



Experimental Study on the Free-Radical Copolymerization Kinetics with Crosslinking of Styrene and Divinylbenzene in Supercritical Carbon Dioxide¹



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Introduction

Supercritical carbon dioxide (scCO₂) is important as solvent in polymerization processes^{1,2}. The copolymerization of styrene and divinylbenzene (DVB) in scCO₂ has already been reported^{3,4}. Poly(styrene-co-divinylbenzene) PSDVB, is important for chromatographic columns, ion exchange resins, immobilization of enzymes, catalytic supports^{5,6}, etc. The homogeneity of the polymer network is critical for their performance in applications.

A study on the effect of process conditions (temperature and pressure) and formulation (stabilizer concentration, crosslinker concentration, and monomer/solvent ratio) on the kinetics and particle properties (size and shape) in the copolymerization of styrene and DVB in scCO₂ is presented here. Poly(styrene-*b*-dimethylsiloxane), PSDMS, synthesized by anionic polymerization was used as stabilizer (M_n of 55,000 g/mol), with a block ratio of 1 to 9 of polystyrene to polydimethylsiloxane. A 38 mL, high pressure view cell, equipped with one frontal and two lateral sapphire windows was used as the reacting vessel. Total monomer conversion was determined gravimetrically and gel content was determined by extraction with a Soxhlet apparatus, using toluene. Particle size and shape were measured by scanning electron microscopy, SEM. DVB55 was used as crosslinker and AIBN as initiator. Temperature and pressure varied from 65 to 80 ° C and from 172 to 310 bars, respectively¹.

General Objective

Conducting an experimental study of the effect of the type and concentration of surfactant, cross-linker, monomer mass/reaction volume ratio, pressure and temperature on monomer conversion and particle size and shape.

Specific Objectives

➤ Synthesize and evaluate a surfactant of poly(styrene-*b*-dimethylsiloxane) for experimental studies of styrene and DVB copolymerization in scCO₂, and compare the results with a fluorinated commercial surfactant, Krytox 257FSL.

➤ Synthesize copolymers of PSDVB in scCO₂ at different temperatures, pressures and compositions of the reaction mixture, and characterize them for monomer conversion, particle size (SEM), sol and gel, molecular weight of the sol, and correlate these parameters with reaction conditions.

The Dispersion Polymerization Process

a) Homogeneous reaction mixture

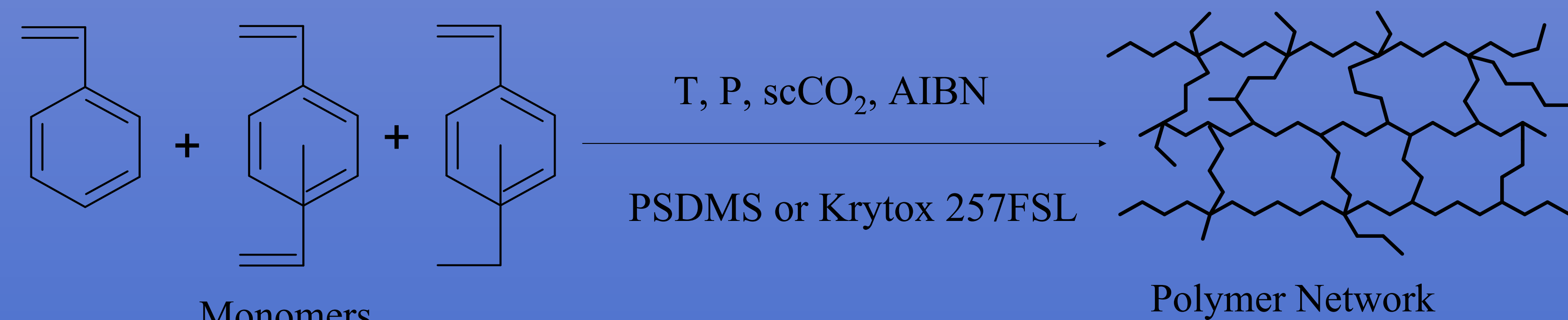
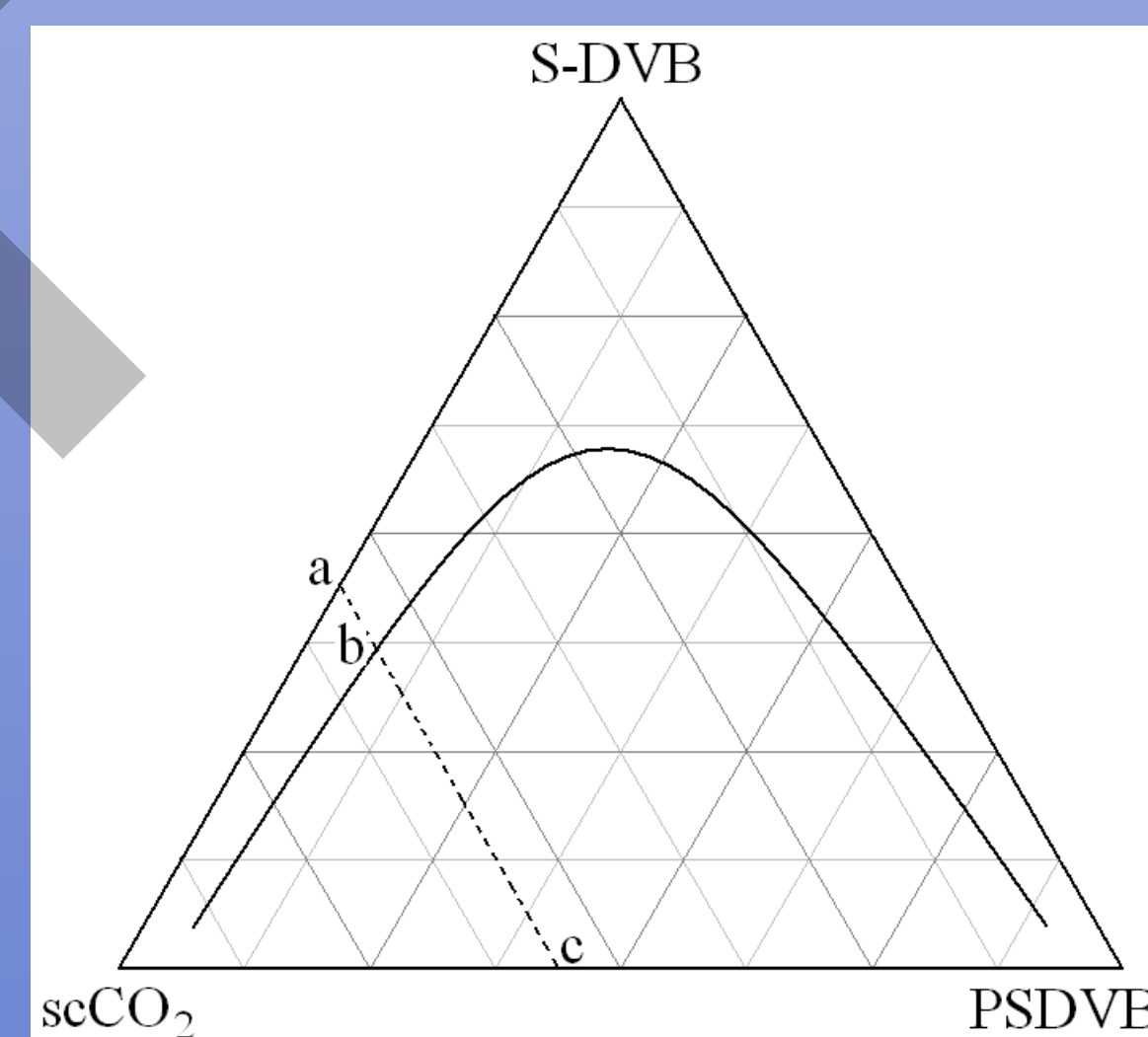
(Styrene, divinylbenzene isomers, ethylvinylbenzene isomers, initiator (AIBN), surfactant (PSDMS or Krytox 257FSL) and scCO₂ as solvent)

b) Appearance of a dispersed phase

(continuous (scCO₂) and dispersed phase (polymer particles))

c) Polymerization at high conversions proceeds in the dispersed phase

(polymer and supercritical CO₂)



Experimental development: Sequence of filling the cell reaction.



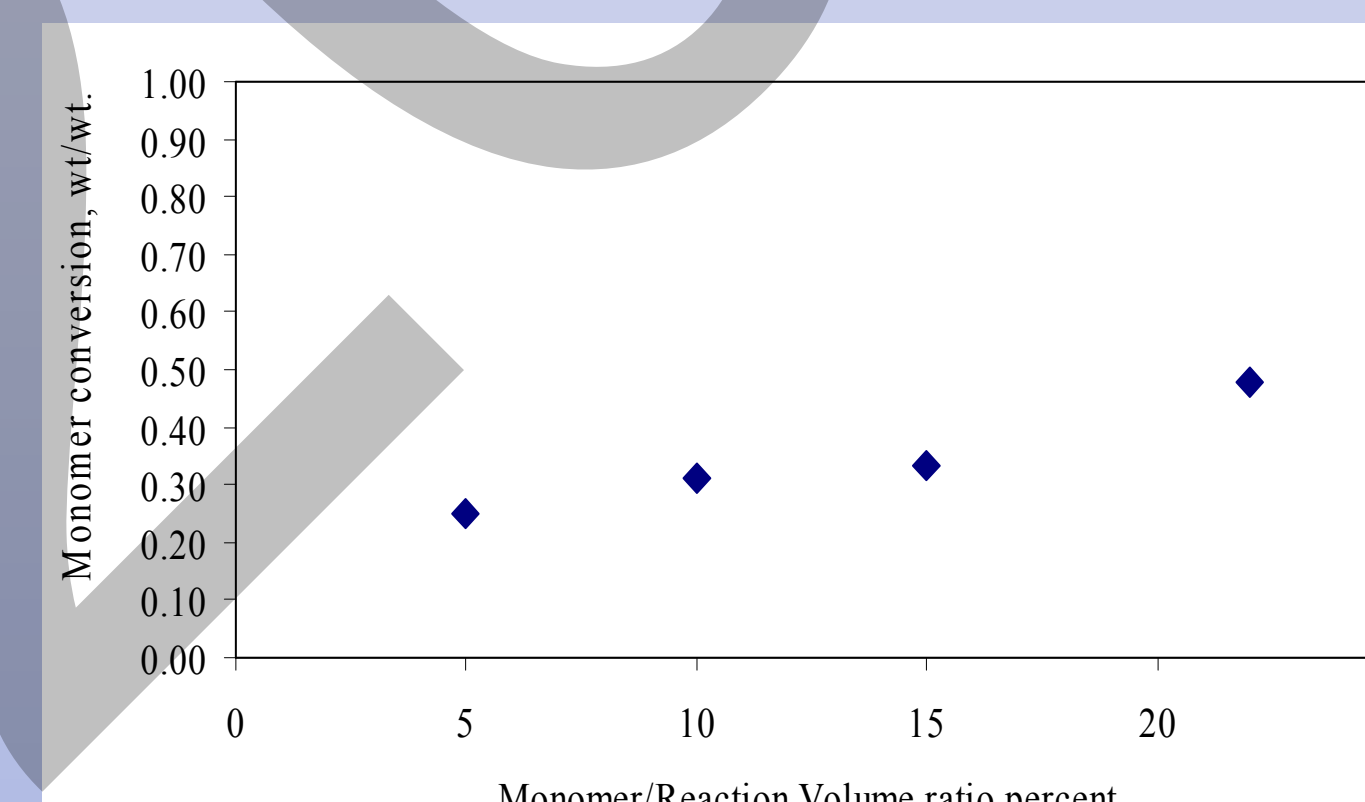
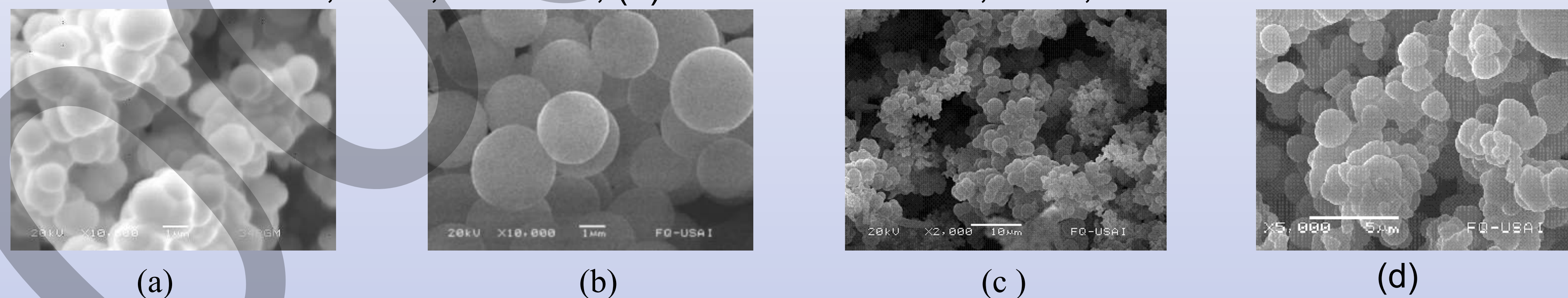
Results:

After a given reaction time, the cell is cooled to about 4 ° C, and opened. Polymer is recovered as granules.

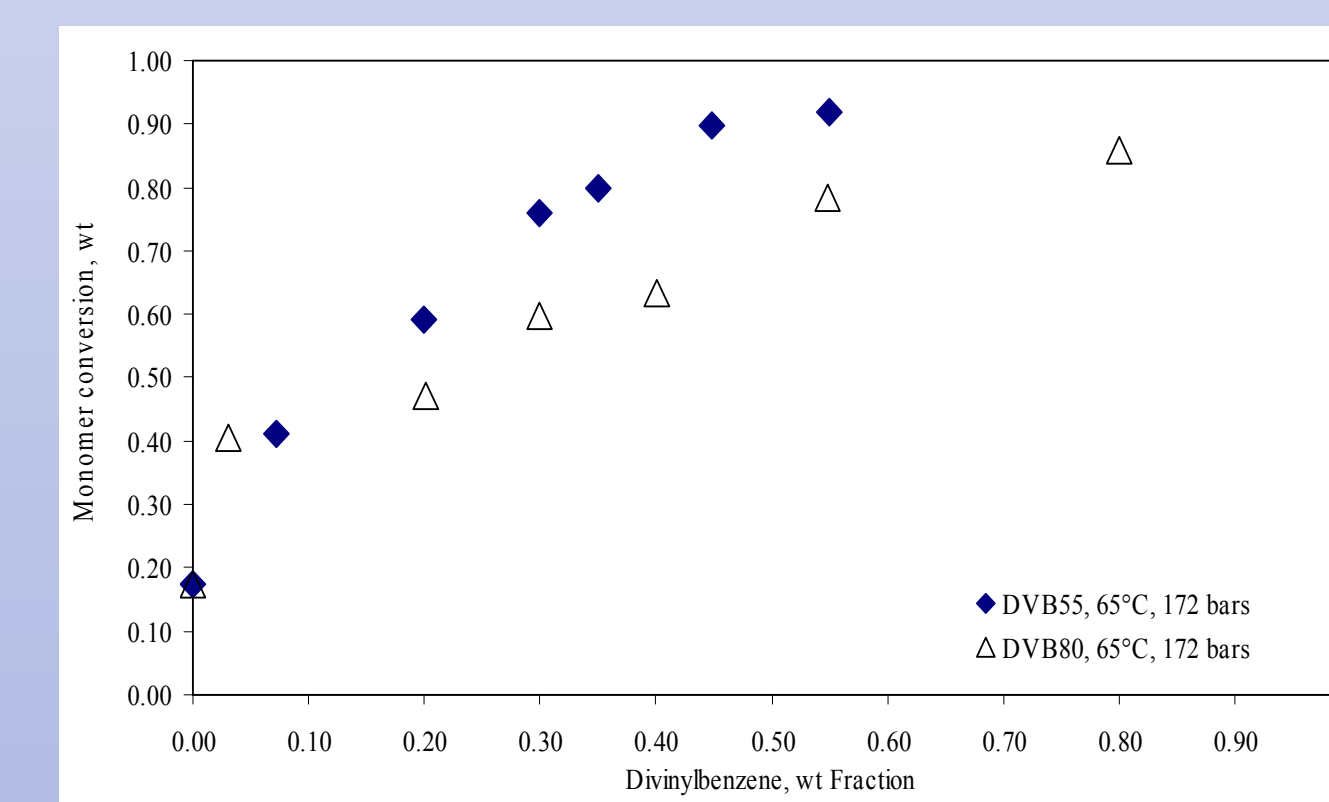


Cell full of PSDVB. Final product, not high monomer conversion. PSDVB with Krytox 257FSL as surfactant. PSDVB with PSDMS as surfactant.

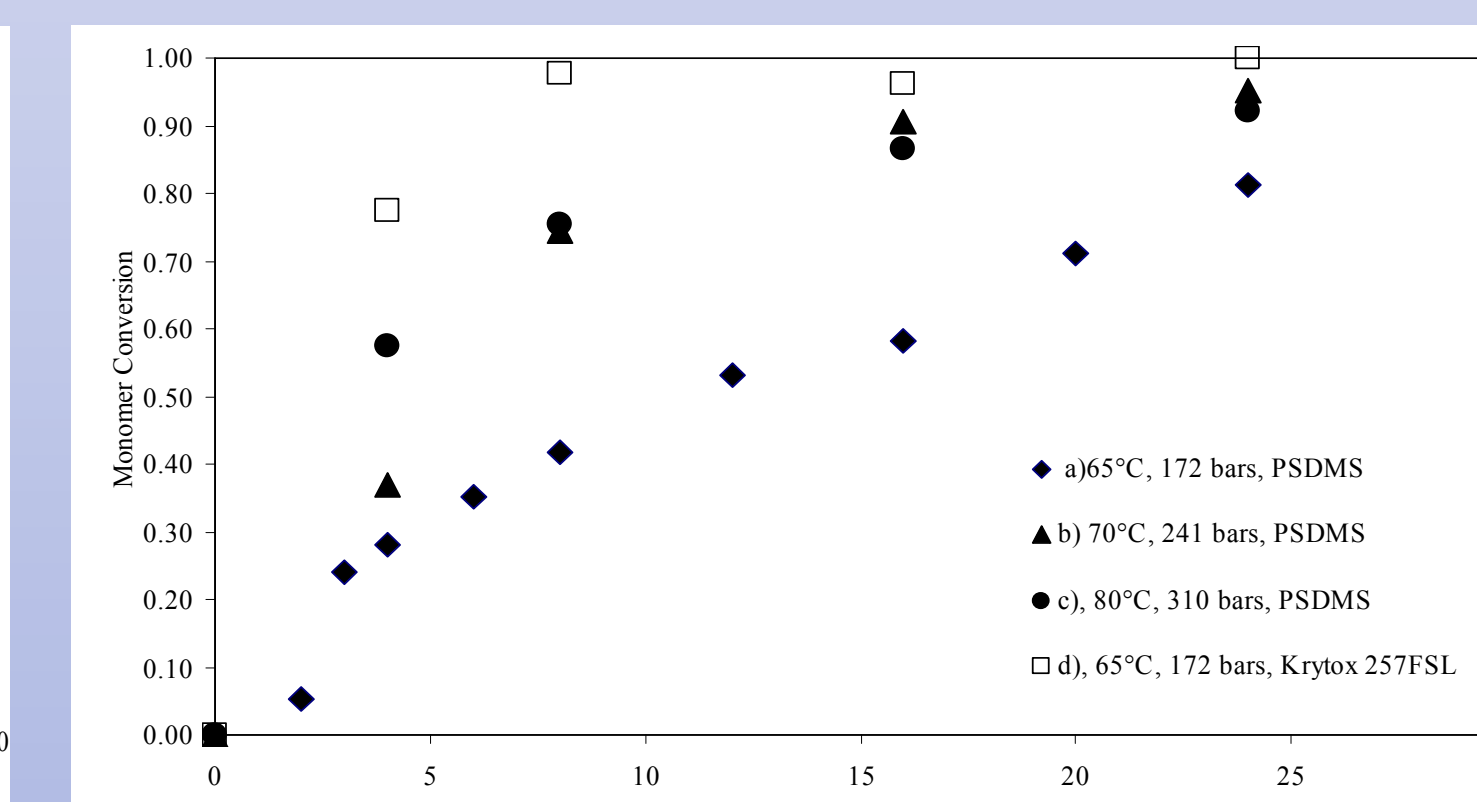
Particles of PSDVB synthesized with 5%w of surfactant, 1%w AIBN, 24 hours of reaction time. (a) Surfactant PSDMS, 65°C, 172 bar, (b) Surfactant Krytox 257FSL, 65°C, 172 bar, (c) Surfactant PSDVB, 70°C, 241 bars, (d) surfactant PSDMS, 80°C, 310 bar.



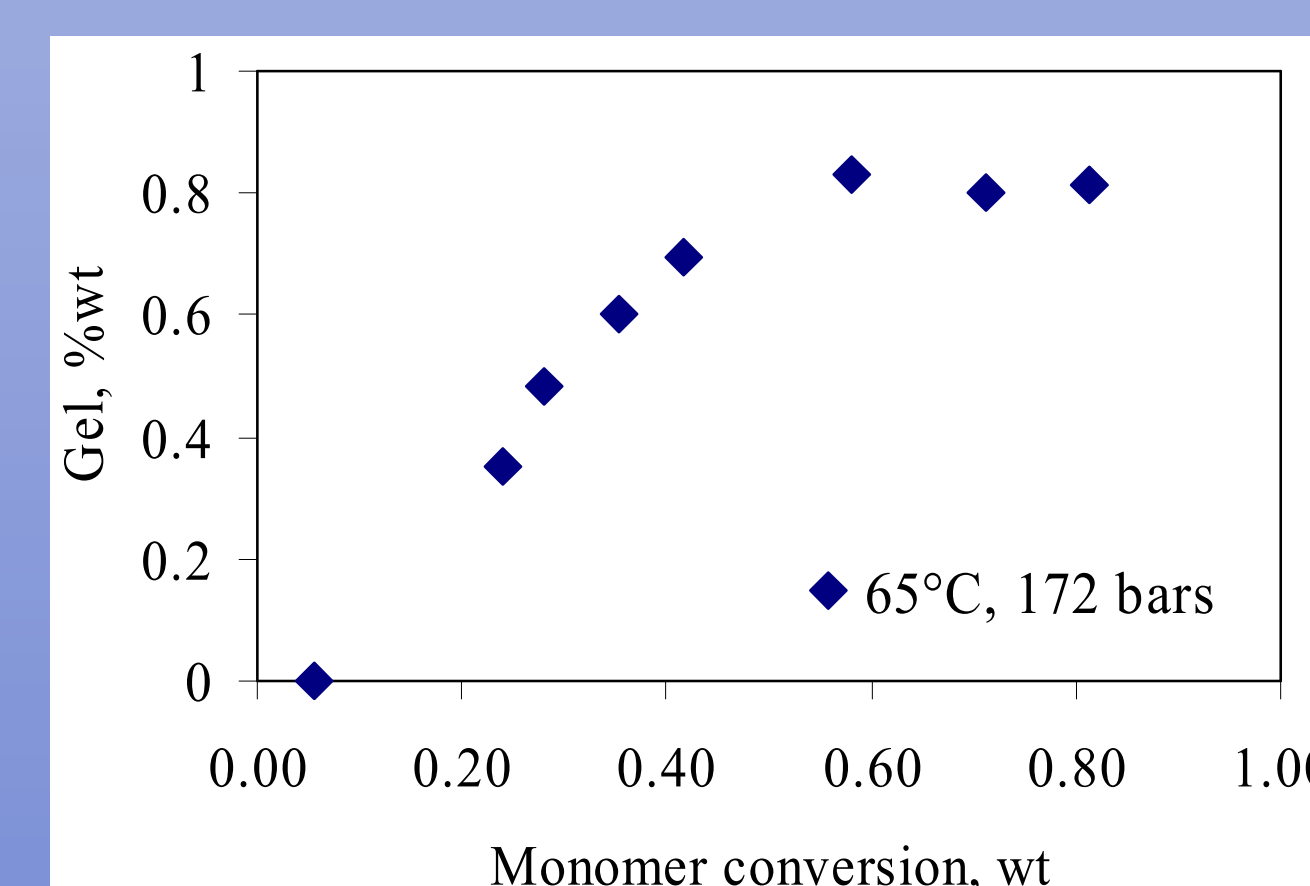
Effect of Monomer mass/reaction volume ratio on monomer conversion. 172 bar, 65°C, 5wt.% PSDMS as surfactant, 1wt.% AIBN, 19wt.% of DVB, all respect monomer mass and 16 hour of reaction time.



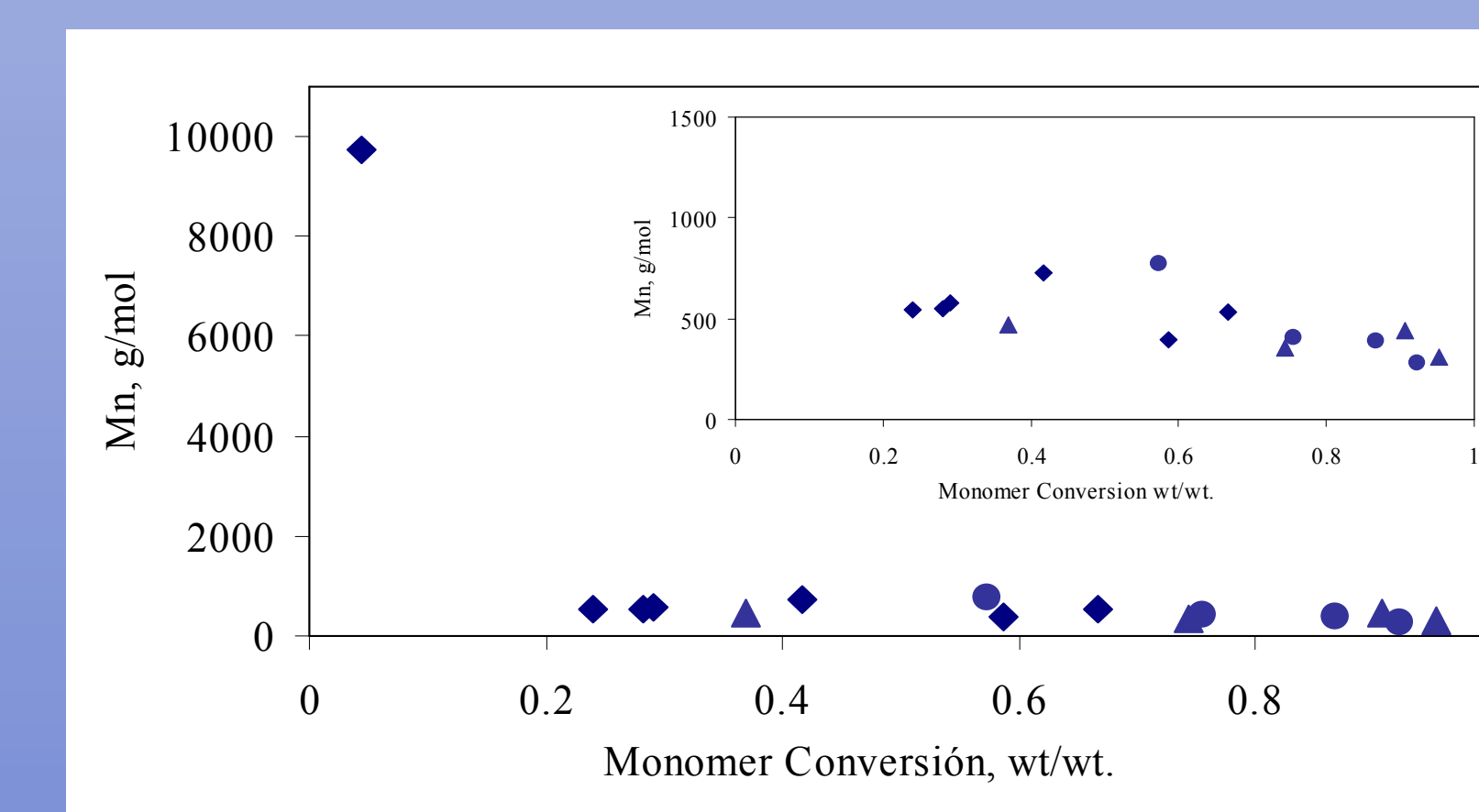
Effect of crosslinker type (DVB55 or DVB80) and concentration on monomer conversion. 1wt% of AIBN, 3wt% of PSDMS, 172 bar, 65°C. ♦ DVB55, Δ DVB80.



Effect of surfactant, temperature and Pressure on rate of STY/DVB copolymerization. 5wt% of surfactant (PSDMS in a, b & c; Krytox257FSL in d), 19wt.% of DVB and 1wt% of AIBN. (a) & (d) 172 bar, 65°C, (b) 241 bar, 70°C, (c) 310 bar, 80°C.



Gel fraction from copolymerization of styrene-DVB at 65°C and 172 bar. 5wt.% PSDMS as surfactant, 1wt.% AIBN, 19wt.% of DVB, all respect monomer mass.



Number average molecular weight, M_n of sol from copolymerization of styrene-DVB (5wt% of surfactant (PSDMS), 19wt.% of DVB and 1wt% of AIBN. ▲ 65°C, 172 bares, ● 70°C, 241 bares, ■ 80°C, 241 bares.

Conclusions:

➤ This study has shown that scCO₂ is viable as a means of reaction medium for vinyl/divinyl copolymerization. The conditions of pressure and temperature were moderate. Reasonably high monomer conversions were reached (82%w at 65°C and 172 bars with 5% PSDMS, and about 99%w with Krytox257FSL).

➤ The surfactant plays a key role in the monomer conversion achieved, as well as in the shape and size of the particles. When PSDMS was used as a surfactant the particle size ranged between 1 to 2 μm, and particle agglomeration was observed. When Krytox was used, the average particle size ranged between 2 to 3 μm and well defined spherical particles were produced.

➤ The value of M_n of the sol fraction was lower than 1000 g/mol.

References

- Some of the information displayed on this poster was published in this article. García-Morán, P. R.; Jaramillo-Soto, G.; Albores Velasco, Eduardo Vivaldo-Lima An Experimental Study on the Free-Radical Copolymerization Kinetics with Crosslinking of Styrene and Divinylbenzene in Supercritical Carbon Dioxide. *Macromol. React. Eng.* 2009, 3, 58–7.
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