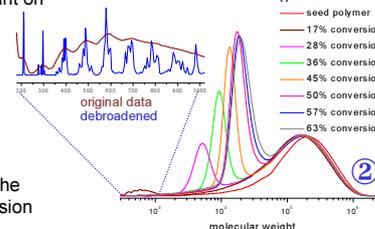
## 3b. Molecular Weight Control

- $M_n$  (from sampled and dilatometry experiments) is in reasonable agreement with the predicted value (④):

$$M_n^{\text{pred}} = \frac{x m_{\text{mon}}}{n_{\text{RAFT}}}$$

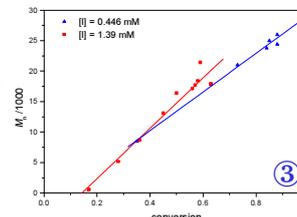
where  $m_{\text{mon}}$  is the mass of monomer used,  $n_{\text{RAFT}}$  is the amount of RAFT agent and  $x$  is the fractional conversion

- data shown is over wide range of initiator and monomer levels (Interval II and Interval III)



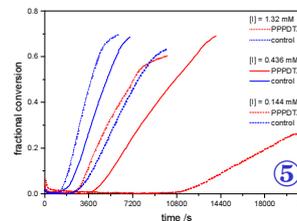
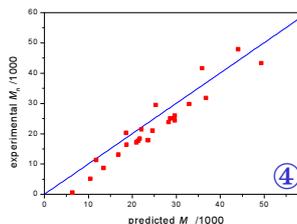
## 3c. Rate of Polymerization

- conversion vs time plots for experiments with same conditions except for amount of initiator added (⑤)
- rate of polymerization reduced by presence of RAFT agent
- long induction period due to RAFT agent; can be reduced by using higher initiator levels



## 3d. Further Observations & Mechanistic Discussion

- in ① & ②, samples show "seed" peak reproducibly shifted to lower MW than in the original seed latex
  - is this dead polymer formed at the beginning of the reaction? if so, why is the MW so low?
- $M_n$  vs conversion plot ③ indicates 14% conversion before significant living polymerization starts (for high initiator expt)
  - is this linked to the broader seed latex peak?
- low molecular weight peak ( $<10^3$ ) of first sample from ② can be "debroadened" to give set of peaks ~100 apart in MW
  - peaks not observable in subsequent samples and fall on  $M_n$  vs conversion plot; these are living oligomers
- causes of induction period unclear at this stage:
  - could be due to high exit of radicals from particles; cumyl radical is small & has high diffusion coefficient
  - could also be due to poor re-initiation by the cumyl radical to give new oligomeric radicals
  - styrene has poor aqueous phase initiation efficiency in emulsion systems;<sup>3</sup> exacerbated by above effects



## References

- Rizzardo, E.; Chiefari, J.; Mayadunne, R.; Moad, G.; Thang, S. H. *ACS Symp. Ser.* 2000, 768, 278.
- Moad, G.; Chiefari, J.; Chong, Y. K.; Kristina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Intnl* 2000, 49, 993.
- Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995.
- Monteiro, M. J.; Hodgson, M.; De Brouwer, H. J. *Polym. Sci. A-Polym. Chem.* 2000, 38, 3864.
- Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* 2000, 150, 33-38.

## Acknowledgements

- Mr Heng Taing & Ms Amanda Finlay (CSIRO) for assistance with experimental techniques and fruitful discussions
- Mr David Sangster & Dr Hank De Bruyn (KCPC) for helpful discussions about dilatometry
- The Key Centre for Polymer Colloids is established and supported under the Australian Research Council's Research Centres Programme