Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization in supercritical Carbon Dioxide (scCO$_2$)

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• Controlled Radical Polymerization
• RAFT Polymerization
• Why polymerization in scCO$_2$?
• State of the Art
• Model and Simulation
• Experimental Results
• Conclusions
Living polymer chains with active end groups

Predetermined MW and narrow MWD.

Applications include adhesives, coatings, electronics, nano-technology, and biomaterials.
**RAFT**


✓ Applicable to a large range of monomers
✓ Polymeric materials with controlled structure
✓ Success under a wide range of reaction conditions
✓ Wide variety of RAFT agents structures

RAFT

Weak C-S bond

Free radical leaving group, R^*
(must be able to reinitiate polymerization)

Z-group controls the reactivity of the
C-S double bond; influences the rate
of radical addition and fragmentation

Reactive C-S double bond

$k_{addition}$ +

$k_{fragmentation}$ -

$Z$: Ph $>>$ SCH$_3$ $>$ CH$_3$ $>$ N

$k_{addition}$ -

$k_{fragmentation}$ +

MMA $\rightarrow$ S, MA, AM, AN

S, MA, AM, AN $\rightarrow$ VAc, NVP

MMA $\rightarrow$ S, MA, AM, AN

VAc $\rightarrow$
RAFT

initiation

\[ I^* \xrightarrow{\text{monomer (M)}} P_n^* \]

chain transfer

\[ P_n^* + S \xrightarrow{k_{\text{add}}} P_n - S \xrightarrow{k_{\beta}} P_n - S \]

reinitiation

\[ R^* \xrightarrow{\text{monomer (M)}} P_m^* \]

chain equilibration

\[ P_m^* + S \xrightarrow{\text{equilibration}} P_m - S \xrightarrow{\text{equilibration}} P_n^* \]

termination

\[ P_n^* + P_m^* \rightarrow \text{dead polymer} \]

**scCO\textsubscript{2}**

<table>
<thead>
<tr>
<th></th>
<th>Liquid</th>
<th>Supercritical</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho) [kg m(^{-3})]</td>
<td>1000</td>
<td>100-800</td>
<td>1*</td>
</tr>
<tr>
<td>(\eta) [Pa S]</td>
<td>(10^{-3})</td>
<td>(10^{-5}-10^{-4})</td>
<td>(10^{-5})</td>
</tr>
<tr>
<td>(D) [m(^2) s(^{-1})]</td>
<td>(10^{-9})</td>
<td>(10^{-8})</td>
<td>(10^{-5})</td>
</tr>
</tbody>
</table>

*NIST Chemistry Webbook, NIST Standard Reference Database 69, National Institute of Standards and Technology, Gaithersburg MD, http://webbook.nist.gov*

- Critical Point: \(T_c = 304.13\) K, \(P_c = 73.773\) bar
- Triple point: \(T_t = 216.58\) K, \(P_t = 5.18\) bar
- Sublimation curve
- Vapour-pressure curve
- Melting curve

**Table**: Critical Points

<table>
<thead>
<tr>
<th>Substance</th>
<th>(T_c)</th>
<th>(P_c)</th>
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</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>31 °C</td>
<td>73.8 atm</td>
</tr>
<tr>
<td>Ethanol</td>
<td>240.9 °C</td>
<td>64.1 atm</td>
</tr>
<tr>
<td>CO(_2)+7 mol% Eth</td>
<td>52 °C</td>
<td>97 atm</td>
</tr>
<tr>
<td>Water</td>
<td>374 °C</td>
<td>220 atm</td>
</tr>
</tbody>
</table>
High purity, low toxicity, low cost.
Controllable dissolving power.
Inert solvent.
Low viscosity favors mass transportation.
Advantages in the operation.

- Elevated pressures required.
- Compression costs.
- High capital equipment investment.
• Complexity of the kinetics and mechanisms presents
• Solubility of the RAFT agent, Z and R• groups
• Interaction between controller and surfactant in dispersion polymerization
STATE OF THE ART


- Andrew M. Gregory, Kristofer J. Thurecht and Steven M. Howdle Controlled Dispersion Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide via RAFT American Chemical Society. Macromolecules 2008, 41, 1215-1222

EXPERIMENTAL REPORTS, NOT SIMULATION OR MODELING STUDIES!
To develop a model, using Predici, for RAFT polymerization processes in dispersion systems in scCO₂.
T = 80°C
P = 300 bar
scCO2 = 20% v/w
[AIBN] = 2.6X10^{-3}M
[STY] = 6.49 M
[RAFT] = 7.0X10^{-3}M

*Cumil Ditiobenzoate (CDB)*

T. Arita, S. Beuermann, M. Buback, P. Vana
T = 65°C
P = 200 bar
scCO₂ = 20% v/w
[AIBN] = 1.19 \times 10^{-2}\text{M}
[MMA] = 1.96 \text{M}
[RAFT] = 1.19 \times 10^{-2}\text{M}
The model captured the expected effects of RAFT agent to initiator ratio, pressure and temperature on polymerization rate and molecular weight development.

More detailed and systematic experimental studies on this topic are needed for model validation purposes.
To evaluate RAFT agents, commercially available or synthesized in dispersion polymerization in scCO2

Evaluate the effect of operating conditions, P, T on monomer conversion and MWD

Designing and improved recipes and operating conditions for the RAFT dispersion polymerization in scCO2
EXPERIMENTAL RESULTS

IPR 2009
EXPERIMENTAL SYSTEM
EXPERIMENTAL SYSTEM
MMA RAFT POLYMERIZATION IN scCO₂

S-Thiobenzoyl thioglycolic acid

**Krytox® 257 FSL.**

Effect of the Operating Pressure and Temperature on RAFT Mediated Dispersion Polymerization of MMA in scCO₂
Gabriel Jaramillo-Soto, Pedro R. García-Morán and Eduardo Vivaldo-Lima
To be submitted.
MMA RAFT POLYMERIZATION IN scCO₂
Effect of Stabilizer Concentration and Controller Structure and Composition on Polymerization Rate and Molecular Weight Development in RAFT Polymerization of Styrene in Supercritical Carbon Dioxide. G. Jaramillo-Soto et al. Submitted to Polymer, under corrections.
There are too many experimental factors to study.

Results strongly depend on the RAFT agent structure.

S-(thiobenzoil) thioglicolic better results with STY than MMA.

Stabilizer concentration importance.

Model optimization.
ACKNOWLEDGMENTS

Facultad de Química, Universidad Nacional Autónoma de México (FQ-UNAM), project PAIP 5290-28

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THANK YOU