



# AN EXPERIMENTAL AND MODELING STUDY OF THE REVERSIBLE ADDITION-FRAGMENTATION TRANSFER (RAFT) DISPERSION POLYMERIZATION OF STYRENE AND MMA IN SUPERCRITICAL CARBON DIOXIDE (scCO<sub>2</sub>)



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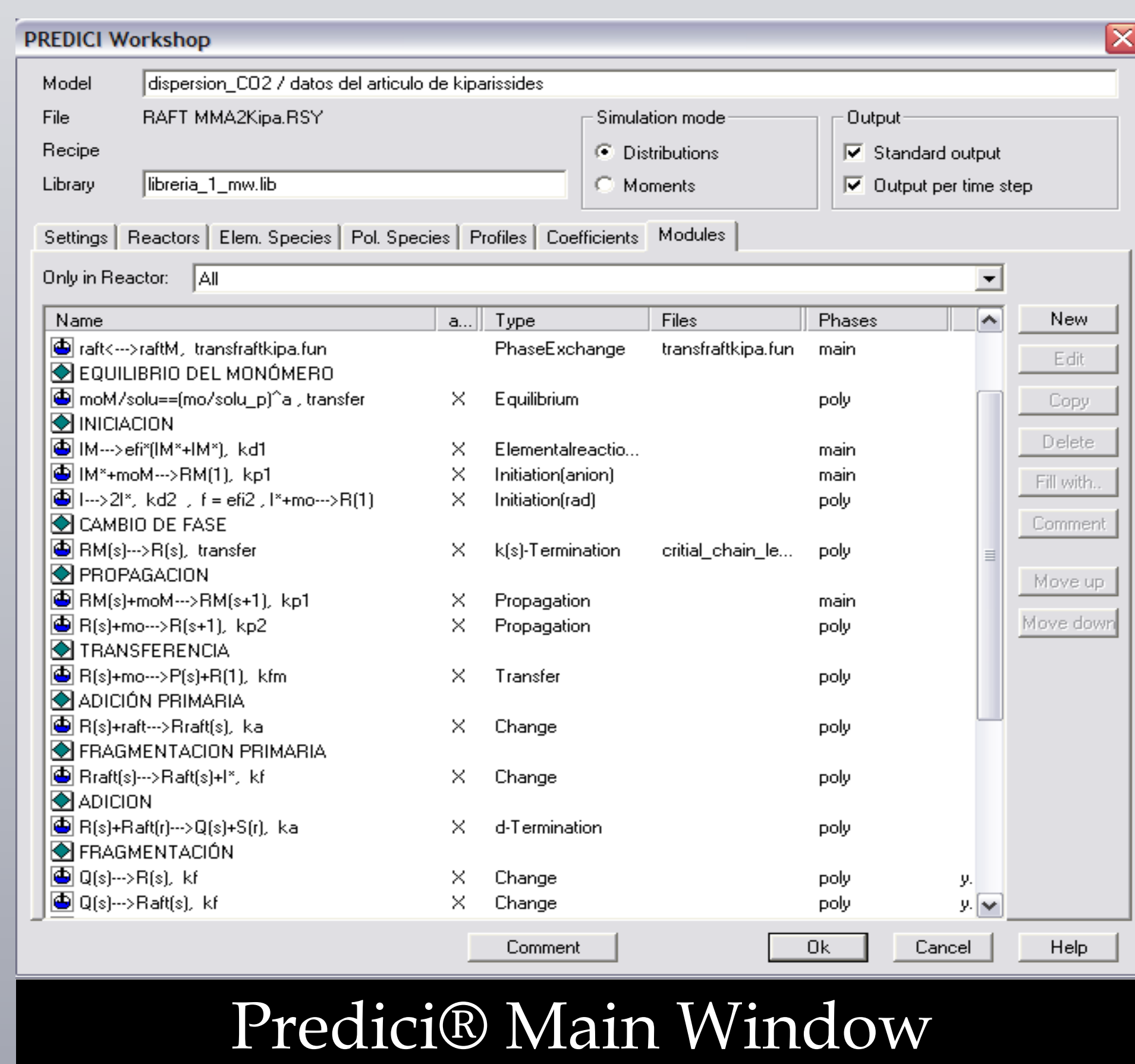
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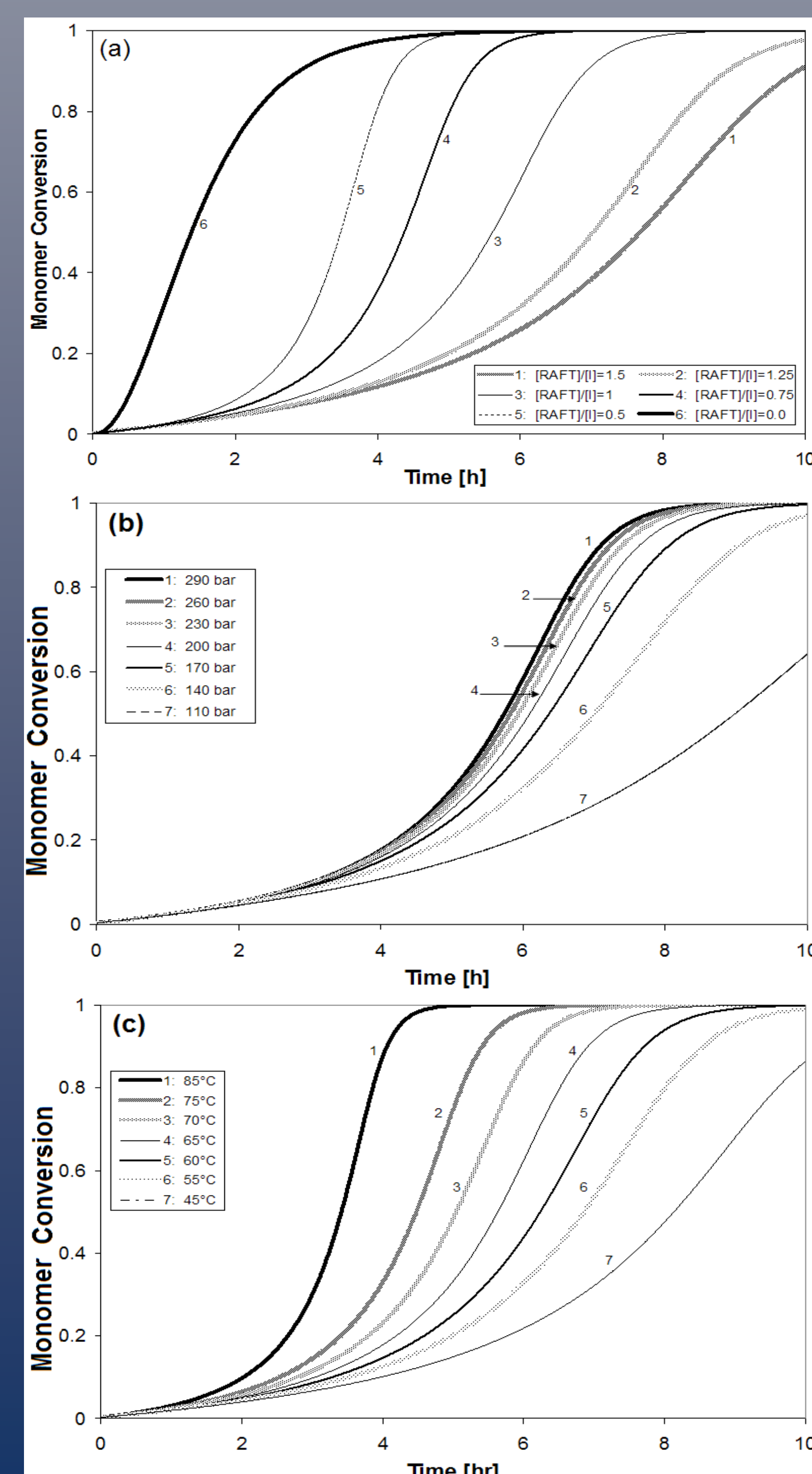
## OBJECTIVES

- Modeling the RAFT polymerization of MMA, carried out by dispersion polymerization in scCO<sub>2</sub>.
- Experimental study of the effect of changes in operating conditions initial concentration of the stabilizer, temperature and pressure, on the polymerization rate and MWD in the MMA polymerization system in scCO<sub>2</sub>.
- Evaluate RAFT agents for STY polymerization carried out by dispersion in scCO<sub>2</sub>.

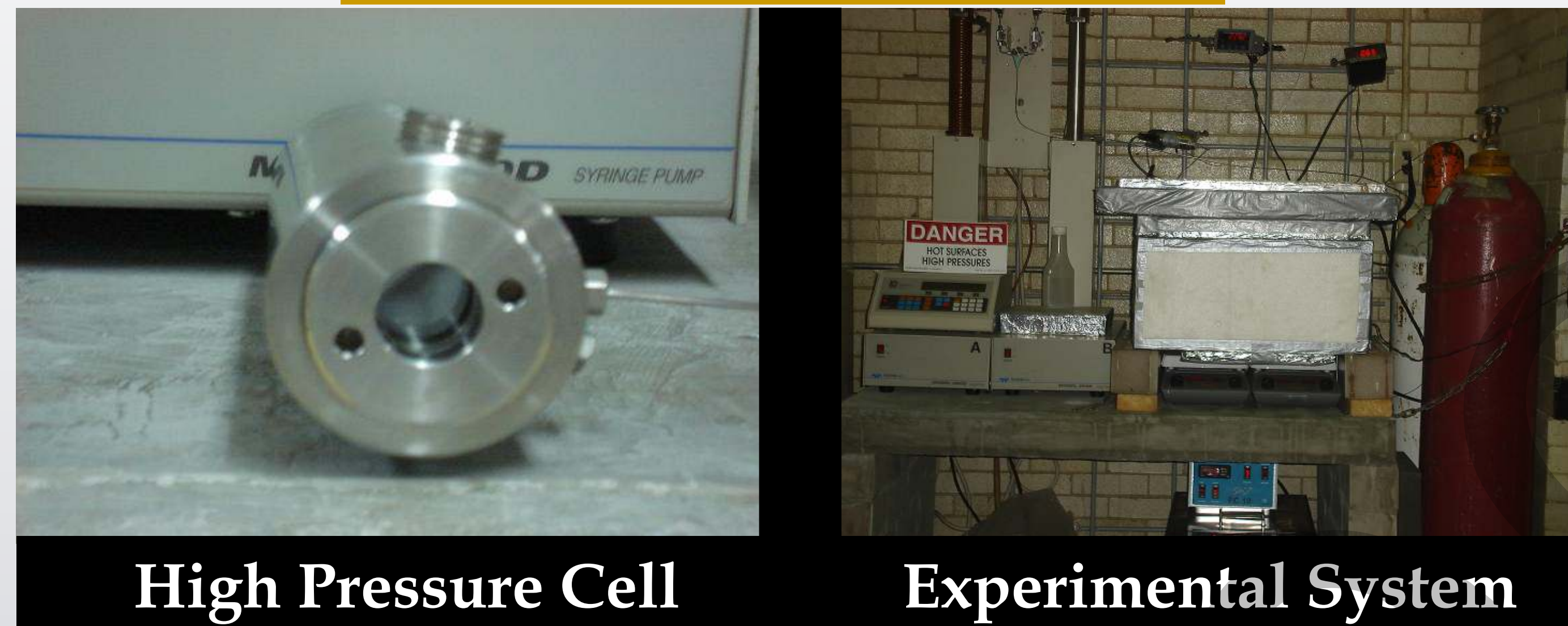
## MODELING [1]



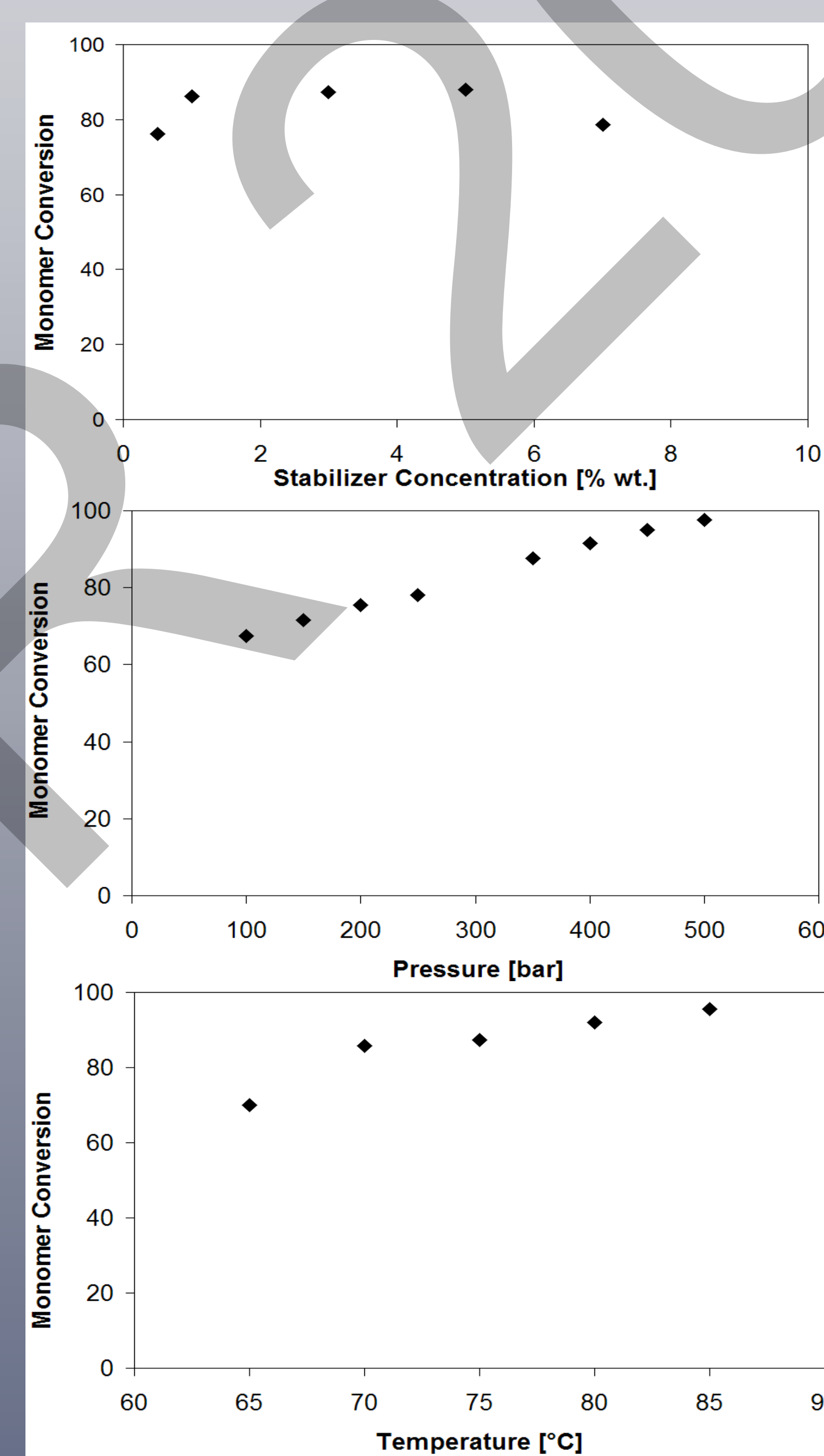
The simulations were carried out using kinetic and physical parameters corresponding to the polymerization of MMA in scCO<sub>2</sub>, using AIBN as initiator, at 65 °C and 200 bar, using values of the addition and fragmentation kinetic rate constants of a "typical" RAFT agent, as reference conditions.



## EXPERIMENTAL [2-3]



An experimental study on the kinetics and the effect of changes in operating conditions, temperature (65 to 85 °C) and pressure (100 to 500 bar), and the initial concentration of the stabilizer on the polymerization rate and molecular weight development in the RAFT mediated polymerization in dispersion of MMA in scCO<sub>2</sub> are reported. AIBN was used as initiator, S-Thiobenzoyl thioglycolic acid as RAFT agent and Krytox® as stabilizer.

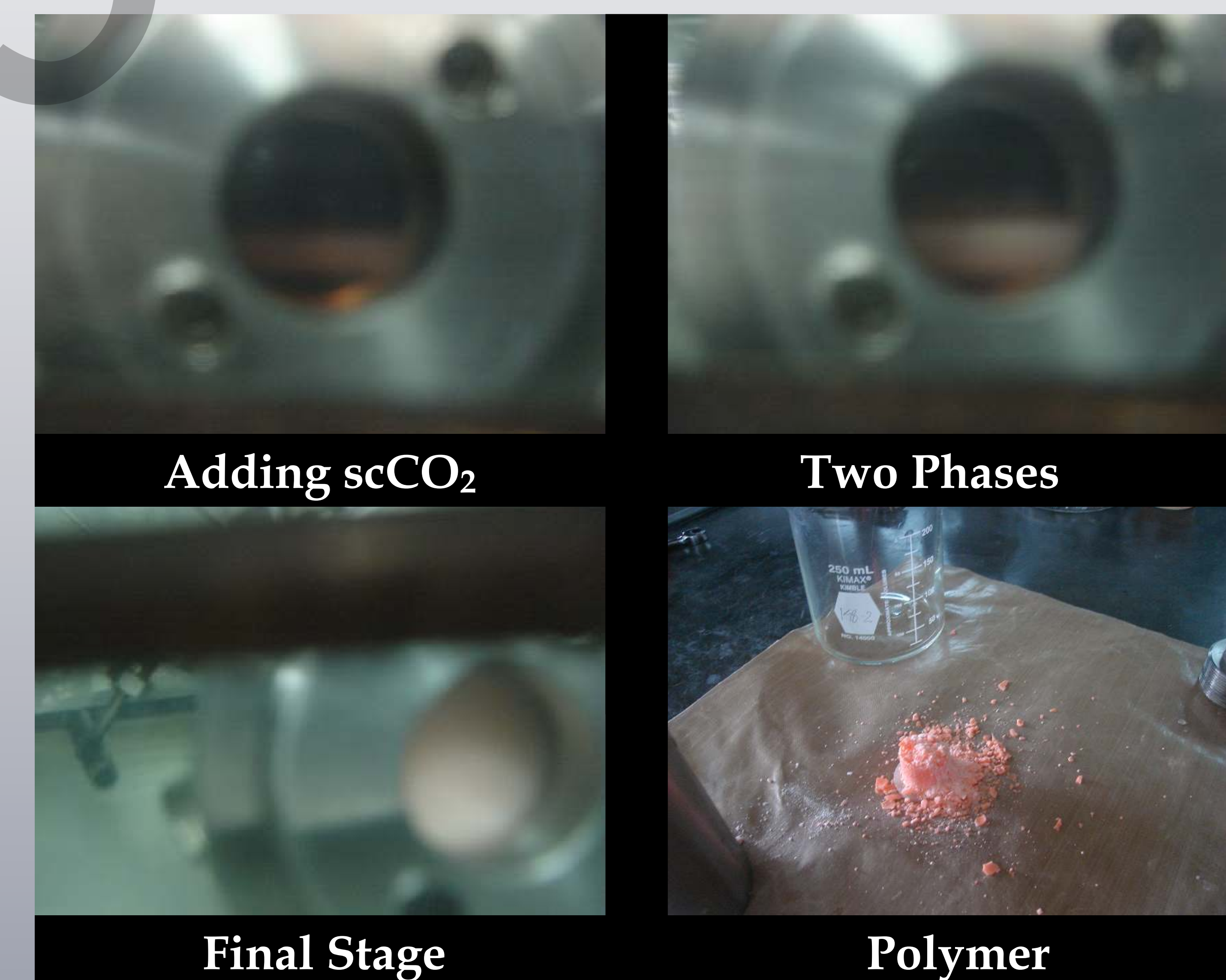
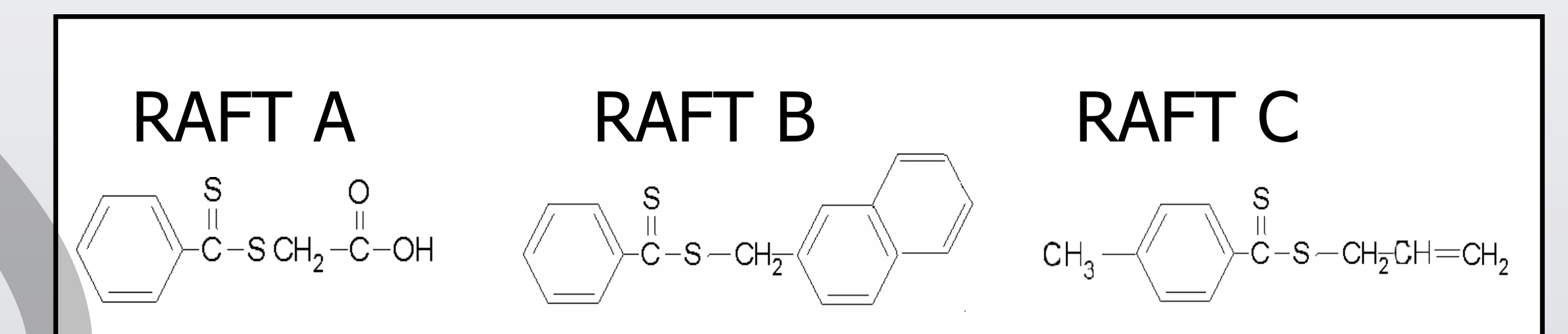


## CONCLUDING REMARKS

- The expected effects of controller to initiator ratio, pressure, temperature, and rate of transfer of polymer radicals from the continuous to the dispersed phase, on polymerization rate and molecular weight development, were adequately captured with our model.
- The polymerization rate and MWD strongly depend on the operating conditions, temperature and pressure. The experimental results confirmed the results predicted and allowed us to improve the model.
- Polymerizations of STY using either of the three controllers present low polymerization rates. The results obtained suggest that the addition and fragmentation reactions proceeded mainly in the dispersed phase.

[1] Gabriel Jaramillo-Soto, M. Luz Castellanos-Cárdenas, Pedro R. García-Morán, Eduardo Vivaldo-Lima, Gabriel Luna-Bárceñas, Alexander Penlidis. "Simulation of RAFT Dispersion Polymerization in Supercritical Carbon Dioxide" *Macromol. Theory Simul.* 2008, 17, 280–289  
 [2] Gabriel Jaramillo-Soto, Pedro R. García-Morán and Eduardo Vivaldo-Lima  
 "MMA RAFT Dispersion Polymerization in scCO<sub>2</sub>, the Effect of Operating Pressure and Temperature on MWD" To be submitted.  
 [3] Gabriel Jaramillo-Soto, Pedro R. García-Morán, Francisco J. Enríquez-Medrano, Hortensia Maldonado-Textle, Martha E. Albores-Velasco, Ramiro Guerrero-Santos, and Eduardo Vivaldo-Lima. "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" Submitted to *Polymer*, February 2009

A comprehensive investigation of RAFT mediated styrene polymerization comparing three control agents, S-Thiobenzoyl thioglycolic acid, Methyl naphthalene dithiobenzoate and 4-Methyl allyl dithiobenzoate, is presented.



Polymerizations were carried out using AIBN as initiator and Poly(styrene-b-dimethylsiloxane), P(S-b-DMS) as surfactant.

The influence of the structure of the RAFT agent over the Monomer Conversion, Molecular Weight and Poldispersity is shown in the next figures.

