



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

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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;^{1,2} emulsion polymerization allows fast polymerization rates and high molecular weights³
- previous studies have reported quite slow rates and high levels of coagulum^{4,5}

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

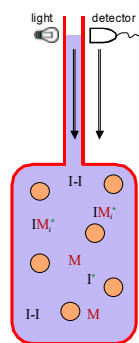
- polystyrene seed latex synthesized
- final latex statistics
size: $r_w/r_n = 1.18$
MW: $M_n = 74700$, $M_w/M_n = 3.3$
- water added (to final dilution for latex)
- acetone added (20% w/w on total water)
- RAFT agent added as crystalline solid
- stirred for 24 to 72 h
- acetone assists RAFT agent transport 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

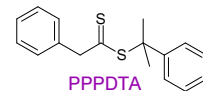
- 10 mL samples taken at intervals throughout experiment, short-stopped using hydroquinone (10 ppm)
- particle size, conversion (by gravimetry) and molecular weight distribution determined for each sample

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. γ -relaxation) required to fully understand reduction in rate and inhibition period

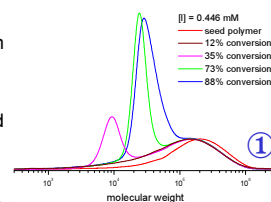
1. Introduction: Reversible Addition-Fragmentation Chain Transfer (RAFT)

- 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)



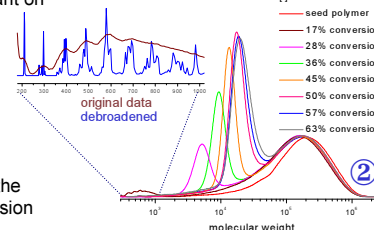
3b. Molecular Weight Control

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

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

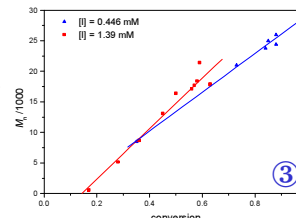
where m_{mon} is the mass of monomer used, n_{RAFT} is the amount of RAFT agent and x is the fractional conversion

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



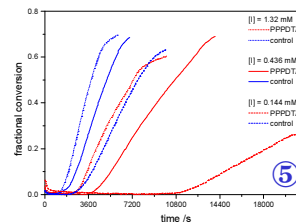
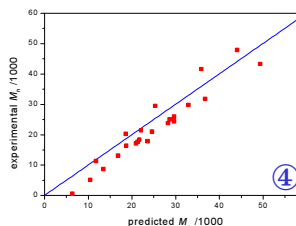
3c. Rate of Polymerization

- 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 "debrodened" 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;³ exacerbated by above effects



References

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