UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO

PROGRAMA DE DOCTORADO EN INGENIERÍA

FACULTAD DE QUÍMICA

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization in supercritical Carbon Dioxide ($scCO_2$)

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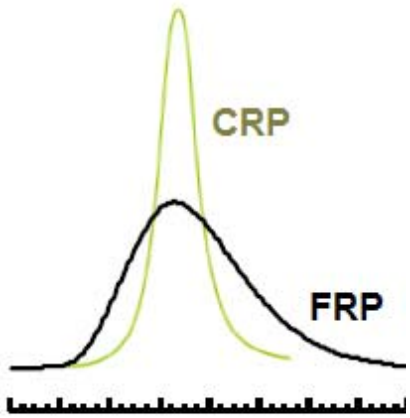
University of Waterloo, Waterloo, Ontario. Friday, May 1, 2009

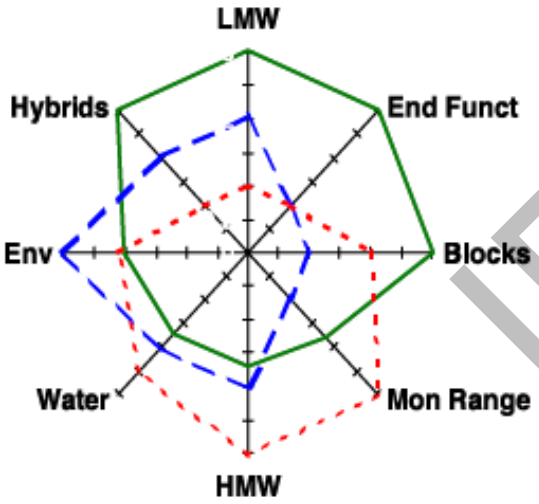
OUTLINE

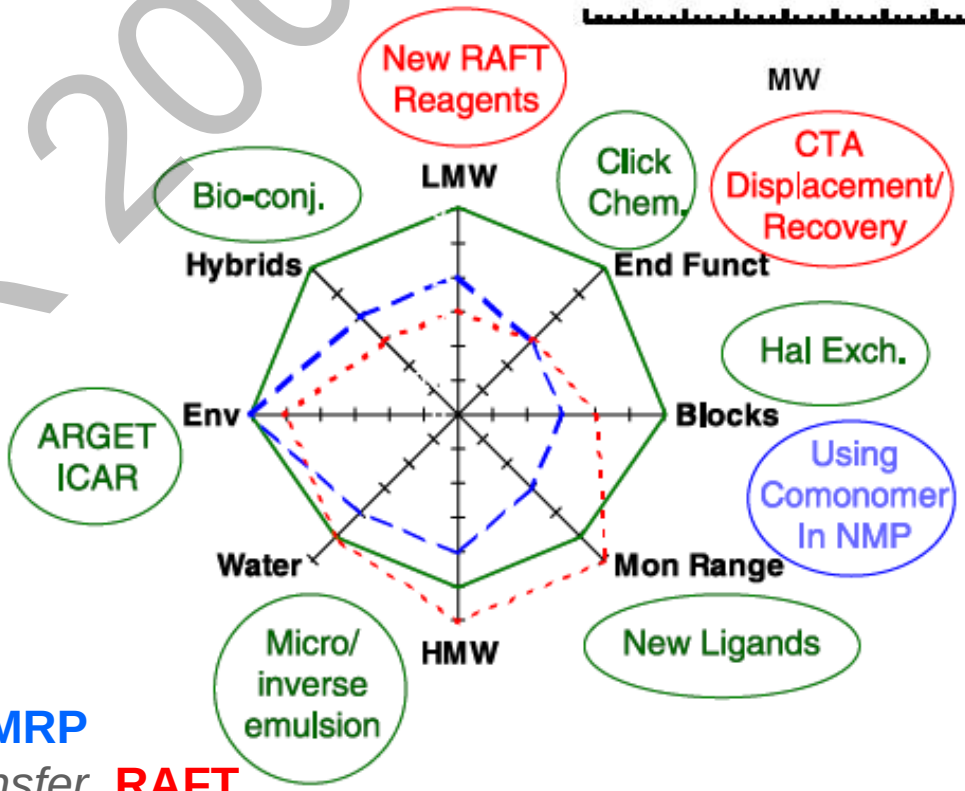
- Controlled Radical Polymerization
- RAFT Polymerization
- Why polymerization in $scCO_2$?
- State of the Art
- Model and Simulation
- Experimental Results
- Conclusions

CRP

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







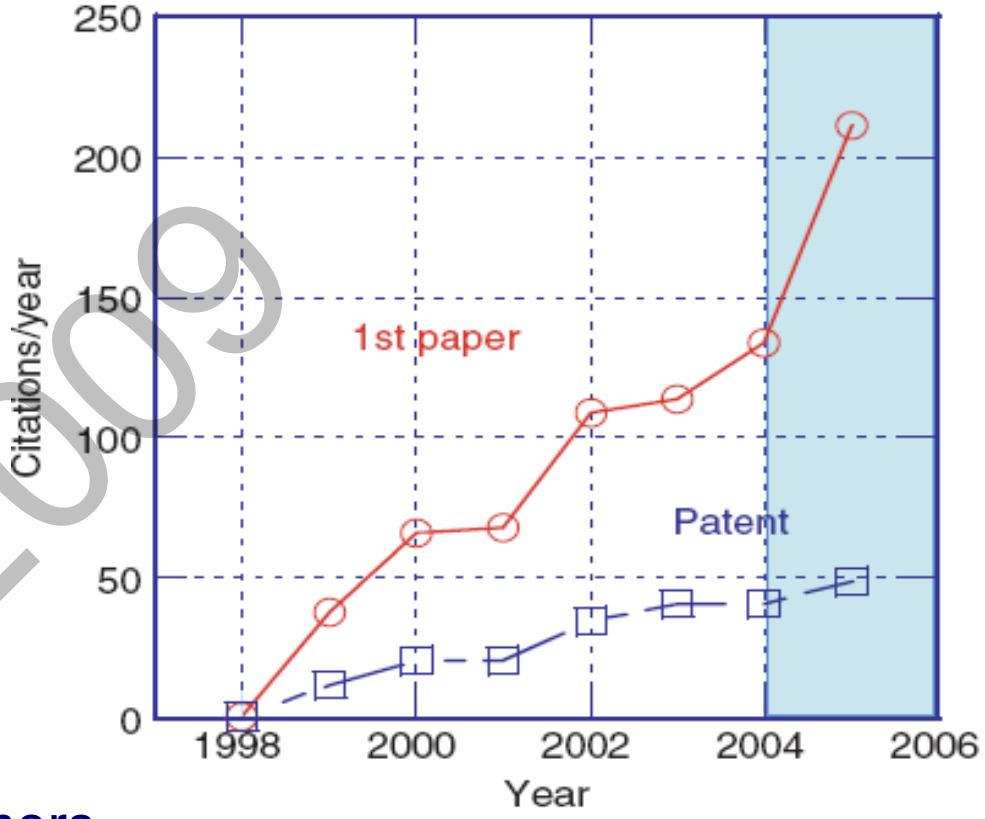
Atom Transfer Radical Polymerization, **ATRP**
Nitroxide Mediated Radical Polimerization, **NMRP**
Reversible Addition Fragmentation chain Transfer, **RAFT**

Prog. Polym. Sci. 32 (2007) 93–146. Wade A. Braunecker, Krzysztof Matyjaszewski

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.*

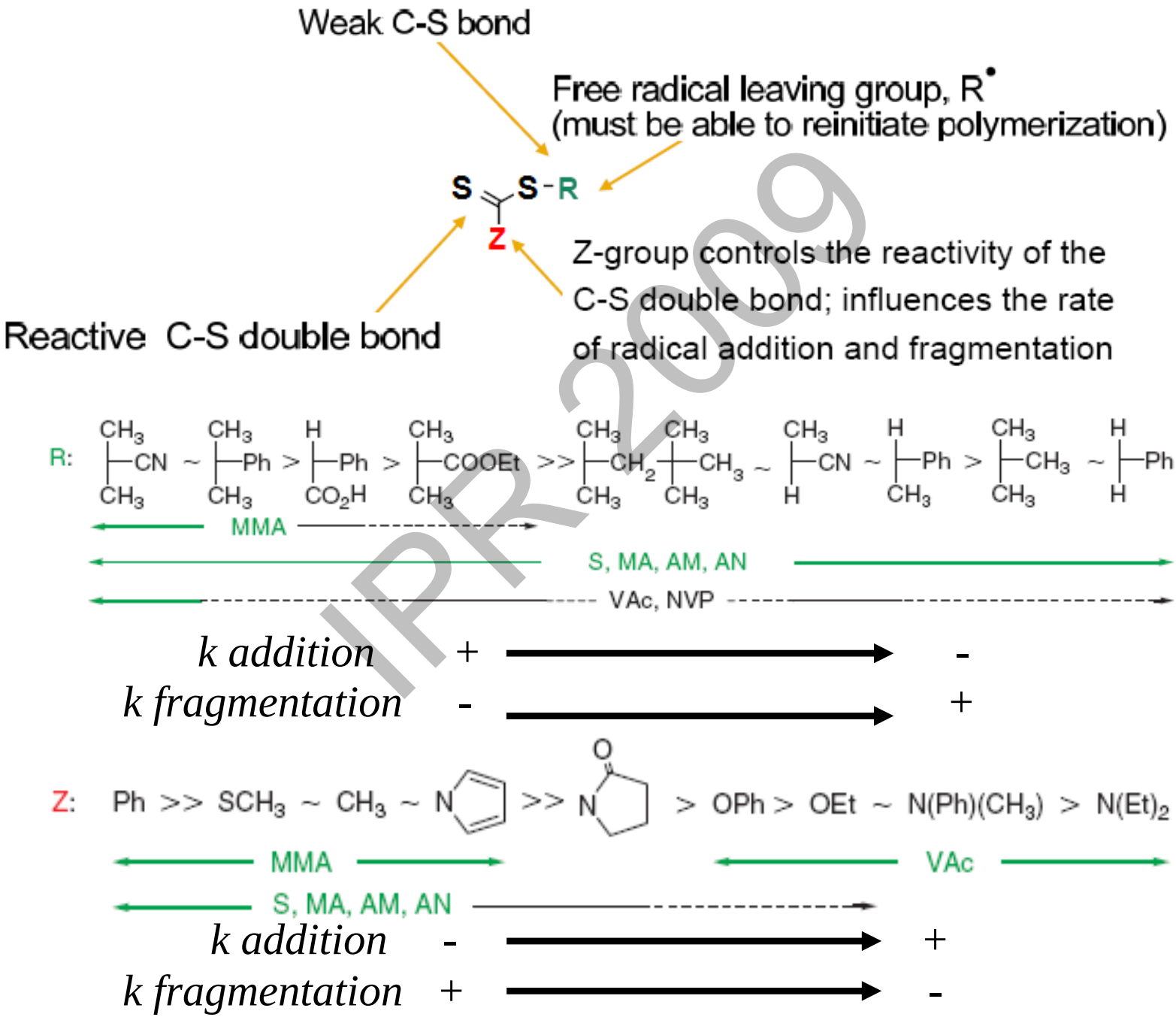
- First patent: *T. P. Le, G.Moad, E. Rizzardo, S. H.Thang, Int.Pat.WO9801478* ***1998*** *[Chem. Abs.* ***1998****, 128, 115390f].*



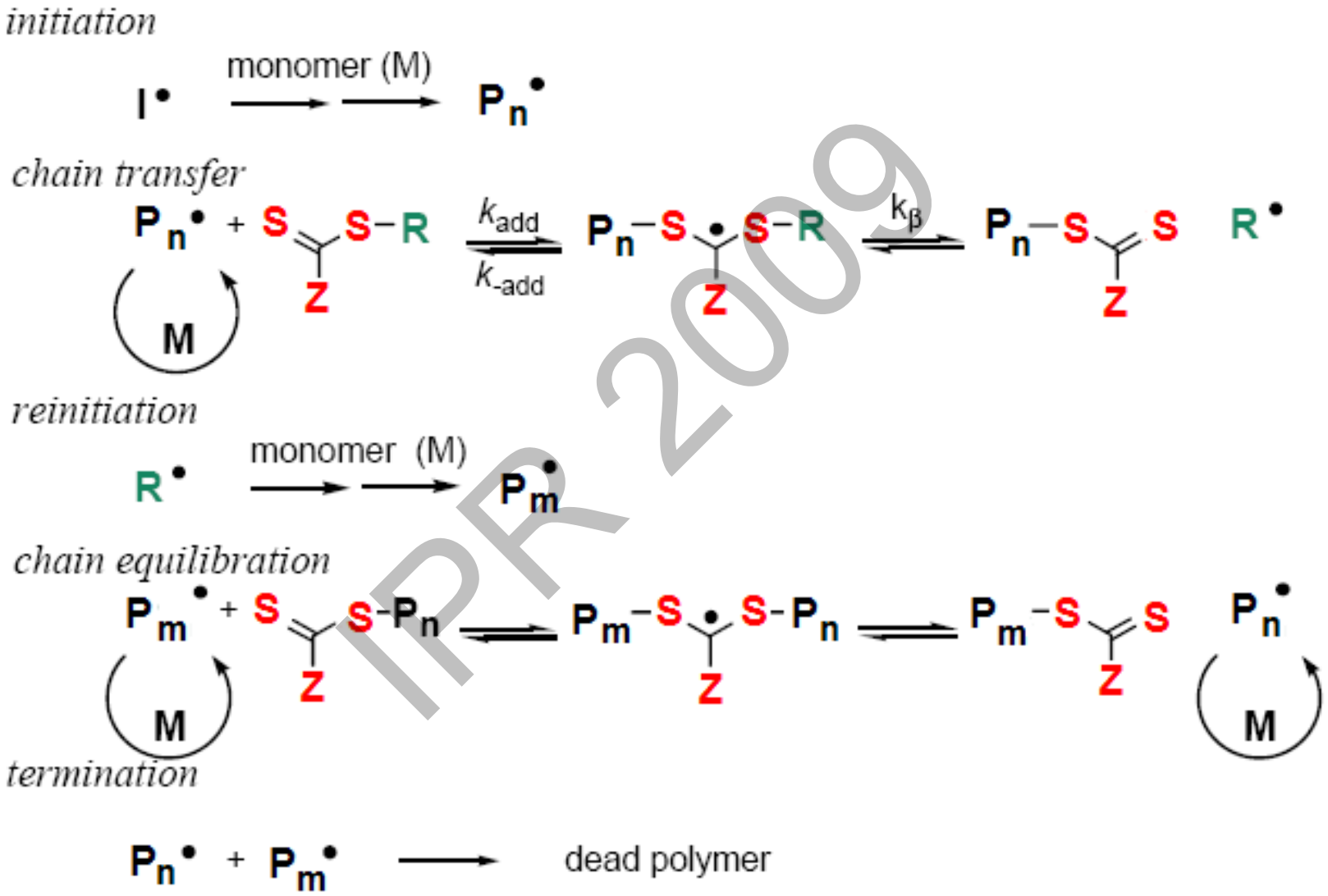
- ✓ Applicable to a large range of monomers
- ✓ Polymeric materials with controlled structure
- ✓ Success under a wide range of reaction conditions
- ✓ Wide variety of RAFT agents structures

Aust. J. Chem. **2006**, *59*, 669–692. *Graeme Moad*, *Ezio Rizzardo*, *and San H. Thang*

RAFT



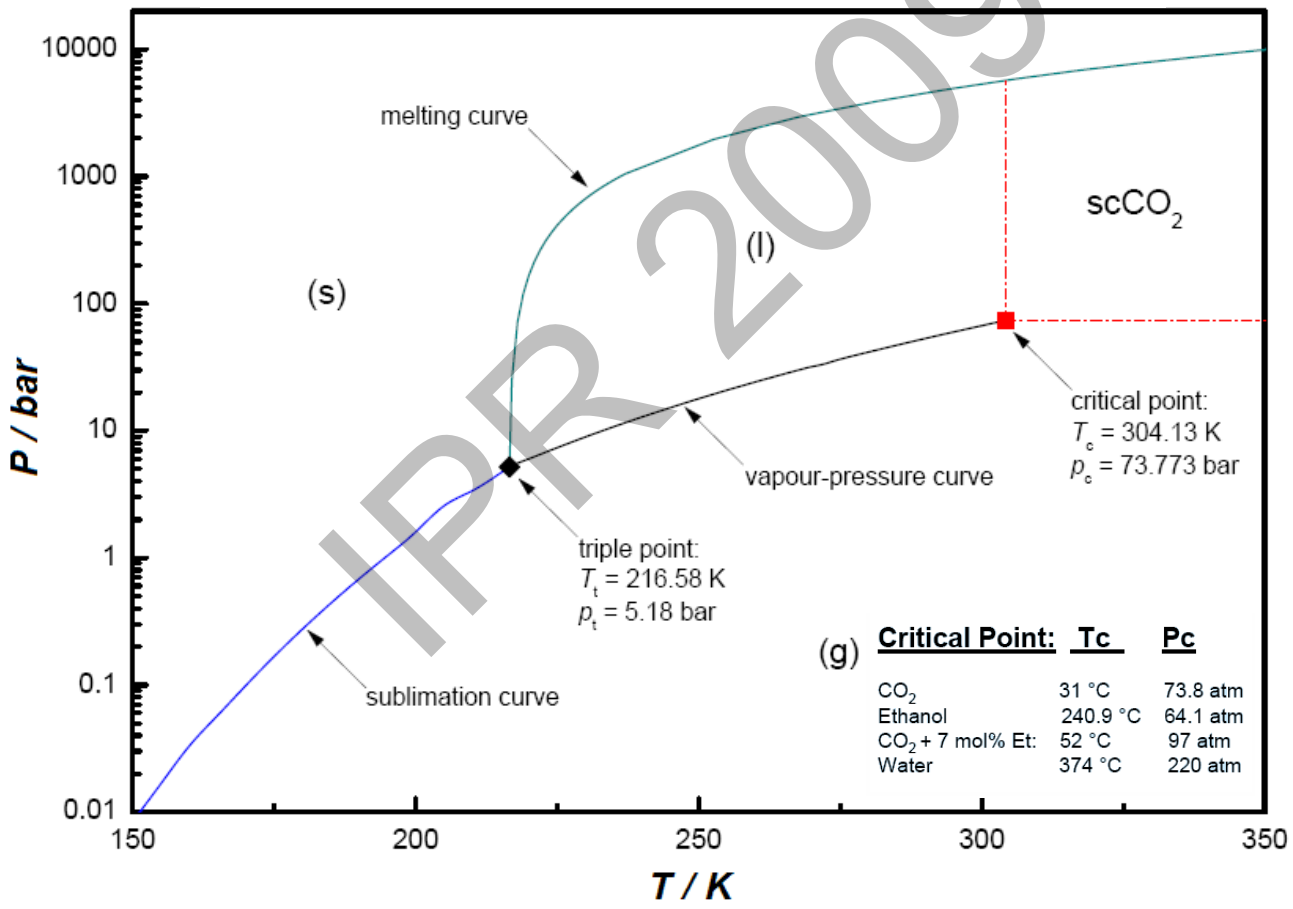
RAFT



Aust. J. Chem. 2005, 58, 379-410. Moad, G.; Rizzardo, E.; Thang, S. H.

$scCO_2$

	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*

$scCO_2$

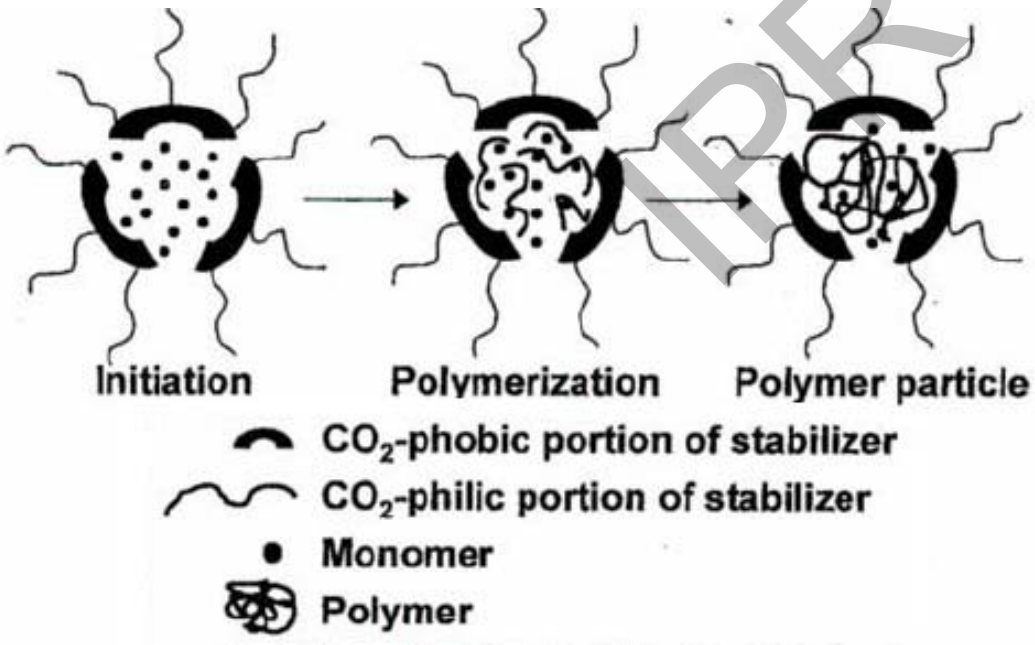
- ✓ High purity, low toxicity, low cost.
- ✓ Controllable dissolving power.
- ✓ Inert solvent.
- ✓ Low viscosity favors mass transportation.
- ✓ Advantages in the operation.

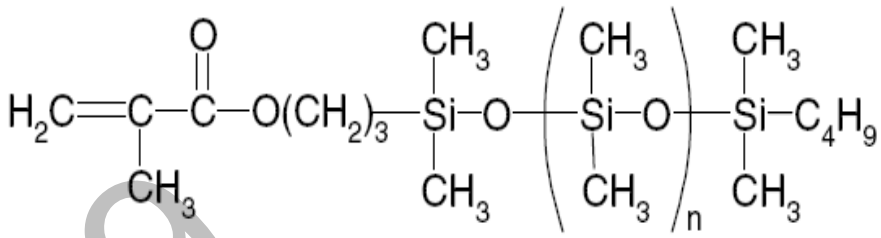
- o Elevated pressures required.
- o Compression costs.
- o High capital equipment investment.

RAFT POLYMERIZATION IN $scCO_2$

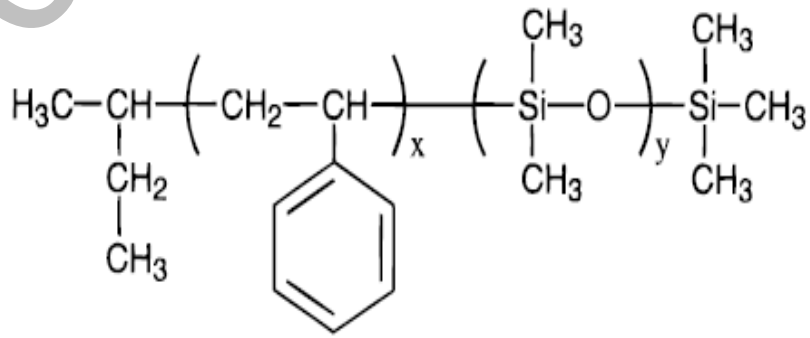
- Complexity of the kinetics and mechanisms presents
- Solubility of the RAFT agent, Z and R• groups
- Interaction between controller and surfactant in

dispersion polymerization

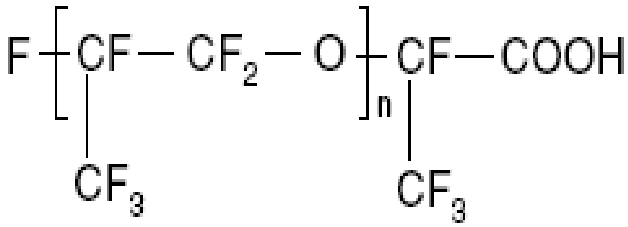




PDMS-MA



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

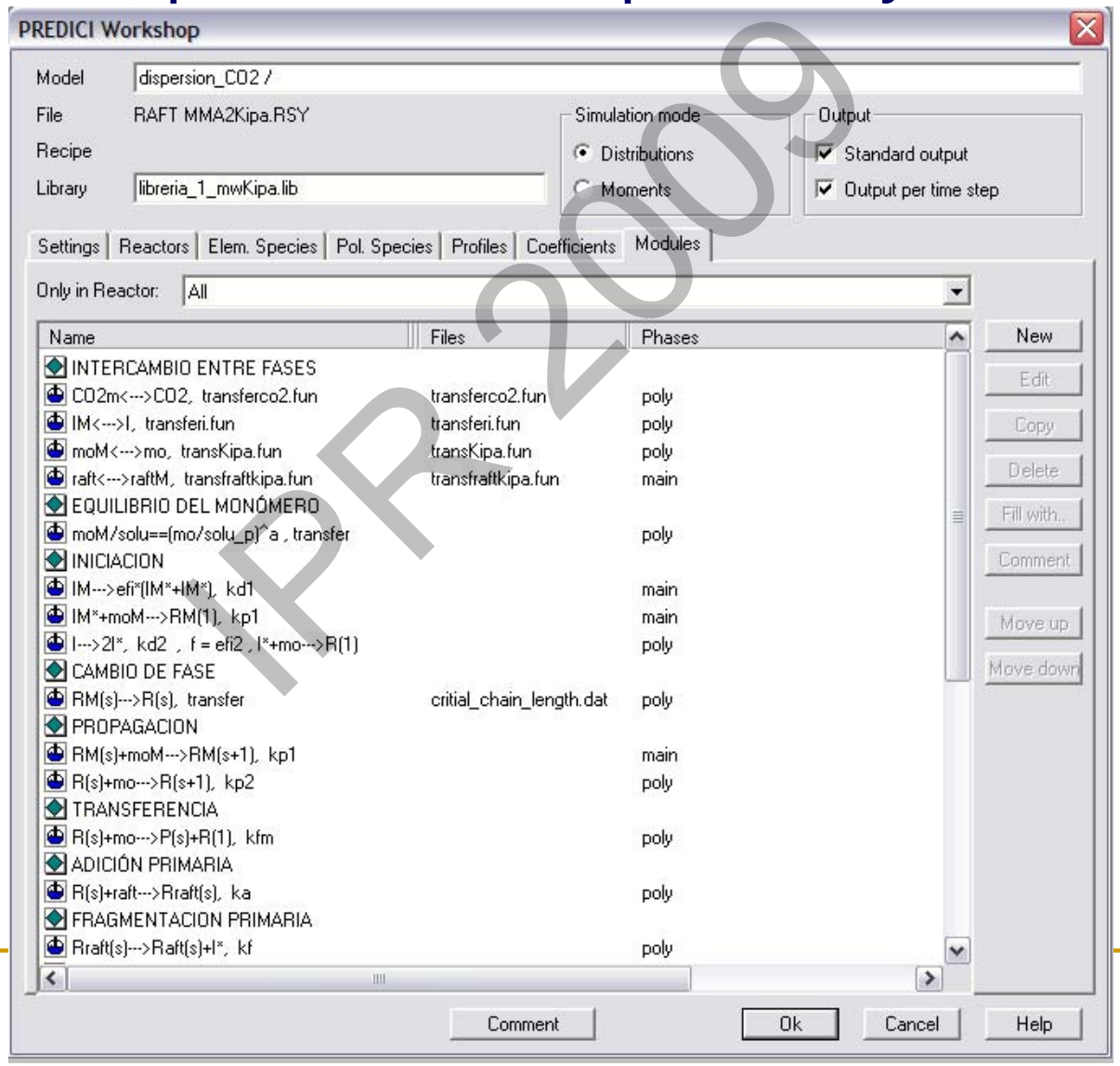
- Kristofer J. Thurecht, Andrew M. Gregory, Wenxin Wang, and Steven M. Howdle, **"***Living" Polymer Beads in Supercritical CO2* Communications to the Editor Macromolecules*, Vol. 40, No. 9, 2007*

- *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*

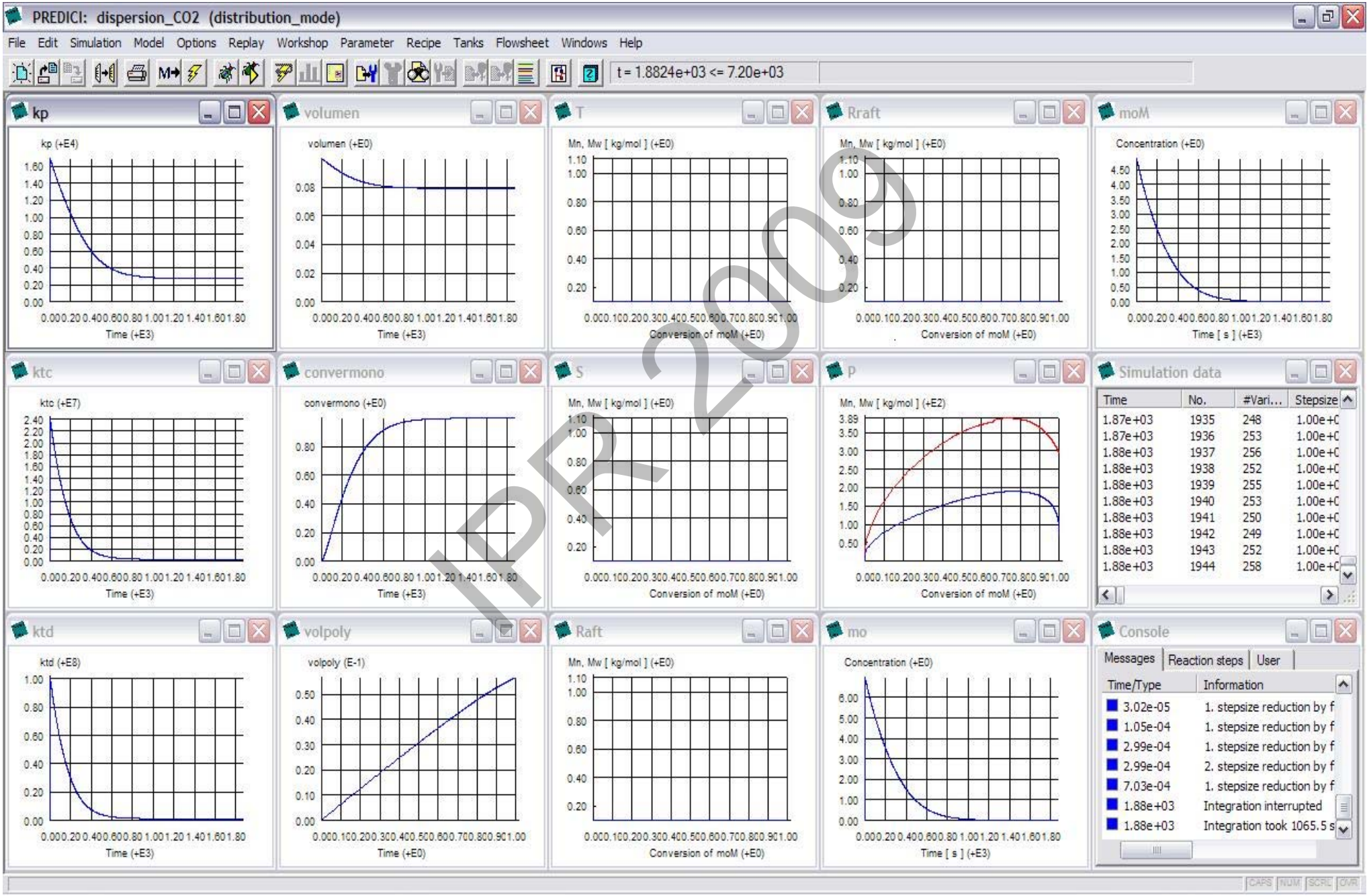
EXPERIMENTAL REPORTS, NOT SIMULATION OR MODELING STUDIES!

MODEL AND SIMULATION

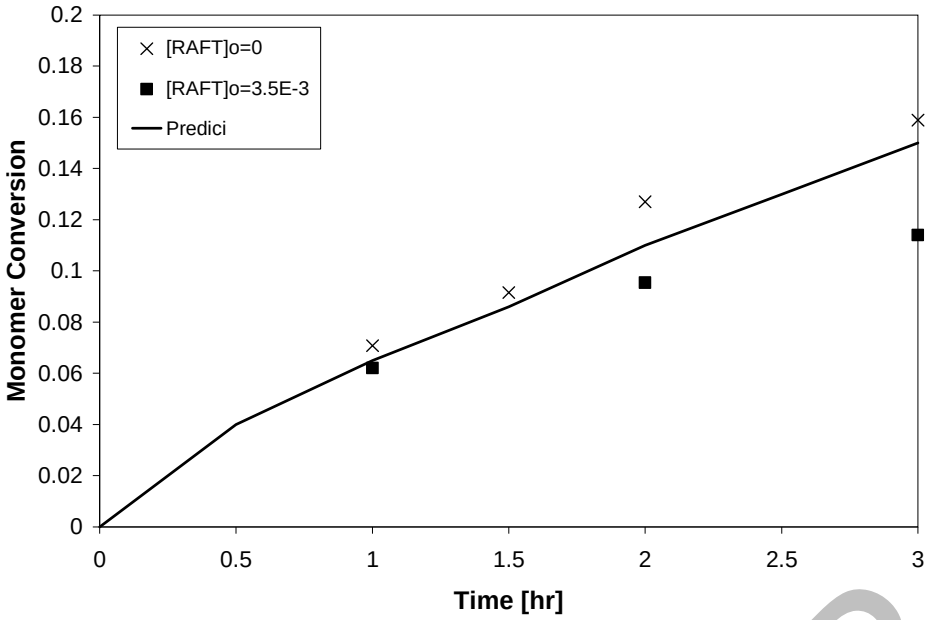
➔To develop a model, using Predici, for RAFT polymerization processes in dispersion systems in $scCO_2$.

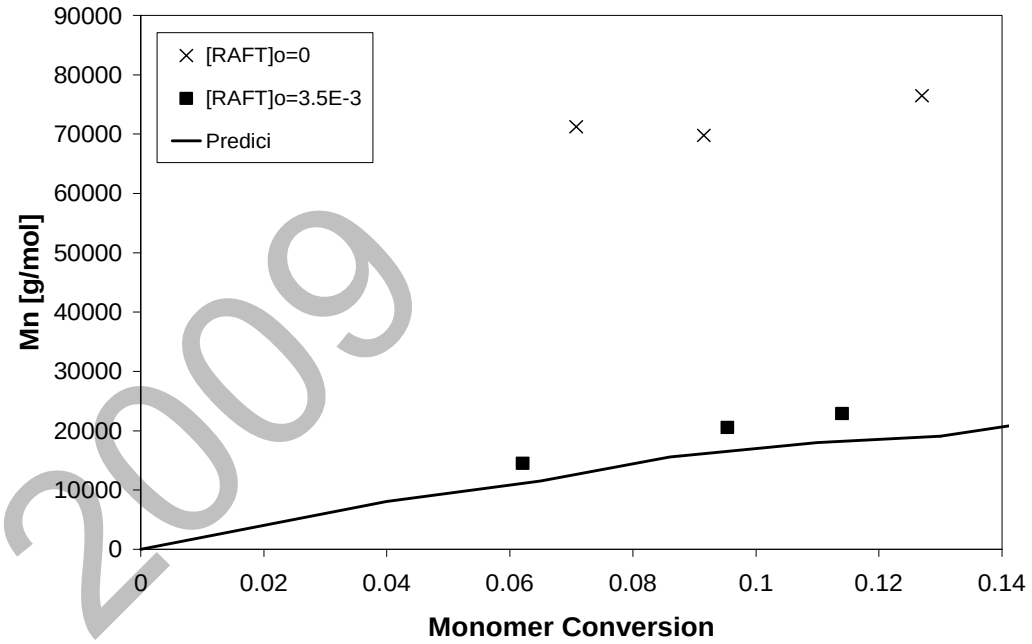


SIMULATION RESULTS



SIMULATION RESULTS





T= 80°C

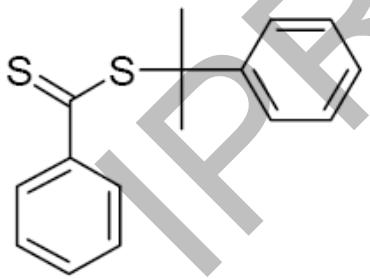
P= 300 bar

scCO2= 20% v/w

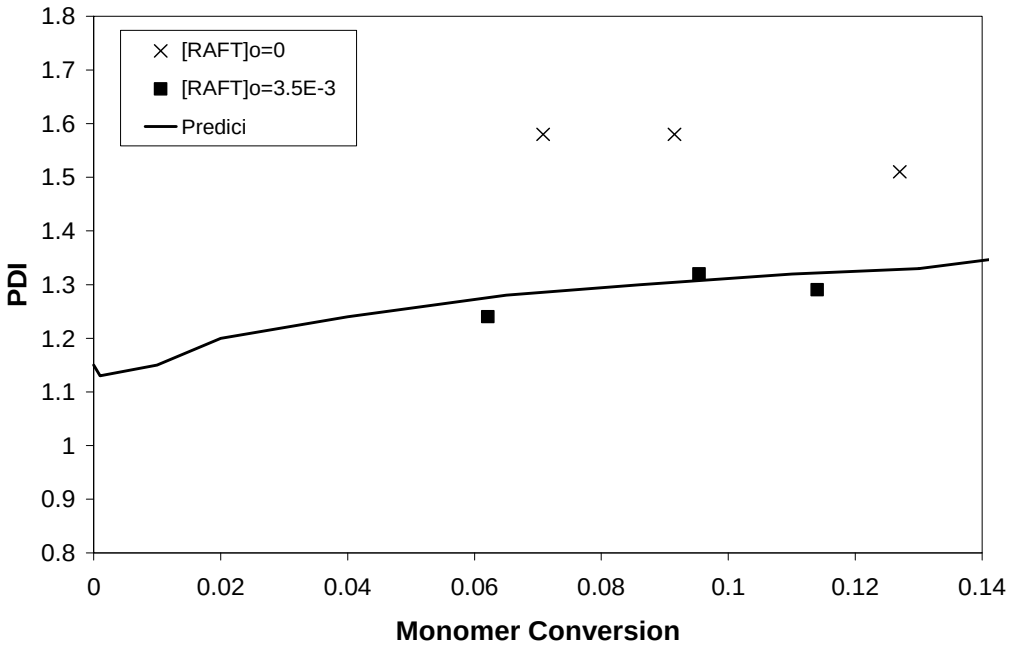
[AIBN]= $2.6X10^{-3}M$

[STY]= 6.49 M

[RAFT]= $7.0X10^{-3}M$



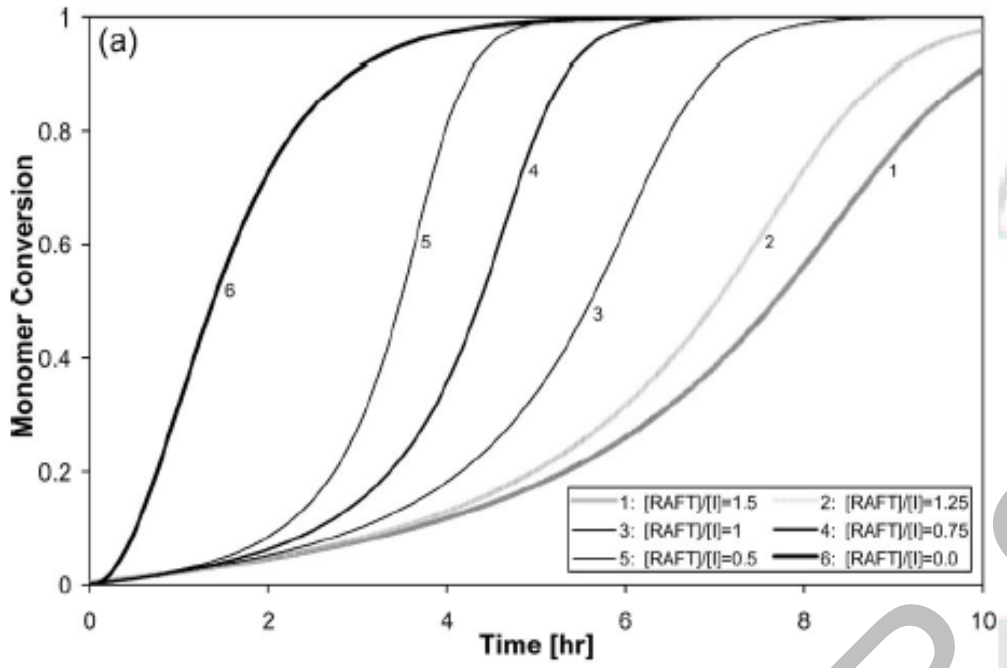
Cumil Ditiobenzoate (CDB)

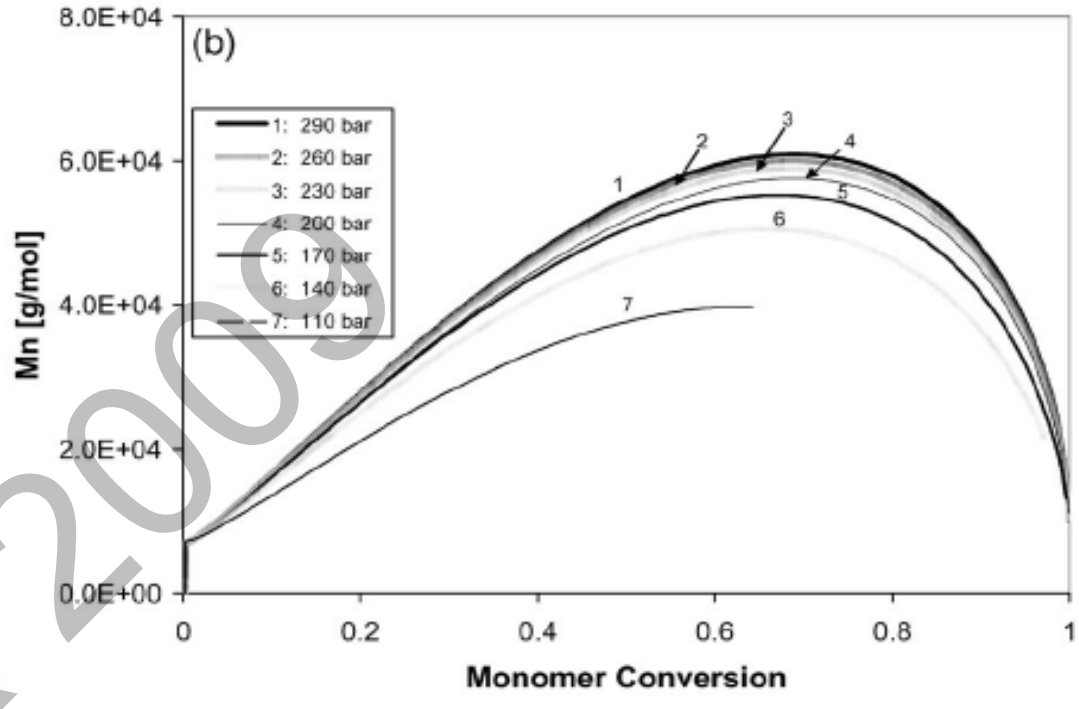


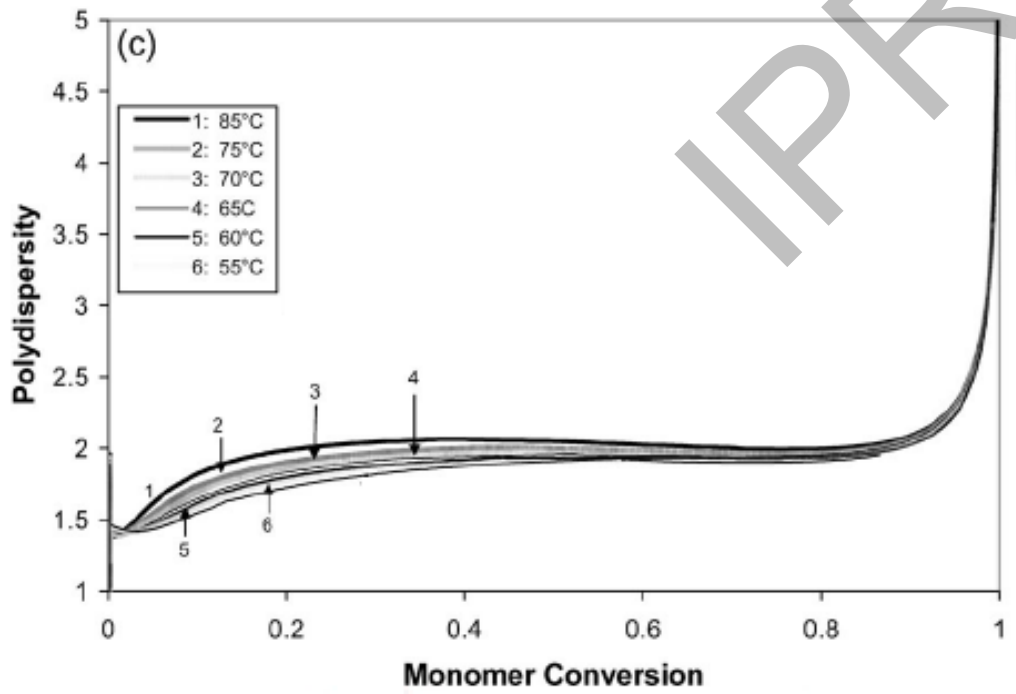
T. Arita, S. Beuermann, M. Buback, P. Vana

*e-Polymers **2004**, no. 003. http://www.e-polymers.org*

SIMULATION RESULTS







T= 65°C

P= 200 bar

scCO2= 20% v/w

[AIBN]= $1.19X10^{-2}M$

[MMA]= 1.96 M

[RAFT]= $1.19X10^{-2}M$

G. Jaramillo-Soto, et. al. Macromol. Theory Simul. 2008, 17, 280–289

SIMULATION CONCLUSIONS

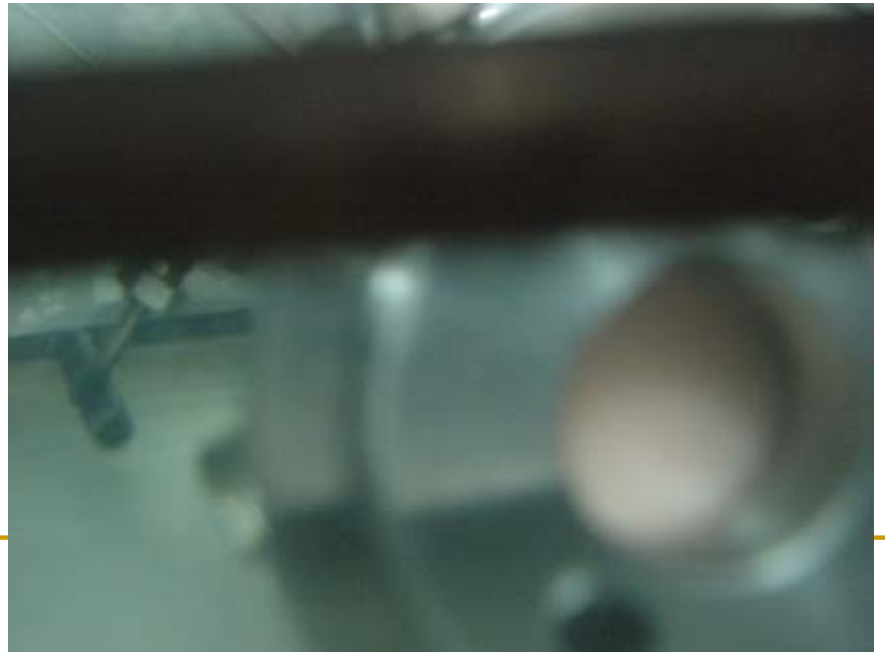
- The model captured the expected effects of RAFT agent to initiator ratio, pressure and temperature on polymerization rate an molecular weight development.

- 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

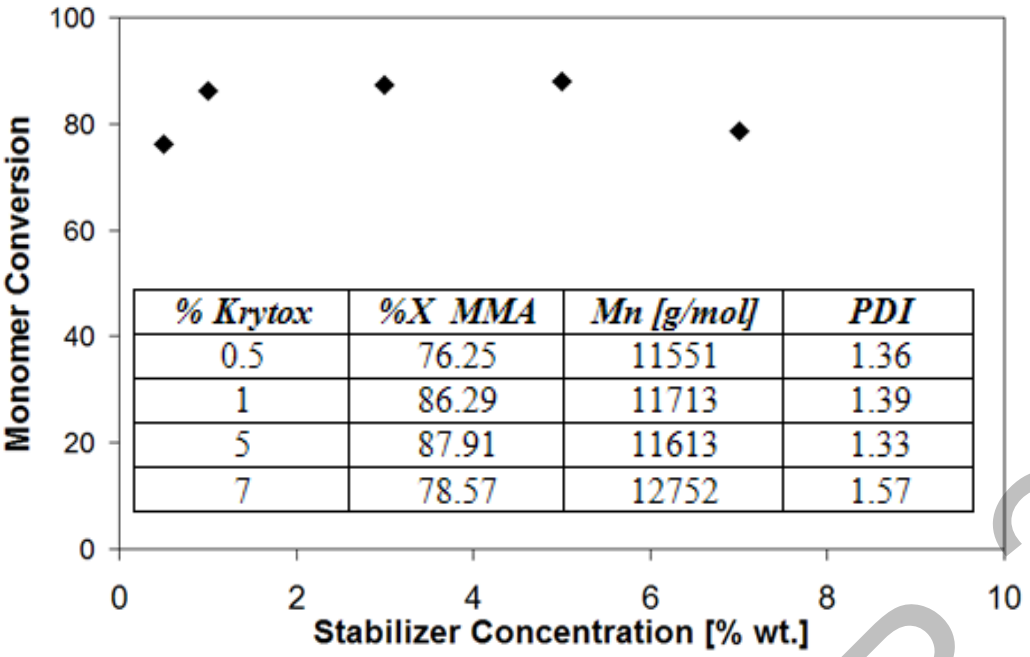
EXPERIMENTAL RESULTS



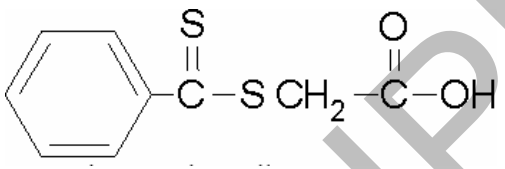
EXPERIMENTAL SYSTEM

EXPERIMENTAL SYSTEM

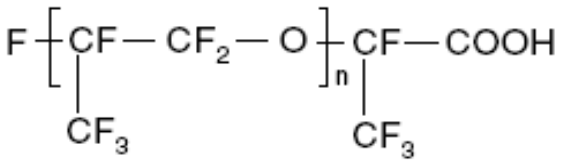
MMA RAFT POLYMERIZATION IN $scCO_2$



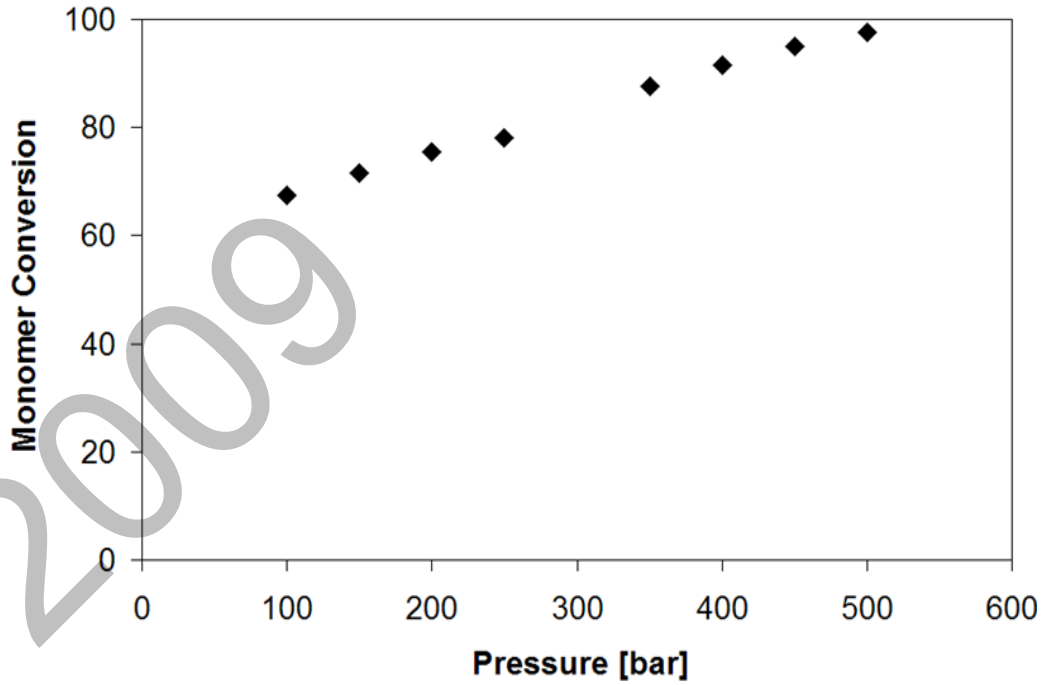
% Krytox	%X MMA	Mn [g/mol]	PDI
0.5	76.25	11551	1.36
1	86.29	11713	1.39
5	87.91	11613	1.33
7	78.57	12752	1.57



S-Thiobenzoyl thioglycolic acid



Krytox® 257 FSL.

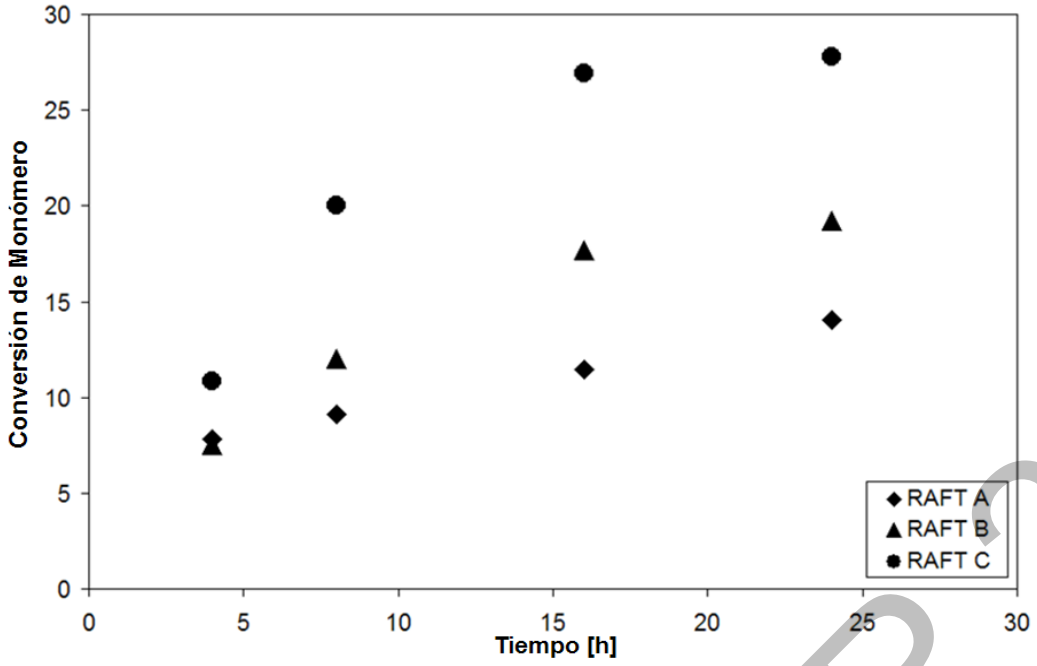


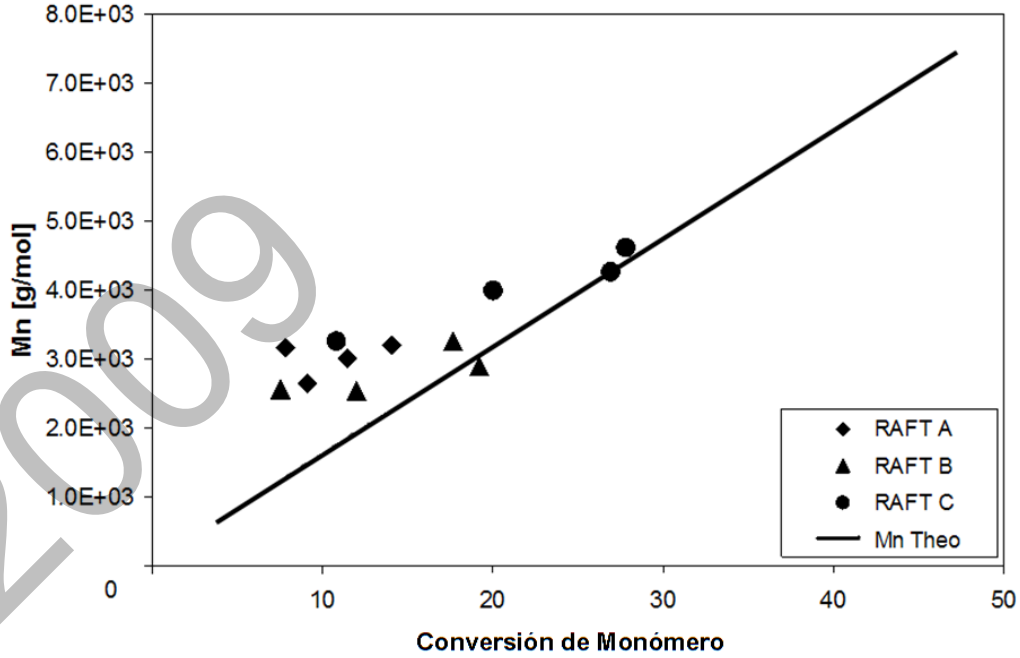
P [bar]	%X MMA	Mn [g/mol]	PDI
100	67.56	12079	1.40
150	71.65	12362	1.68
200	75.57	12782	1.65
250	78.08	12900	1.86
350	87.65	14188	1.42
400	91.57	15060	1.36
450	95.08	15711	1.3
500	97.62	16783	1.29

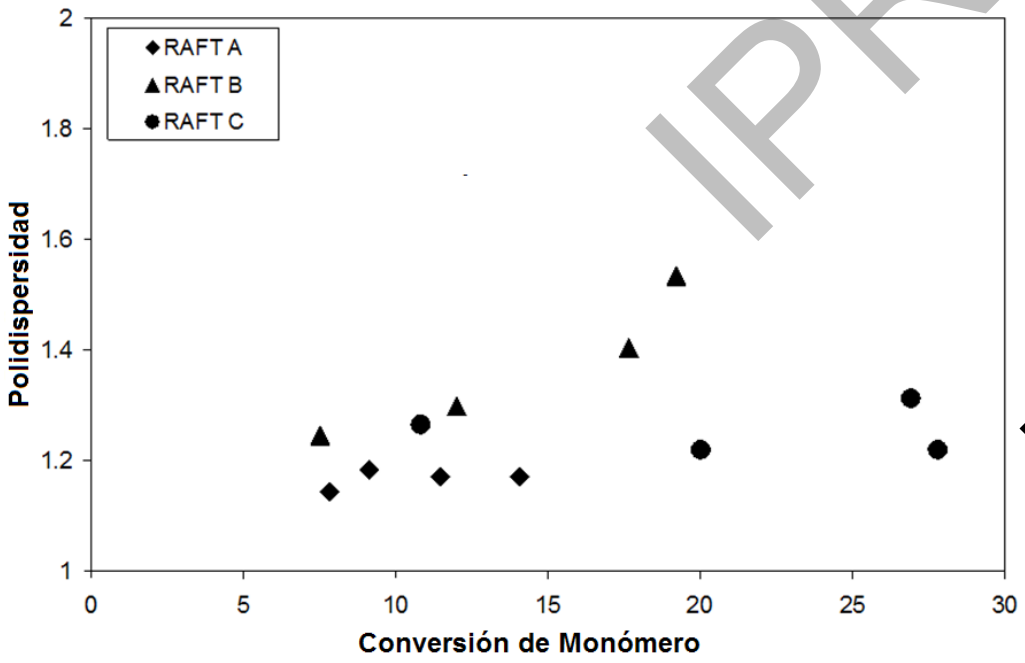
Effect of the Operating Pressure and Temperature on RAFT Mediated Dispersion Polymerization of MMA in scCO2
Gabriel Jaramillo-Soto, Pedro R. García-Morán and Eduardo Vivaldo-Lima
To be submitted.

MMA RAFT POLYMERIZATION IN $scCO_2$

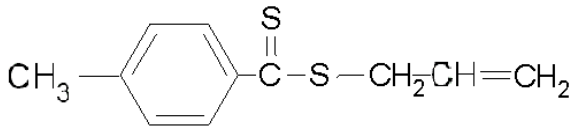
STY RAFT POLYMERIZATION IN $scCO_2$



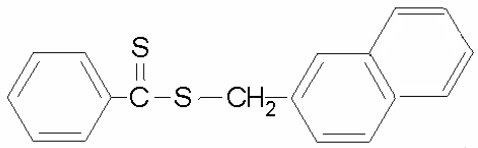




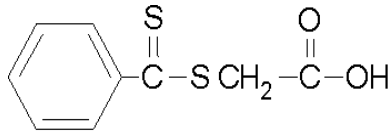
● *4-Methyl- allyl dithiobenzoate*



▲ *Methyl naphtalene dithiobenzoate*



◆ *S-(Thiobenzoil)thioglicolic acid*

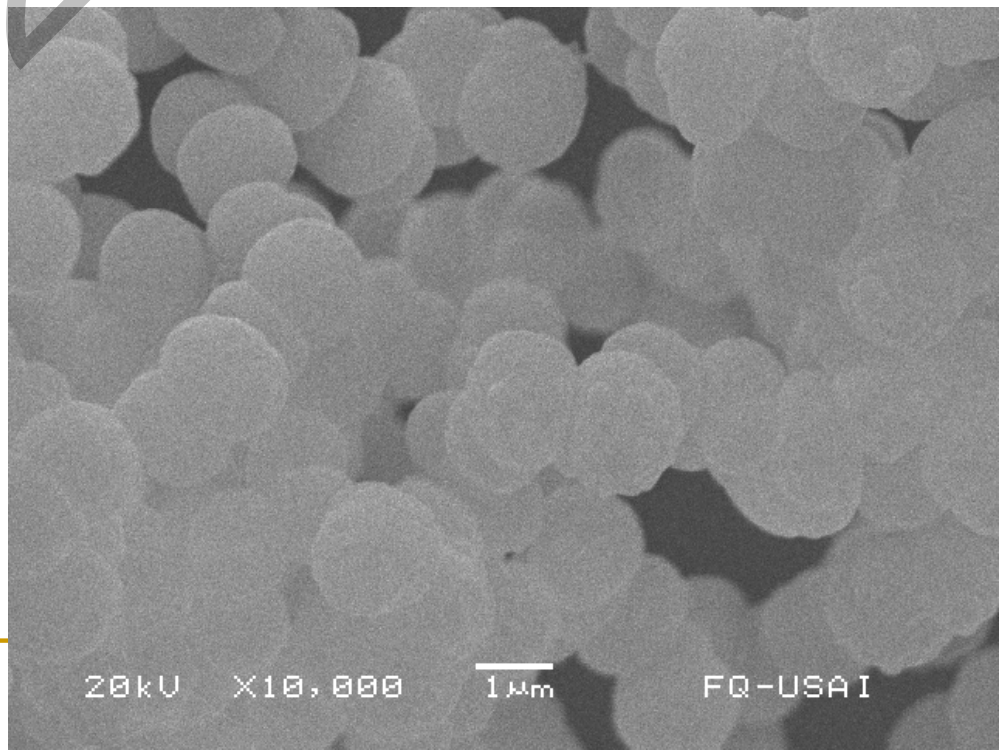


Effect of Stabilizer Concentration and Controller Structure and Composition on Polymerization Rate and Molecular Weight Development in RAFT Polymerization of Styrene in Supercritical Carbon Dioxide. G.Jaramillo-Soto et. al. Submitted to Polymer, under corrections.

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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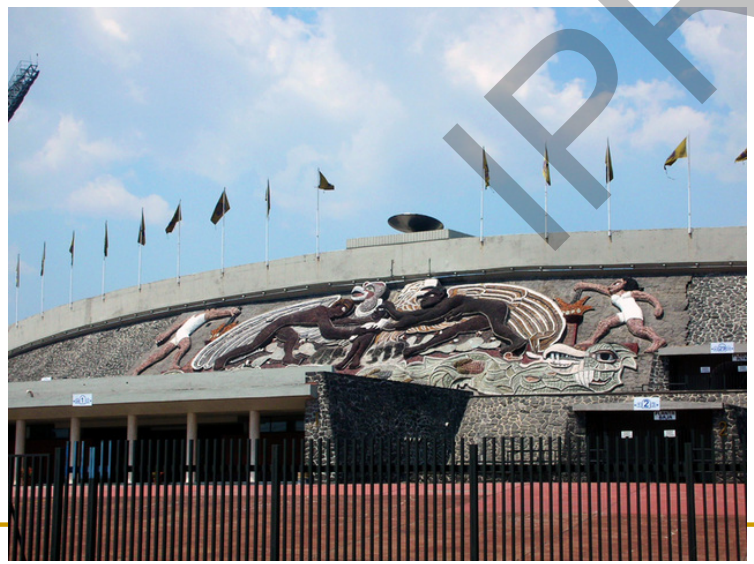

THANK YOU