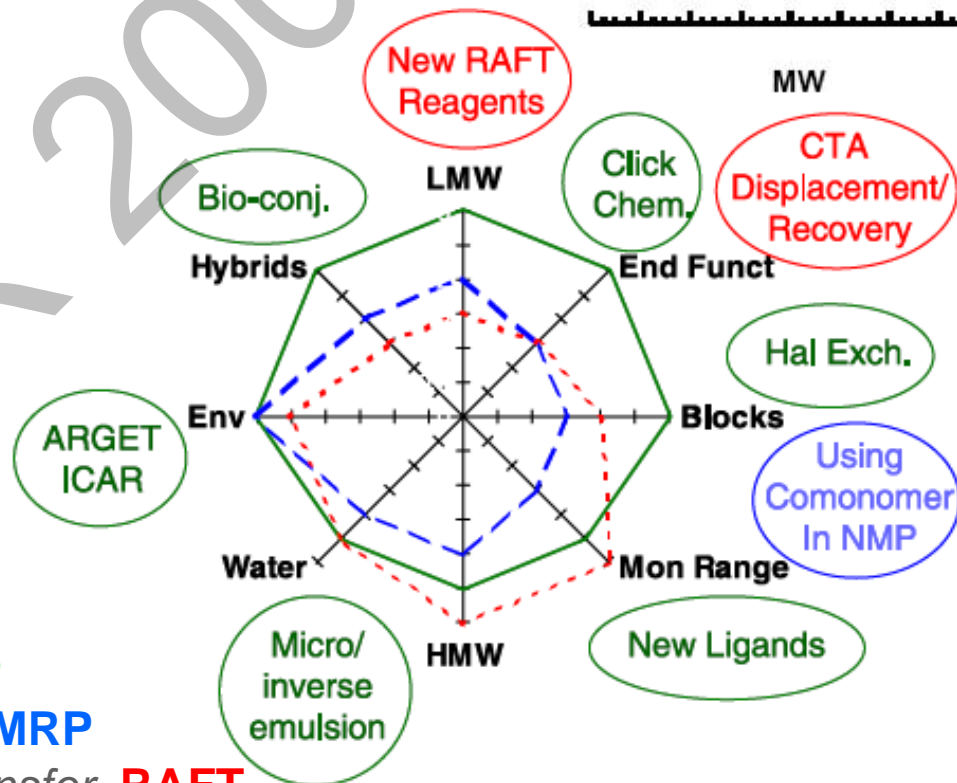
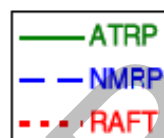
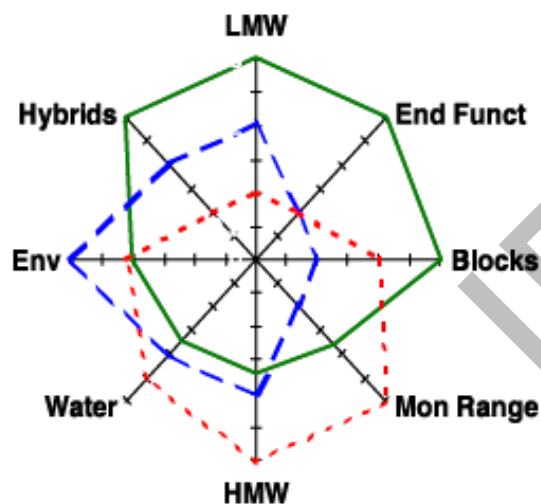
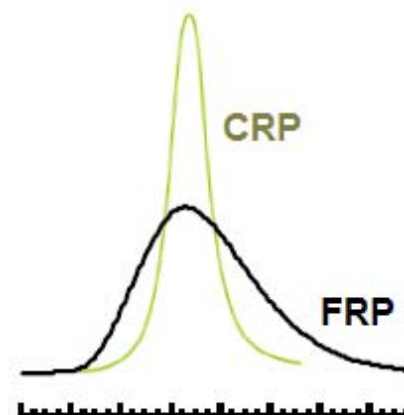


OUTLINE

- Controlled Radical Polymerization
 - **RAFT** Polymerization
 - Why polymerization in scCO_2 ?
 - State of the Art
 - Model and Simulation
 - Experimental Results
 - Conclusions
-

CRP

- Living polymer chains with active end groups
- Predetermined MW and narrow MWD.
- Applications include adhesives, coatings, electronics, nano-technology, and biomaterials.



Atom Transfer Radical Polymerization, **ATRP**

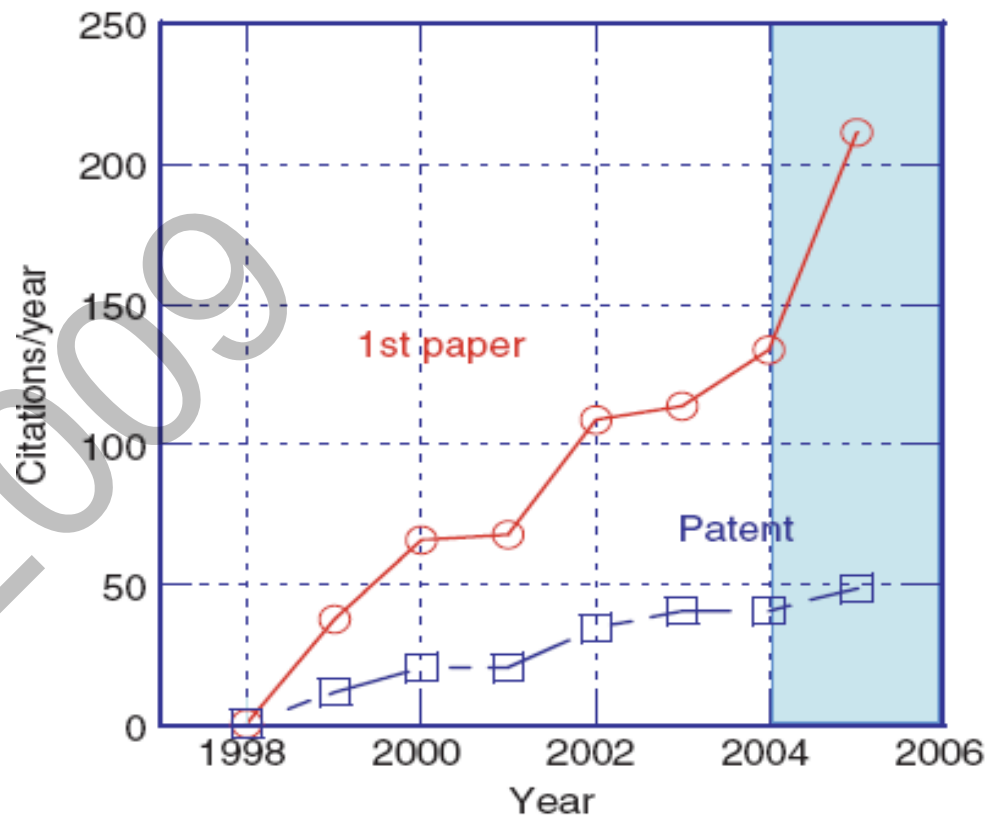
Nitroxide Mediated Radical Polymerization, **NMRP**

Reversible Addition Fragmentation chain Transfer, **RAFT**

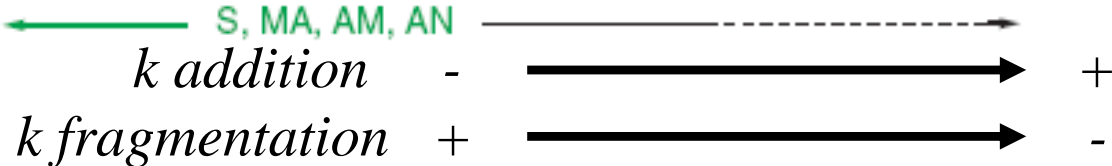
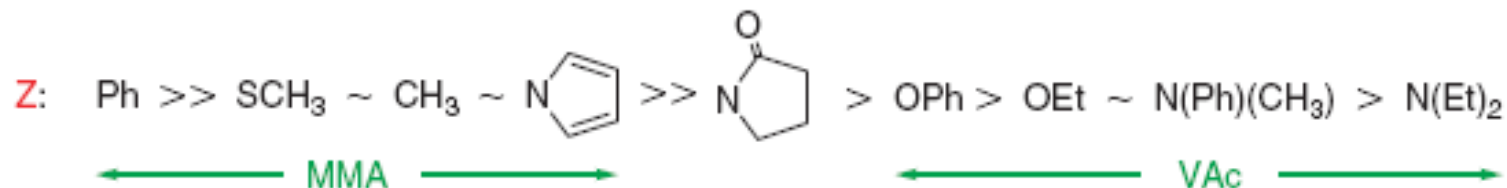
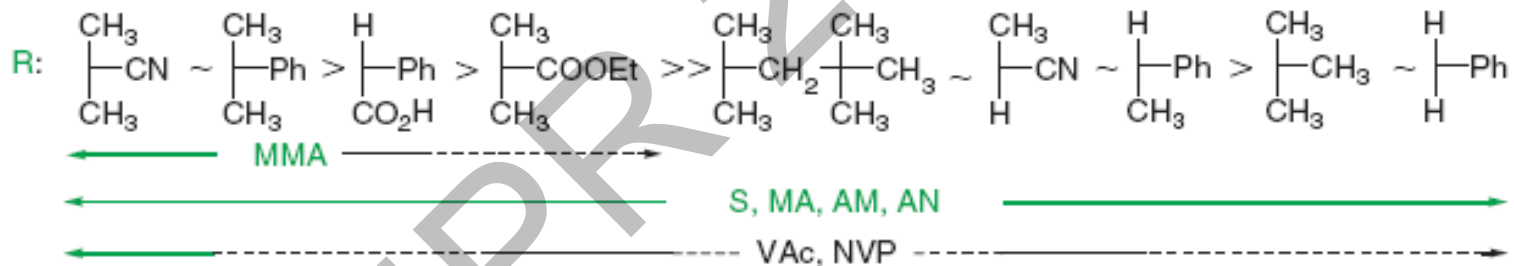
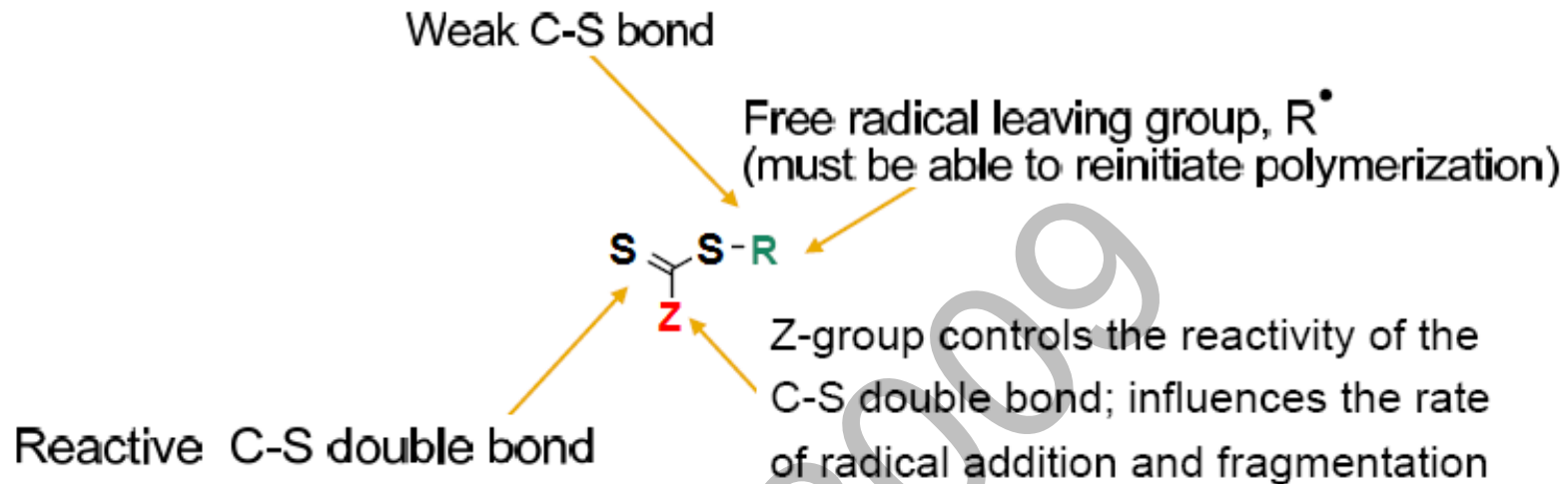
RAFT

- **First communication:** *J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, 31, 5559.*
- **First patent:** *T. P. Le, G. Moad, E. Rizzardo, S. H. Thang, *Int. Pat. WO9801478* **1998** [Chem. Abs. **1998**, 128, 115390f].*

- ✓ 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

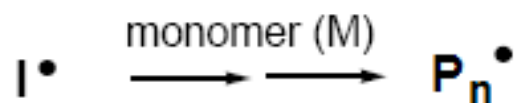


RAFT

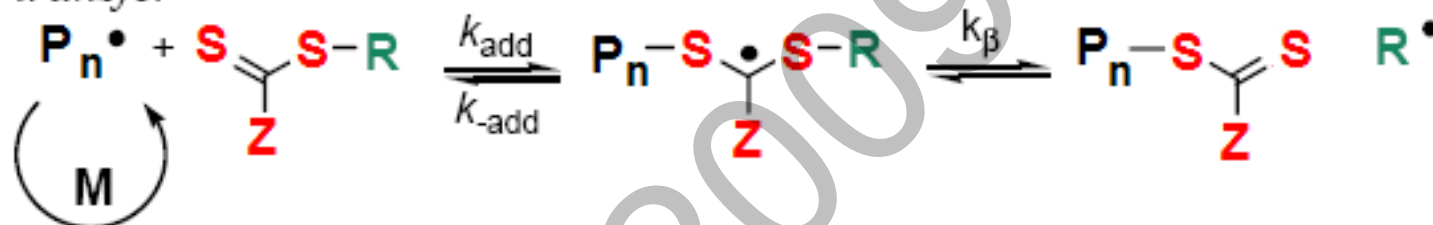


RAFT

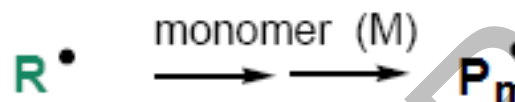
initiation



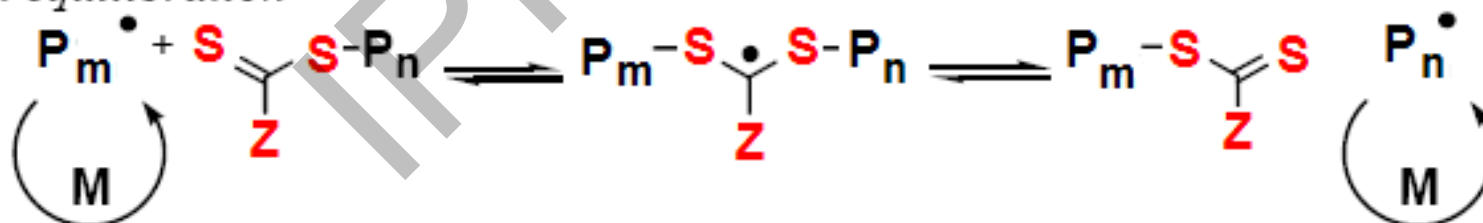
chain transfer



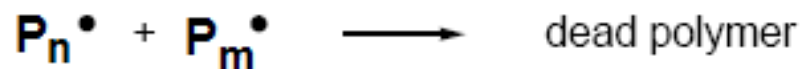
reinitiation



chain equilibration

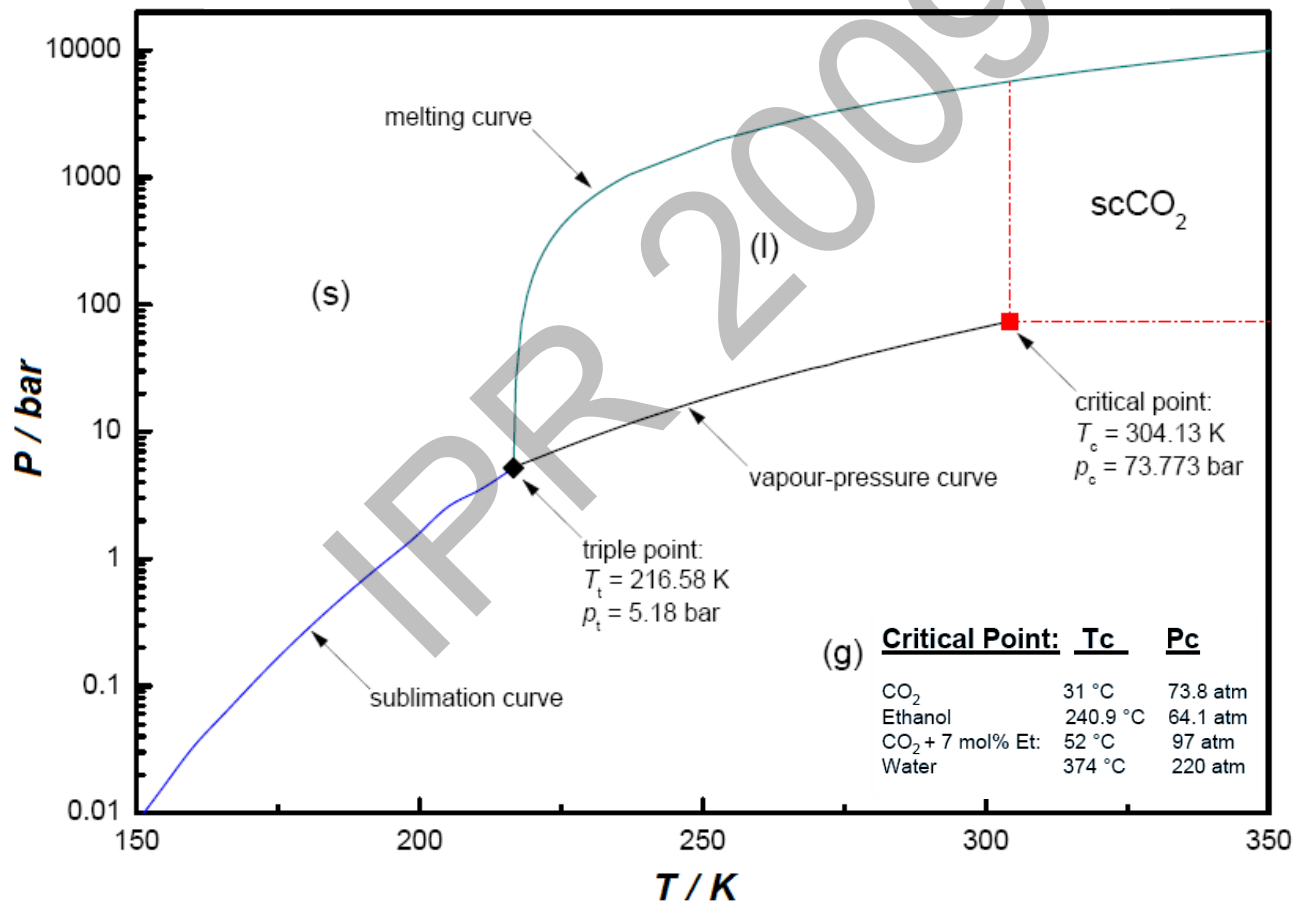


termination



scCO₂

	Liquid	Supercritical	Gas
ρ [kg m ⁻³]	1000	100-800	1*
η [Pa S]	10 ⁻³	10 ⁻⁵ -10 ⁻⁴	10 ⁻⁵
D [m ² s ⁻¹]	10 ⁻⁹	10 ⁻⁸	10 ⁻⁵



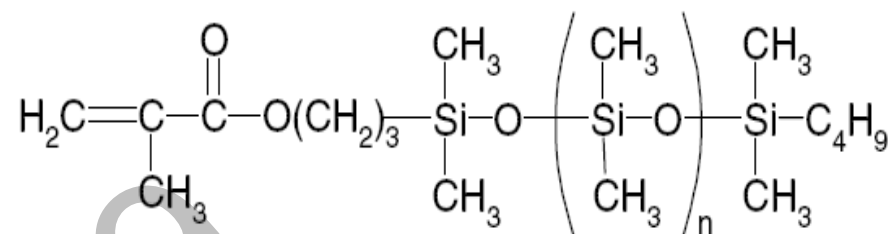
*NIST Chemistry Webbook, NIST Standard Reference Database 69, National Institute of Standards and Technology, Gaithersburg MD, <http://webbook.nist.gov>

scCO₂

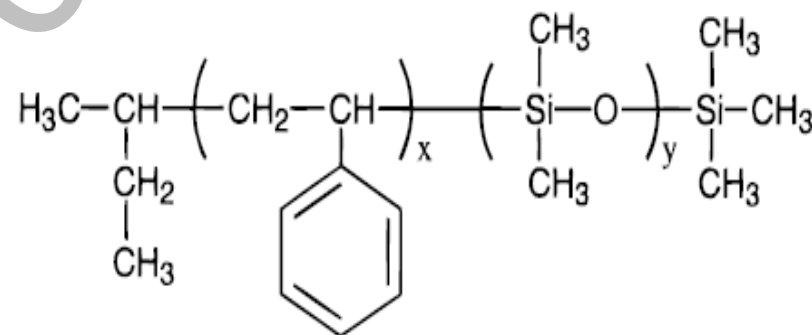
- ✓ High purity, low toxicity, low cost.
 - ✓ Controllable dissolving power.
 - ✓ Inert solvent.
 - ✓ Low viscosity favors mass transportation.
 - ✓ Advantages in the operation.
-
- Elevated pressures required.
 - Compression costs.
 - High capital equipment investment.
-

RAFT POLYMERIZATION IN $scCO_2$

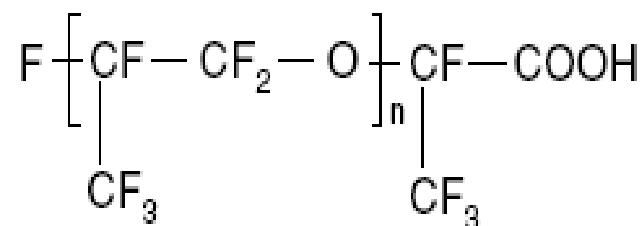
- Complexity of the kinetics and mechanisms presents
- Solubility of the RAFT agent, **Z** and **R•** groups
- Interaction between controller and surfactant in dispersion polymerization



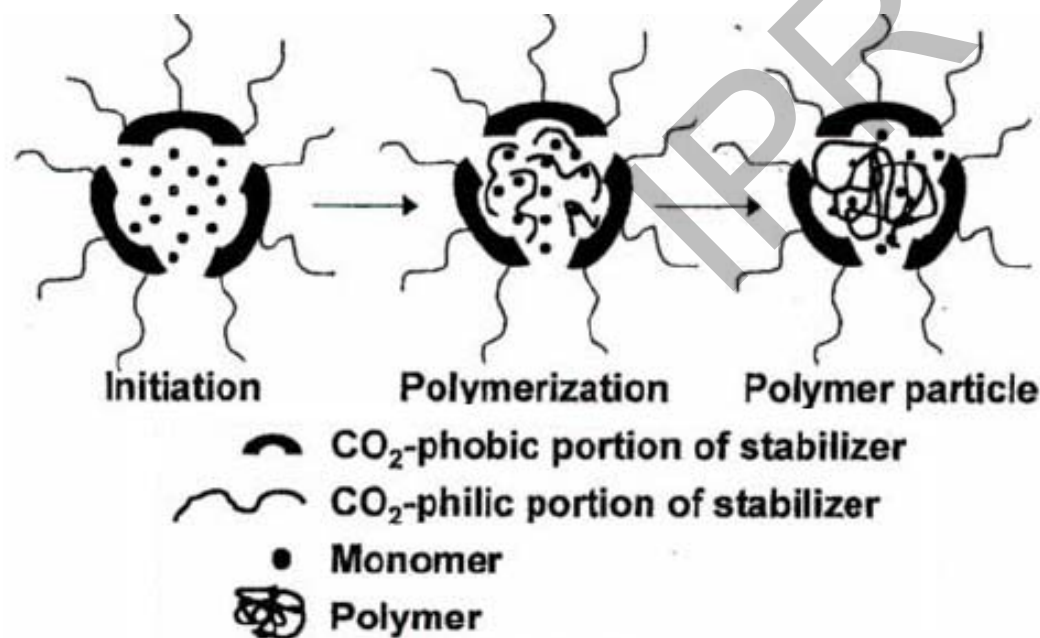
PDMS-MA



PS-PDMS



Krytox 157 FSL



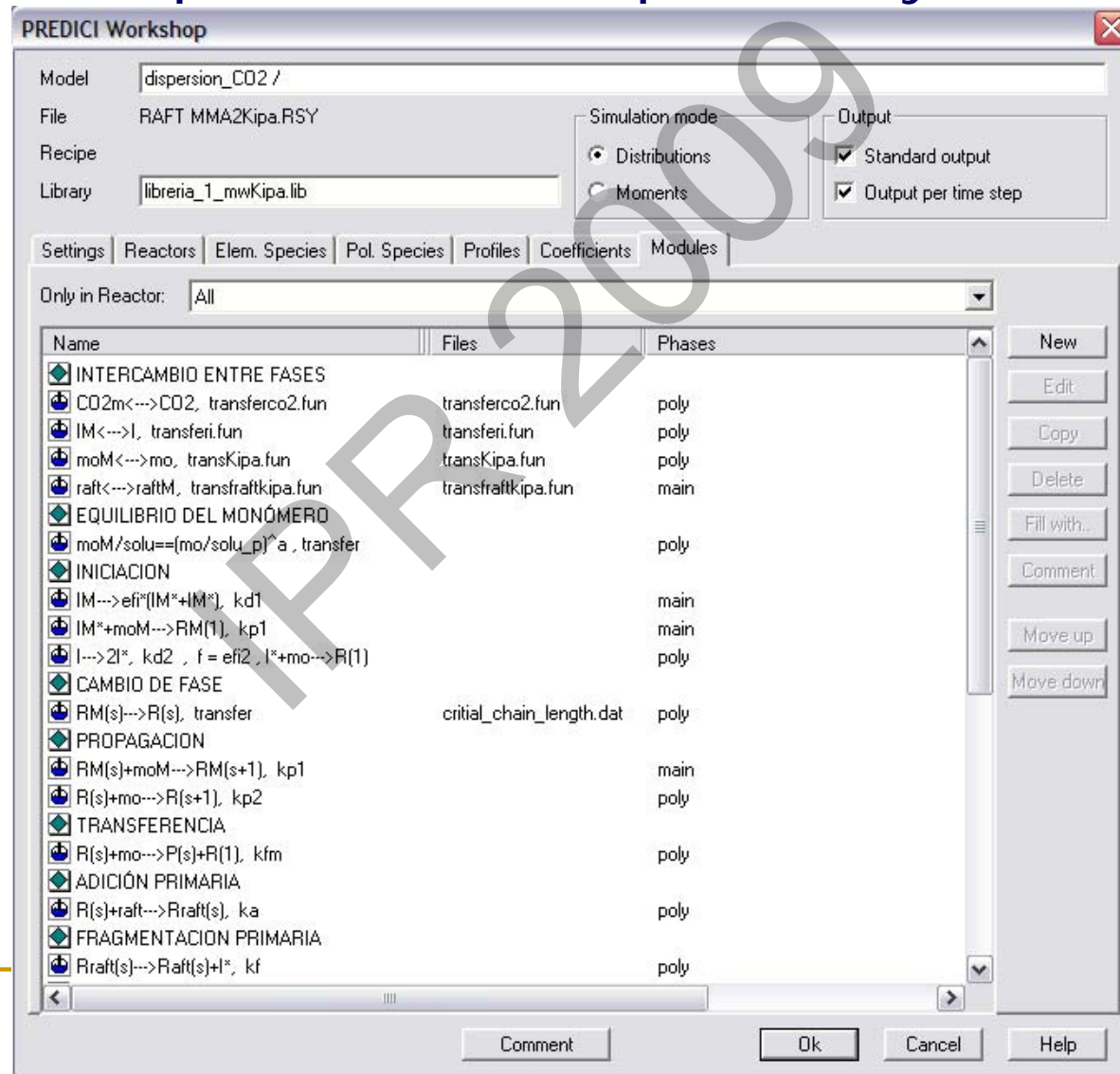
STATE OF THE ART

- ❖ Arita T., Beuermann, S., Vana, P. *Reversible addition fragmentation chain transfer (RAFT) polymerization of styrene in fluid CO₂*, *e-Polymers* **2004**, no. 003. <http://www.e-polymers.org>
- ❖ Arita, T., Beuermann, S. & Vana Philipp *RAFT Polymerization of Methyl Acrylate in Carbon Dioxide* *Macromol. Mater. Eng.* 2005, 290, 283-293
- ❖ Kristofer J. Thurecht, Andrew M. Gregory, Wenxin Wang, and Steven M. Howdle, *"Living" Polymer Beads in Supercritical CO₂* *Communications to the Editor Macromolecules, Vol. 40, No. 9, 2007*
- ❖ 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

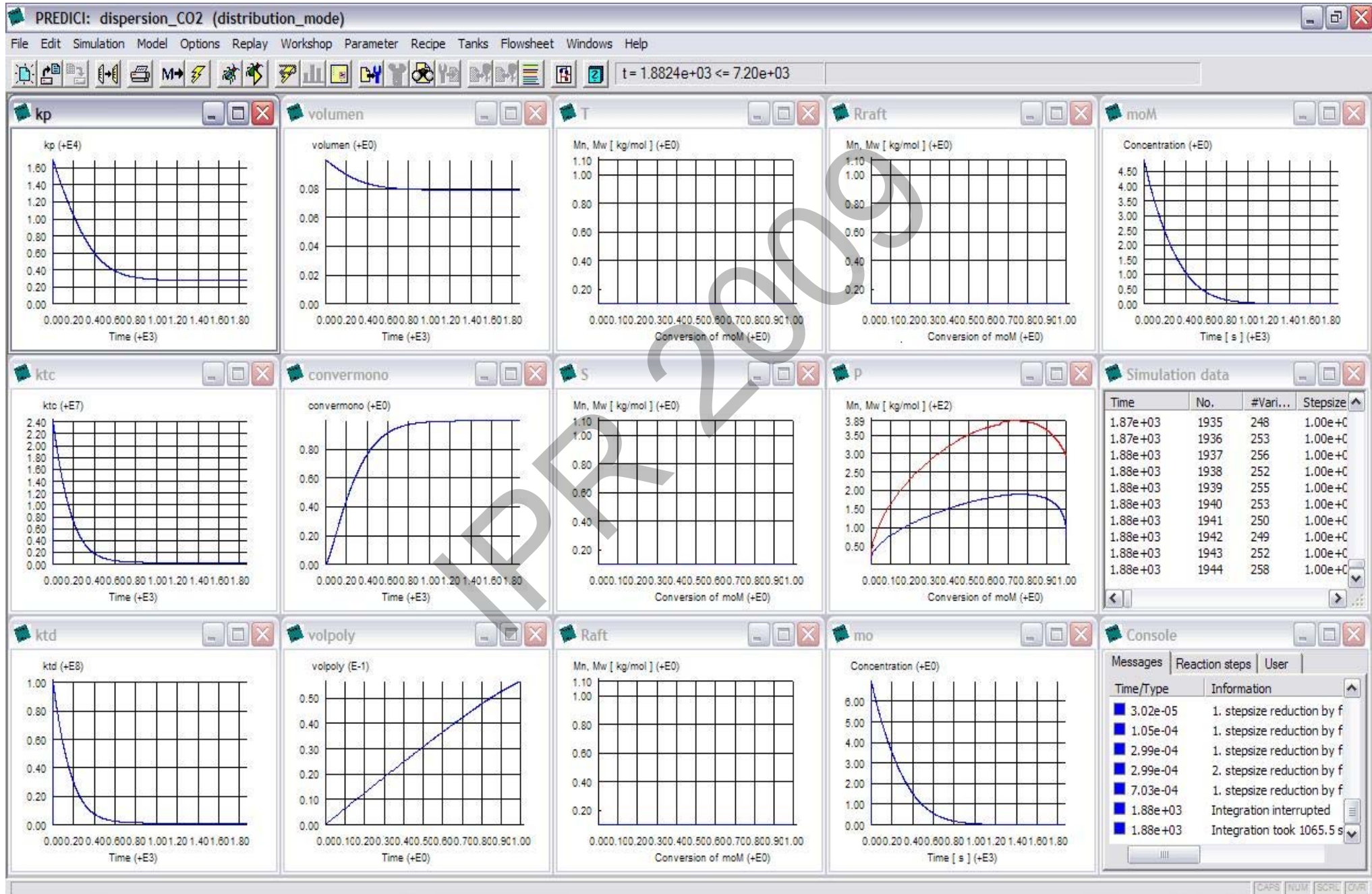
EXPERIMENTAL REPORTS, NOT SIMULATION OR MODELING STUDIES!

MODEL AND SIMULATION

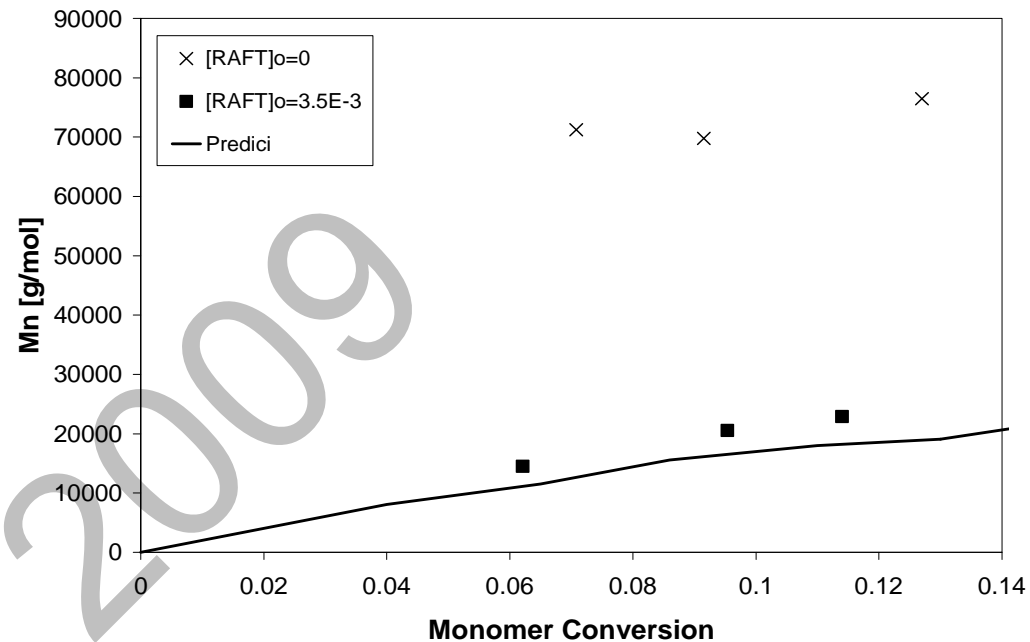
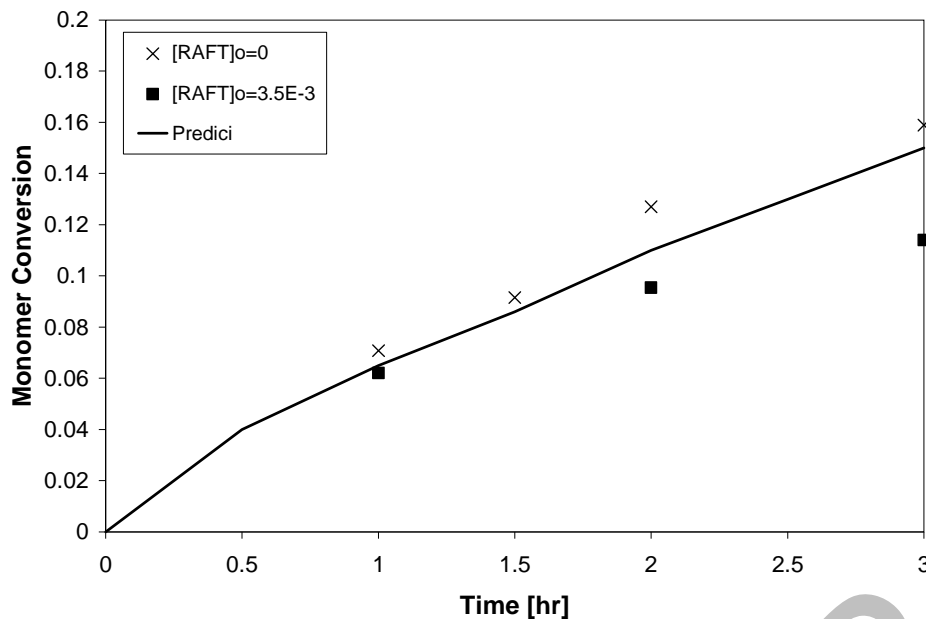
→ To develop a model, using Predici, for RAFT polymerization processes in dispersion systems in $scCO_2$.



SIMULATION RESULTS



SIMULATION RESULTS



$T = 80^{\circ}\text{C}$

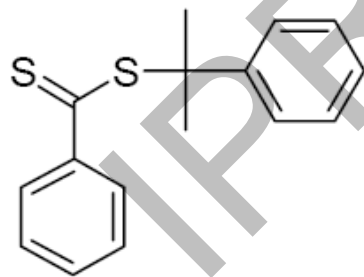
$P = 300 \text{ bar}$

$\text{scCO}_2 = 20\% \text{ v/w}$

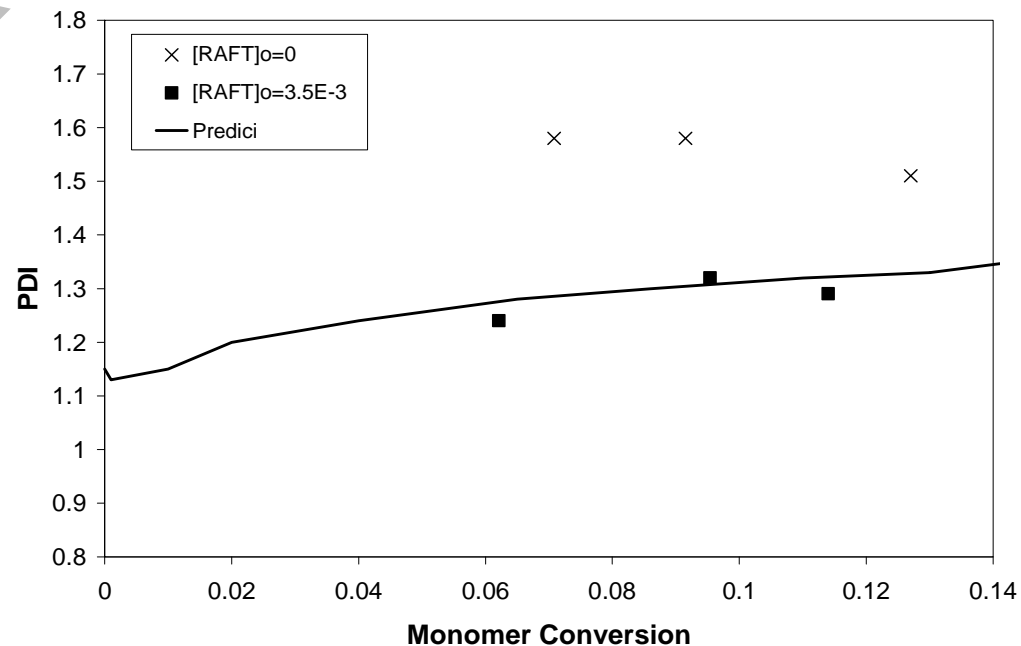
$[\text{AIBN}] = 2.6 \times 10^{-3} \text{ M}$

$[\text{STY}] = 6.49 \text{ M}$

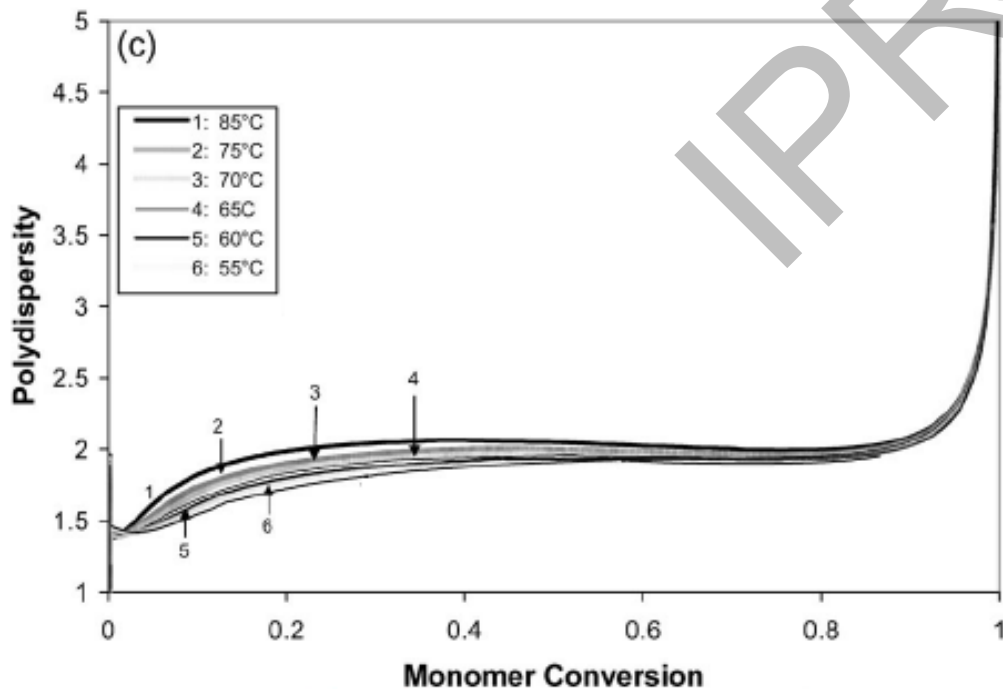
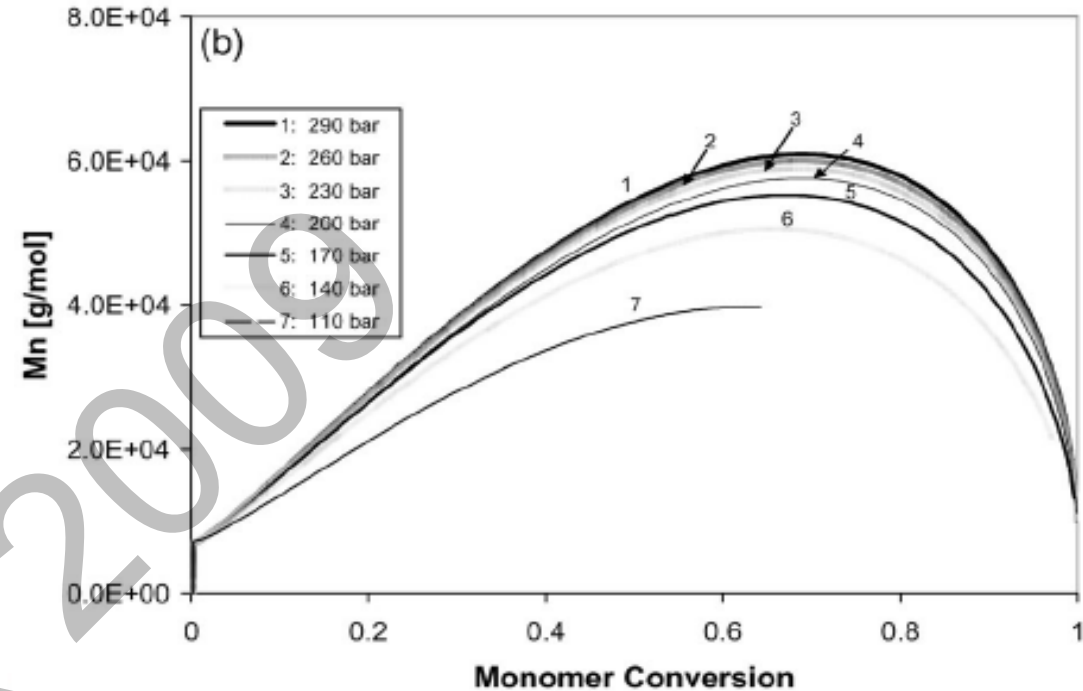
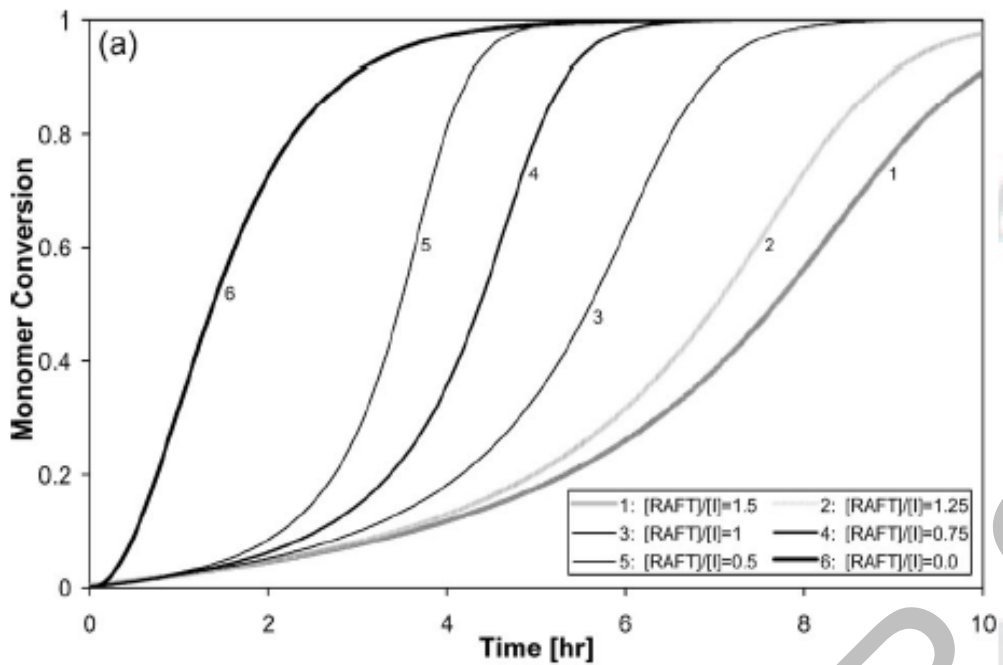
$[\text{RAFT}] = 7.0 \times 10^{-3} \text{ M}$



*Cumil
Dithiobenzoate
(CDB)*



SIMULATION RESULTS



$T = 65^{\circ}\text{C}$

$P = 200 \text{ bar}$

$\text{scCO}_2 = 20\% \text{ v/w}$

$[\text{AIBN}] = 1.19 \times 10^{-2} \text{ M}$

$[\text{MMA}] = 1.96 \text{ M}$

$[\text{RAFT}] = 1.19 \times 10^{-2} \text{ M}$

SIMULATION CONCLUSIONS

- 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.
-

EXPERIMENTAL RESULTS

- 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



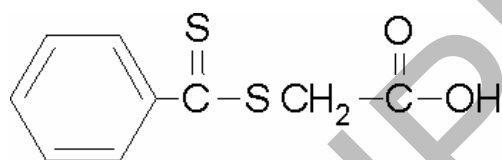
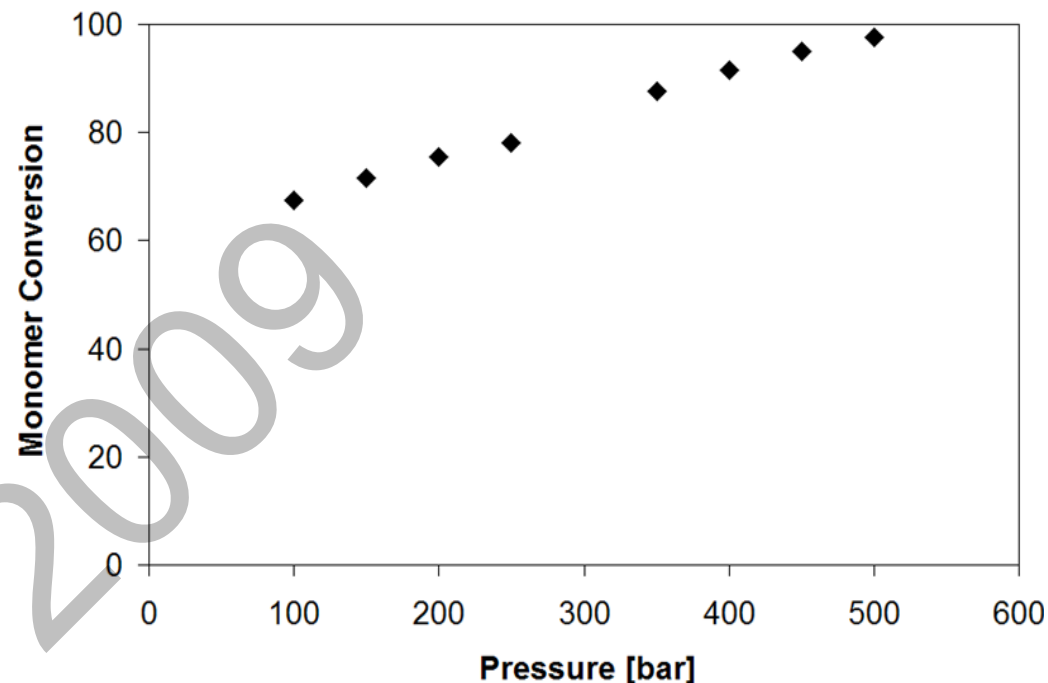
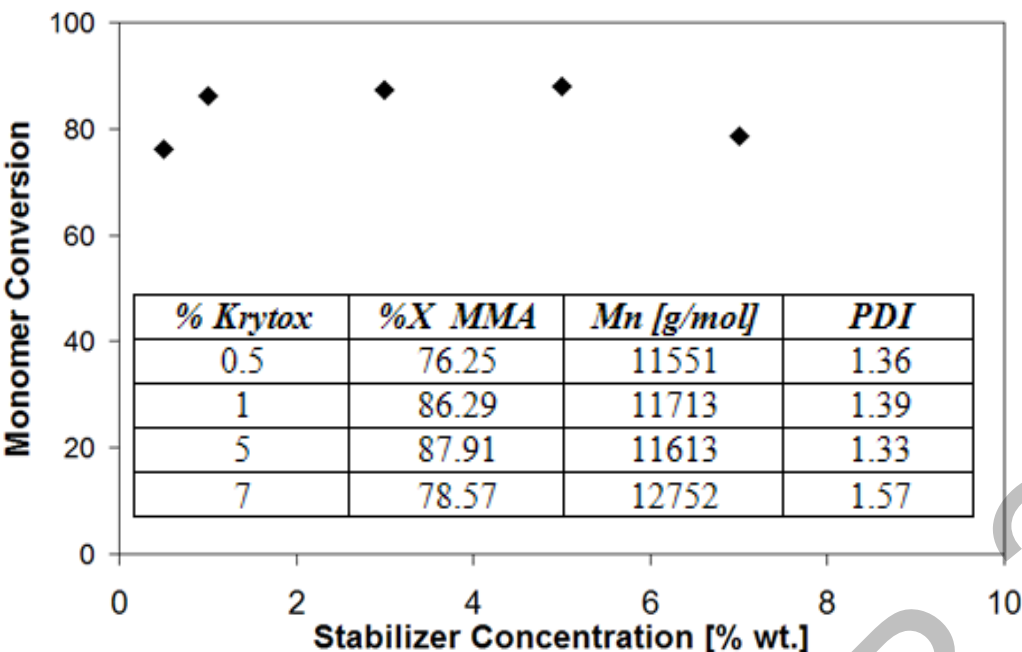
EXPERIMENTAL SYSTEM



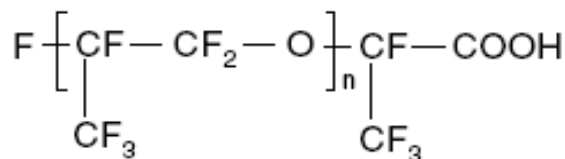
EXPERIMENTAL SYSTEM



MMA RAFT POLYMERIZATION IN $scCO_2$



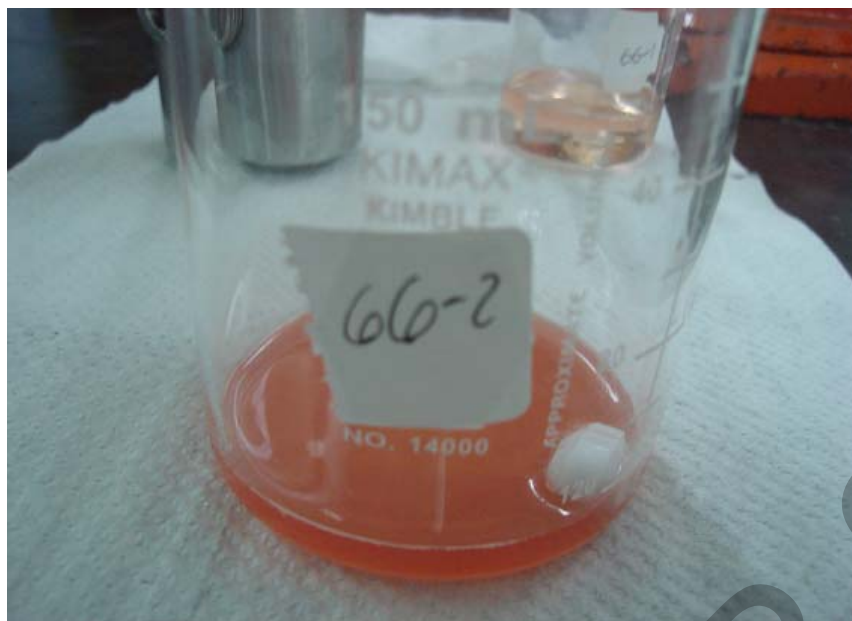
S-Thiobenzoyl thioglycolic acid



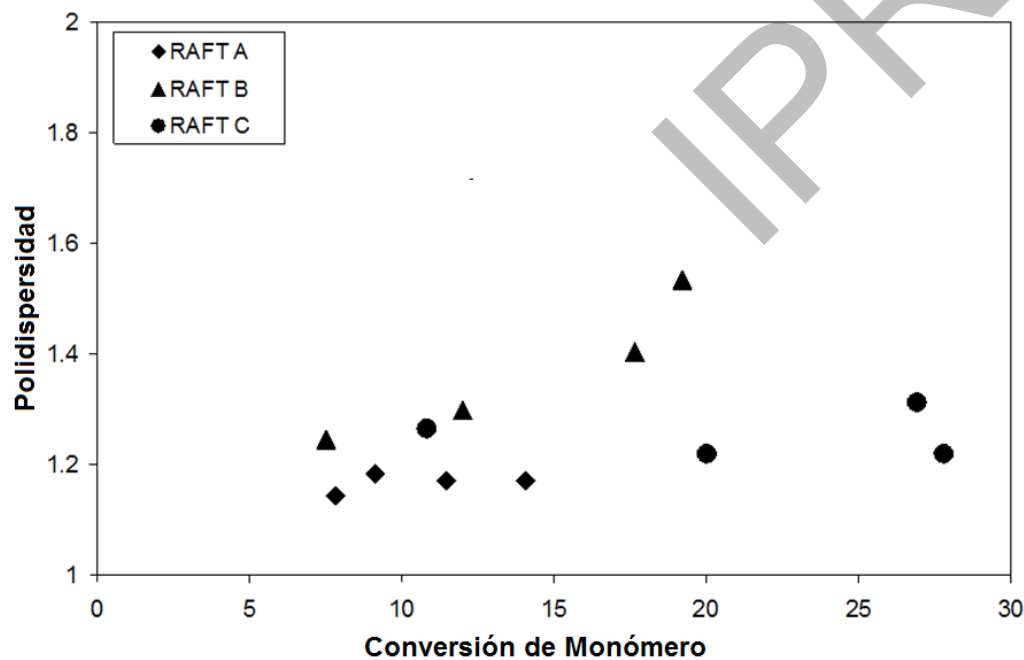
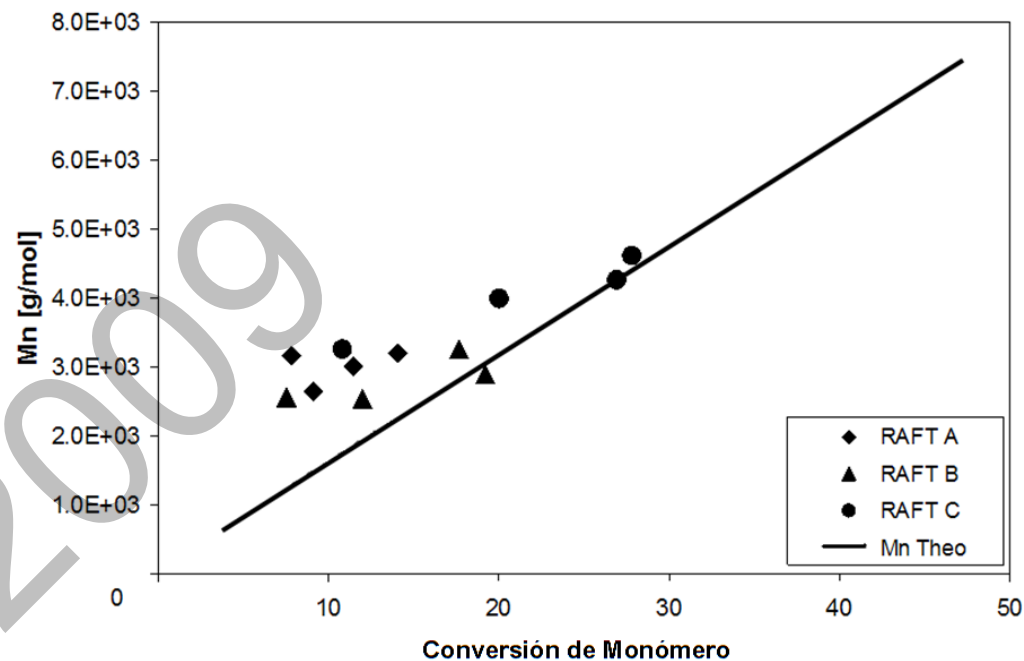
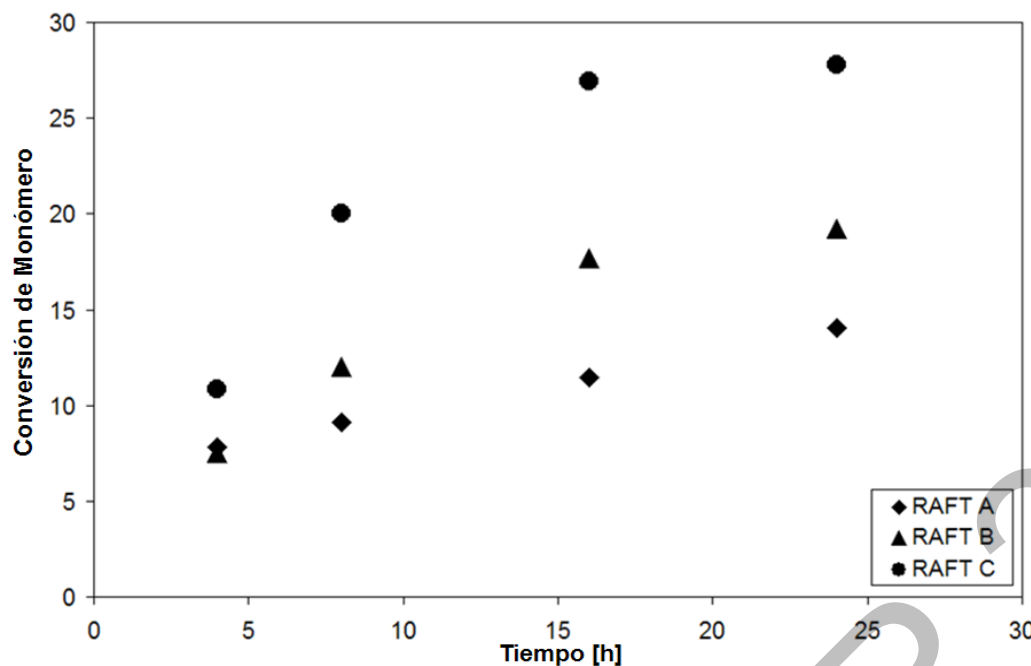
Krytox® 257 FSL.

<i>P</i> [bar]	%X MMA	<i>Mn</i> [g/mol]	<i>PDI</i>
100	67.56	12079	1.40
150	71.65	12362	1.68
200	75.57	12782	1.65
250	78.08	12900	1.86
350	87.65	14188	1.42
400	91.57	15060	1.36
450	95.08	15711	1.3
500	97.62	16783	1.29

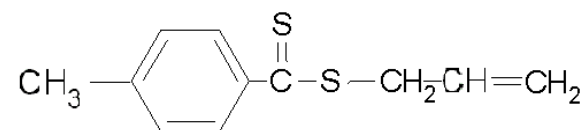
MMA RAFT POLYMERIZATION IN $scCO_2$



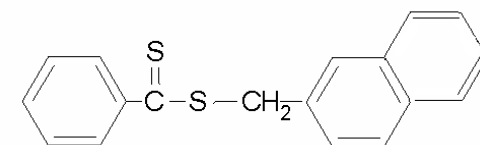
STY RAFT POLYMERIZATION IN $scCO_2$



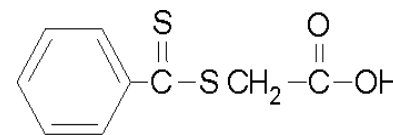
● *4-Methyl- allyl dithiobenzoate*



▲ *Methyl naphthalene dithiobenzoate*



◆ *S-(Thiobenzoil)thioglicolic acid*

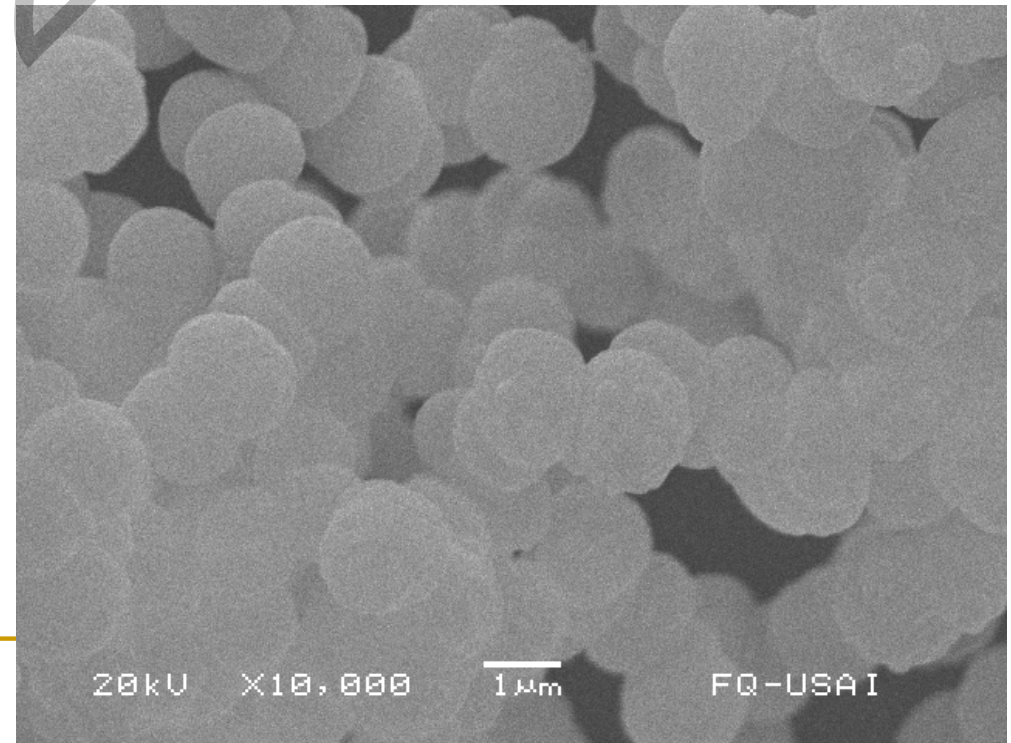


Effect of Stabilizer Concentration and Controller Structure and Composition on Polymerization Rate and Molecular Weight Development in RAFT Polymerization of Styrene in Supercritical Carbon Dioxide. G.Jaramillo-Soto et. al. Submitted to Polymer, under corrections.

EXPERIMENTAL CONCLUSIONS

- There are too many experimental factors to study.
 - Results strongly depends on the RAFT agent structure.
 - S-(thiobenzoil) thioglicolic better results with STY than MMA.
 - Stabilizer concentration importance.
 - Model optimization.
-

PERSPECTIVES

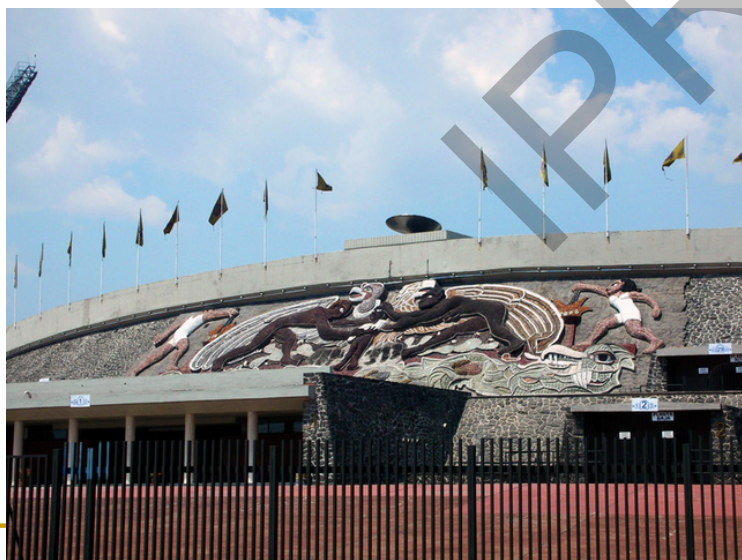


ACKNOWLEDGMENTS

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

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Dirección General de Apoyo al Personal Académico (DGAPA-UNAM) projects PAPIIT IN 10072 and IN 104107.



THANK YOU

