



UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO



UNIVERSITY OF WATERLOO

Polymer Reaction Engineering Issues About Polymerization in Supercritical Carbon Dioxide

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Outline

- What is UNAM?
- Why polymerizations in $sc\text{-CO}_2$?
- What are polymer reaction engineers doing worldwide in the area of polymerization in $sc\text{-CO}_2$?
- What is my group at FQ-UNAM doing?
 - Modeling of vinyl/divinyl copolymerization in $sc\text{-CO}_2$
 - Modeling of homogeneous polymerization
 - RAFT polymerization in $sc\text{-CO}_2$
- What else do we do in the PRE area at FQ-UNAM?



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Faculty of Chemistry at UNAM



Building "A"



Building "B"



Building "C"



Building "D"



Complex "E" (4 Buildings)



UNAM Facts

TOP 50 IN ARTS AND HUMANITIES

RANK	NAME	COUNTRY	PEER SCORE
1	Harvard University	US	100.0
2	Oxford University	UK	84.7
3	Cambridge University	UK	81.2
4	University of California, Berkeley	US	77.8
5	Yale University	US	77.4
6	Beijing University	China	70.9
7	Princeton University	US	69.2
8	Melbourne University	Australia	60.0
9	London School of Economics	UK	58.7
10	Australian National University	Australia	56.7
11	Columbia University	US	56.5
12	Massachusetts Institute Technol	US	53.5
13	Univ Paris 1 Panthéon Sorbonne	France	52.9
14	La Sapienza University, Rome	Italy	51.6
15	McGill University	Canada	50.9
16	Tokyo University	Japan	50.5
17	University of Texas at Austin	US	50.2
18=	Copenhagen University	Denmark	47.7
18=	Kyoto University	Japan	47.7
20	Natl Autonomous Univ of Mexico	Mexico	46.9
21=	Queen Mary, University of London	UK	46.7

THE TIMES
HIGHER
EDUCATION SUPPLEMENT

QS

WORLD UNIVERSITY RANKINGS

OCTOBER 28 2006

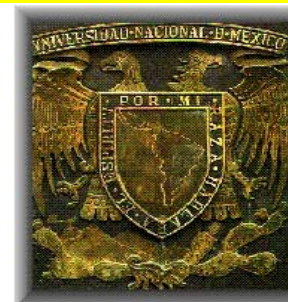
THE REST OF THE WORLD'S TOP 50 UNIVERSITIES

RANK	WORLD RANK	NAME	COUNTRY
1	15	Beijing University	China
2	16	Tokyo University	Japan
3	19	Melbourne University	Australia
4	22	Natl Univ Singapore	Singapore
5	23	Australian Natl University	Australia
6	31	Kyoto University	Japan
7	33	Monash University	Australia
8	38=	Sydney University	Australia
9	40	Univ of New South Wales	Australia
10	41	Hong Kong University	Hong Kong
11	43	Hong Kong Univ Sci & Technol	Hong Kong
12	47	Queensland University	Australia
13	48	Nanyang Technological Univ	Singapore
14	50	Indian Institutes of Technol	India
15	51	Chinese Univ Hong Kong	Hong Kong
16	52	Auckland University	New Zealand
17	62=	Tsing Hua University	China
18	67	Macquarie University	Australia
19	72	Fudan University	China
20	77=	Hebrew Univ Jerusalem	Israel
21=	80=	Adelaide University	Australia
21=	80=	Univ of Western Australia	Australia
23	82	RMIT University	Australia
24	84	Indian Insts of Management	India
25	87	Univ of Technology, Sydney	Australia
26=	93=	China Univ Sci & Technol	China
26=	93=	Seoul Natl University	South Korea
28	95=	Natl Auton Univ of Mexico	Mexico
29	98	La Trobe University	Australia
30	99	Tokyo Inst Technol	Japan

270,000 total students (160,000 Bachelors and graduate students); 33,000 Professional staff (professors, researchers, technicians); 8,500 research projects; 1,144 buildings and 316 "complexes"; 2,104,879 sq meters built infrastructure in Mexico City and other provinces.

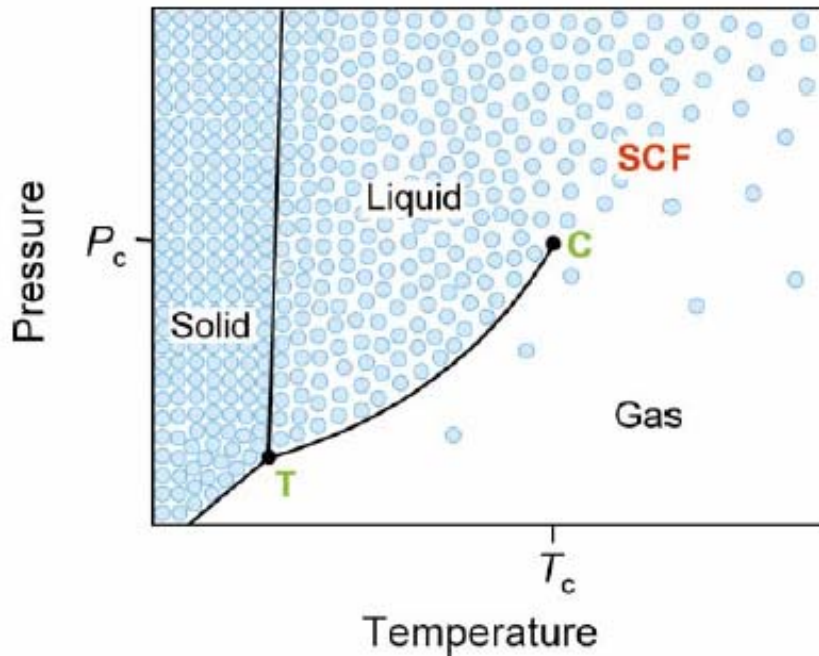
THE WORLD'S TOP 200 UNIVERSITIES

2005 RANK	2004 RANK	NAME	COUNTRY	PEER REVIEW SCORE (40%)	RECRUITER REVIEW (10%)	INT'L FACULTY SCORE (5%)	INT'L STUDENTS SCORE (5%)	FACULTY/STUDENT SCORE (20%)	CITATIONS/FACULTY SCORE (20%)	OVERALL SCORE
1	1	Harvard University	US	100	100	17	23	21	57	100.0
2	3	Massachusetts Institute of Technology	US	84	87	12	41	16	53	86.9
3	6	Cambridge University	UK	96	73	85	34	20	16	85.8
4	5	Oxford University	UK	93	70	58	37	23	15	83.9
5	7	Stanford University	US	78	95	10	30	12	58	83.4
93=	118	Seoul National University	South Korea	39	0	3	5	14	4	28.9
95=	-	Catholic University of Leuven (Flemish)	Belgium	24	10	48	20	23	4	28.8
95=	195	National Autonomous Univ of Mexico	Mexico	33	9	3	1	25	0	28.8
97	170	Nottingham University	UK	22	38	39	30	10	6	28.7
98	142	La Trobe University	Australia	34	0	53	26	6	3	28.6
99	51	Tokyo Institute of Technology	Japan	30	0	6	16	22	10	28.5
100	58	Sussex University	UK	28	0	44	28	15	7	28.4



Founded on Sept. 21, 1551 as "Real and Pontifical University of Mexico"

Why polymerizations in SCF CO₂?

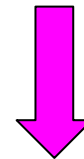


Benefits:

Environmentally-sound technology

Enhanced mass-transfer

“Property” tunability with P/T



Commercial Processes:

-Dupont

(homogeneous, fluoropolymers)

-??

(heterogeneous, unlimited chemistries & architectures)

Polymerizations in Supercritical Carbon Dioxide

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and kinetics. For example, conditions that give a low viscosity supercritical fluid result in diminished solvent cage effects in free-radical initiator decompositions.⁴

When carbon dioxide is used as the supercritical solvent, additional advantages can be realized. The chemical industry has become increasingly aware of environmental concerns over the use of volatile organic solvents and chlorofluorocarbons in the manufacture and processing of commercial polymer products. The use of water alleviates these problems somewhat, but still results in large amounts of hazardous aqueous waste that require treatment. As a result of these environmental concerns, supercritical CO₂ represents a more environmentally friendly alternative to traditional solvents. CO₂ is naturally occurring and abundant: it exists in natural reservoirs of high purity located throughout the world. In addition, it is generated in large quantities as a

PRE Topics about scCO₂*

- Phase behavior of polymer systems in high-pressure CO₂
- Transport properties of scCO₂ (e.g., hydrodynamics and mixing; heat transfer)
- Kinetics of free-radical polymerization in homogeneous phase in scCO₂
- Monitoring reactions in SC media (e.g., online analytical methods as FTIR, Raman spectroscopy, UV/Vis, NMR, etc)
- Heterogeneous homo and co-polymerization in scCO₂ (e.g., Modeling)
- Inverse emulsion polymerization in carbon dioxide (designing and synthesizing CO₂-philic surfactants)
- Catalytic polymerization of olefins in scCO₂ (e.g., phase behavior, cloud point measurements and SAFT modeling of PEP-Ethylene-CO₂ system)
- Production (and modeling) of fluoromonomers in scCO₂
- Polymer processing with SCF
- Synthesis of advanced materials using SCF (e.g., CRP in scCO₂)
- Polymer extrusion with scCO₂
- Chemical modification of polymers in scCO₂
- Reduction of residual monomer in latex products using high-pressure CO₂

*Kemmere and Meyer, *Supercritical Carbon Dioxide in Polymer Reaction Engineering*, Wiley-VCH: Weinheim, Germany, 2005

State of the art on the modeling of polymerization in scCO₂

Only a few scientific papers:

-[De Simone](#), 2002

Homogeneous model for a continuous heterogeneous process (VDF polymerization)

-[Kiparissides](#), 2003; [Morbidelli](#), 2005, 2006

Modeling of heterogeneous homopolymerization process (MMA and VDF polymerization)

-[Our group](#), 2005, 2006.

Modeling of heterogeneous copolymerization with crosslinking (vinyl/divinyl) and homogeneous production of fluoromonomers

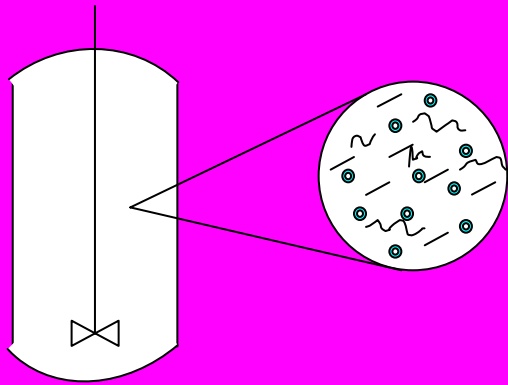
Note: the tools to model these systems have been derived in the last decades by the members of the PRE community; what is new is the application (high P)

Objectives*

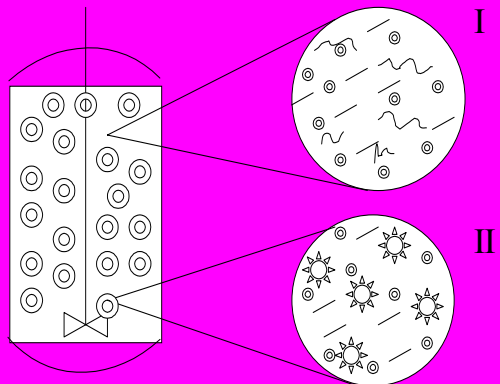
- To develop a mathematical model of copolymerization with crosslinking for the first time in compressible media
- To test the model with vinyl/divinyl monomers in SCF CO₂

Homogeneous & Heterogeneous

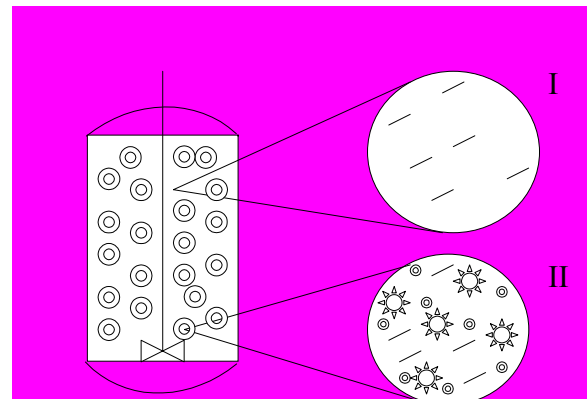
Dispersion Polymerization Process



Stage 1



Stage 2



Stage 3

I. Continuous Phase, rich in CO₂

II. Disperse Phase, rich in polymer

Species:

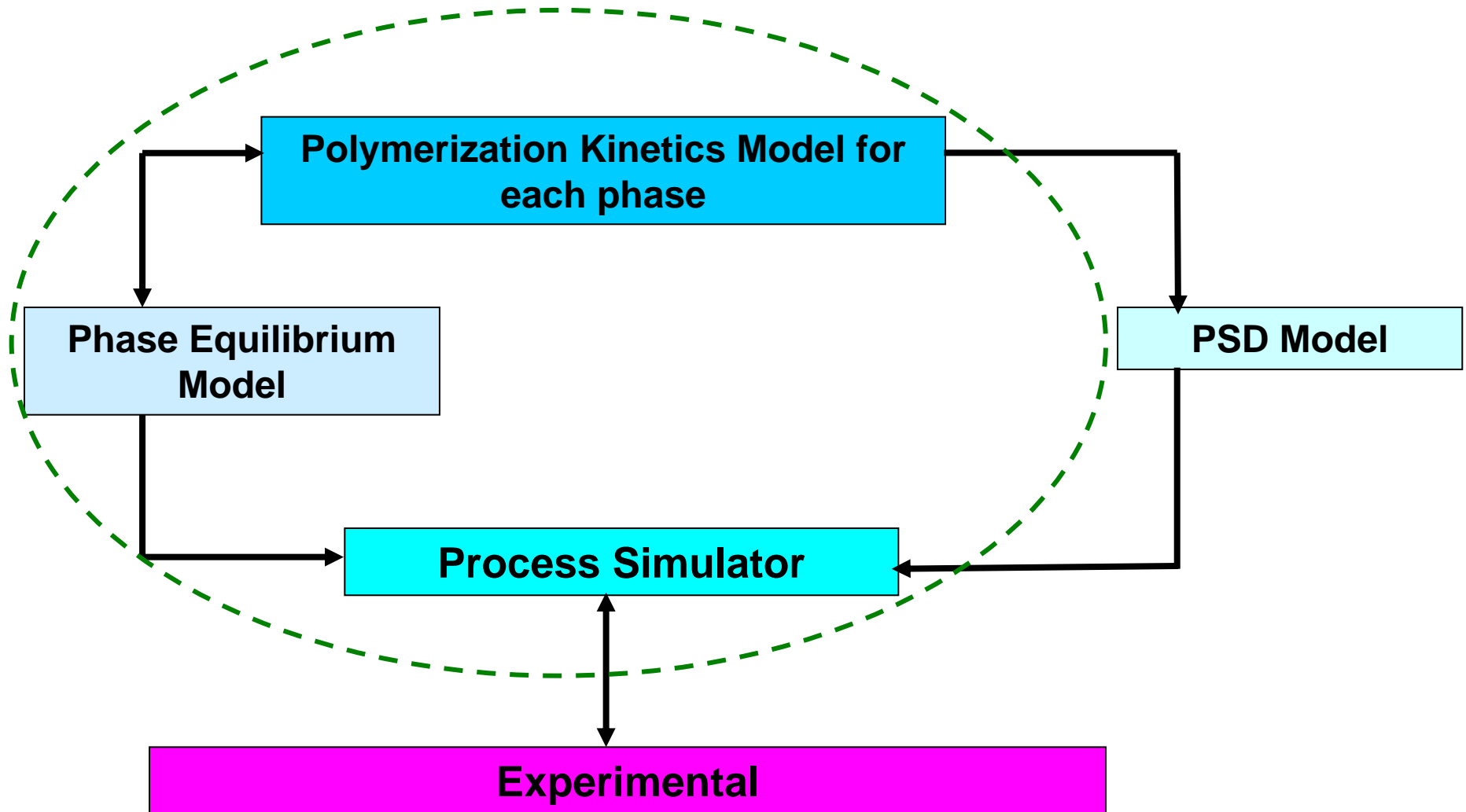
Initiator /

Monomer ⊙

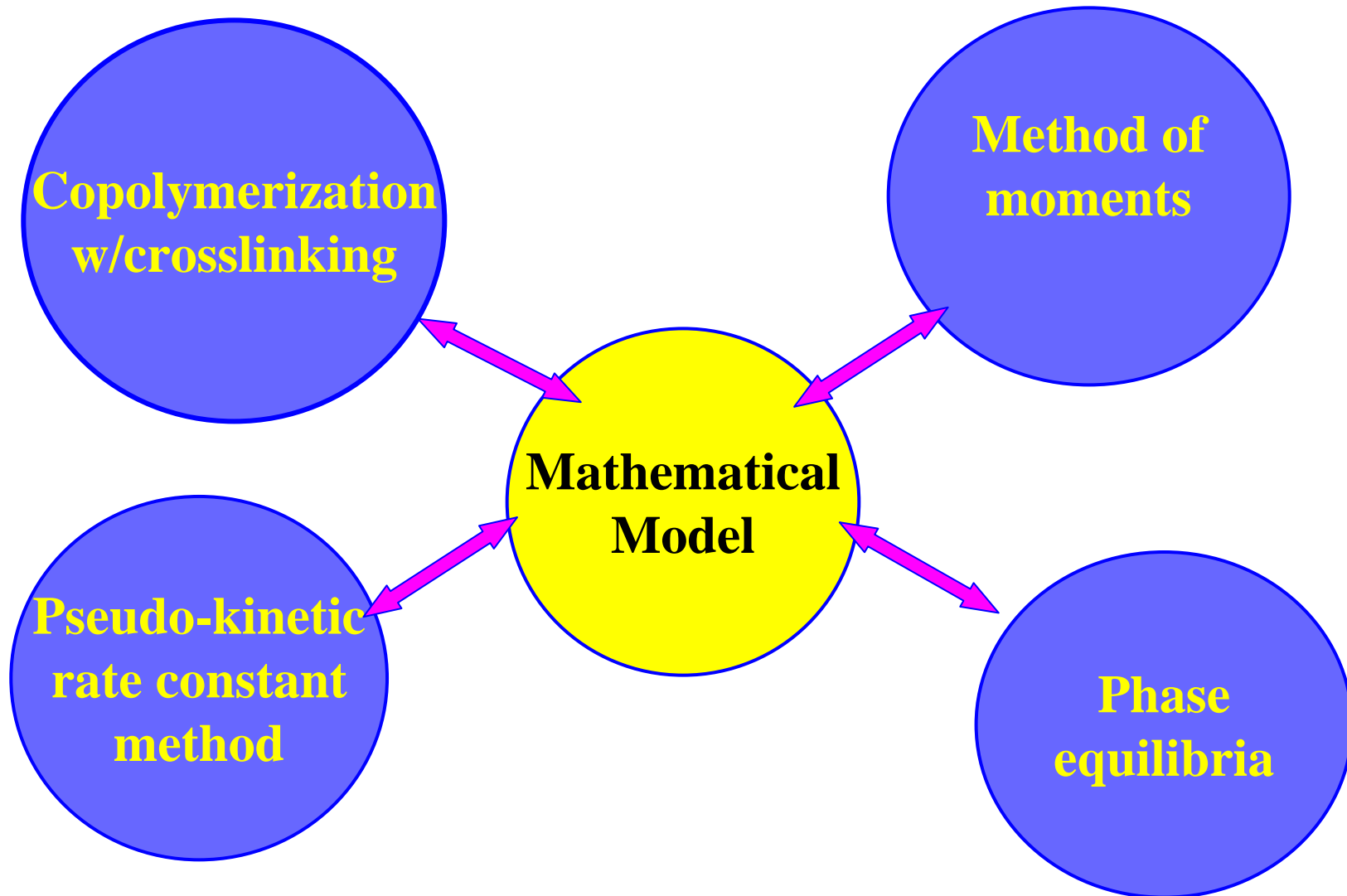
Oligomers ~

Polymer Particles ☀

Strategy



Model Development



Reaction Scheme

Initiation	$I_j \xrightarrow{k_{dj}} 2R_{in,j}^{\bullet}$ $R_{in,j}^{\bullet} + M_j \xrightarrow{k_{I,j}} R_{1,j}^{\bullet}$
Propagation	$R_{r,j}^{\bullet} + M_j \xrightarrow{k_{p,j}} R_{r+1,j}^{\bullet}$
Propagation through double pendant bonds	$R_{r,j}^{\bullet} + P_{s,j} \xrightarrow{k_{p,j}^*} R_{r+s,j}^{\bullet}$
Transfer to monomer	$R_{r,j}^{\bullet} + M_j \xrightarrow{k_{fm,j}} P_r + R_{1,j}^{\bullet}$
Transfer to polymer	$R_{r,j}^{\bullet} + P_{s,j} \xrightarrow{k_{fp}} P_{r,j} + R_{s,j}^{\bullet}$
Termination by disproportionation	$R_{r,j}^{\bullet} + R_{s,j}^{\bullet} \xrightarrow{k_{td,j}} P_r + P_s$
Termination by combination	$R_{r,j}^{\bullet} + R_{s,j}^{\bullet} \xrightarrow{k_{tc,j}} P_{r+s}$

Kinetic Equations for Copolymerization

Initiator Consumption	$\frac{d[I]}{dt} = -k_d[I]; \quad R_I = 2fk_d[I]$
Monomer Consumption	$\frac{d[M]}{dt} = -k_p[M][R^\bullet]; \quad \frac{dx}{dt} = k_p[R^\bullet](1-x)$
Small Molecule Consumption	$\frac{d[T]}{dt} = -k_{fT}[T][R^\bullet]$
Monomer Composition	$\frac{df_i}{dt} = \frac{f_i - F_i}{1-x} \frac{dx}{dt}, \quad i = 1, 2, \dots, \text{número de monómeros}$
Instantaneous Cop. Composition	$F_j = \frac{\sum_{i=1}^N k_{ij}\phi_i^* f_j}{k_p}, \quad N = \text{número de monómeros}$
Accumulated Cop. Composition	$\bar{F}_j = \frac{f_{j0} - f_j(1-x)}{x}$
Crosslink Density	$\frac{d[x\rho_a]_j}{dt} = \frac{k_{pj}^* \bar{F}_{2j} (1 - k_{cpj} - \rho_{aj}(1 + k_{csj}))}{k_{pj}(1-x_j)} \frac{dx_j}{dt}$
Polymer Radicals	$\frac{d[R_r^\bullet]}{dt} = R_I - (k_{tc} + k_{td} + k_{fT})[R_r^\bullet][R^\bullet] + k_p[M][R_{r-1}^\bullet] - k_p[M][R_r^\bullet]$
Dead Polymer	$\frac{d[P_r]}{dt} = k_{td}[R_r^\bullet][R^\bullet] + k_{fT}[T][R_r^\bullet] + \frac{1}{2}k_{tc} \sum_{s=1}^{r-1} [R_s^\bullet][R_{r-s}^\bullet]$

Copolymerization with Crosslinking

$$\frac{d[P_r]}{dt} = k_{td} [R_r^\bullet] [R^\bullet] + k_{fr} [T] [R_r^\bullet] + \frac{1}{2} k_{tc} \sum_{s=1}^{r-1} [R_s^\bullet] [R_{r-s}^\bullet]$$

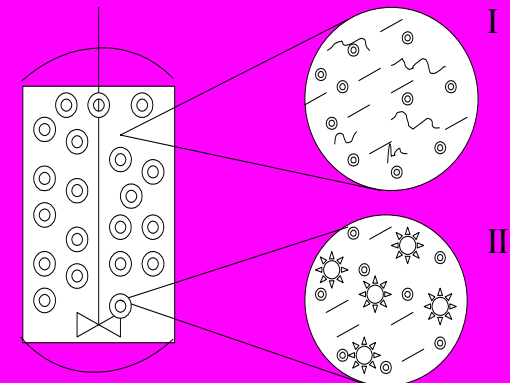
$$\frac{d[R_r^\bullet]}{dt} = R_I - (k_{tc} + k_{td} + k_{fr}) [R_r^\bullet] [R^\bullet] + k_p [M] [R_{r-1}^\bullet] - k_p [M] [R_r^\bullet]$$

Method of Moments

Averages (M_n , M_w , M_z)

All constants are pseudo-kinetic rate constants

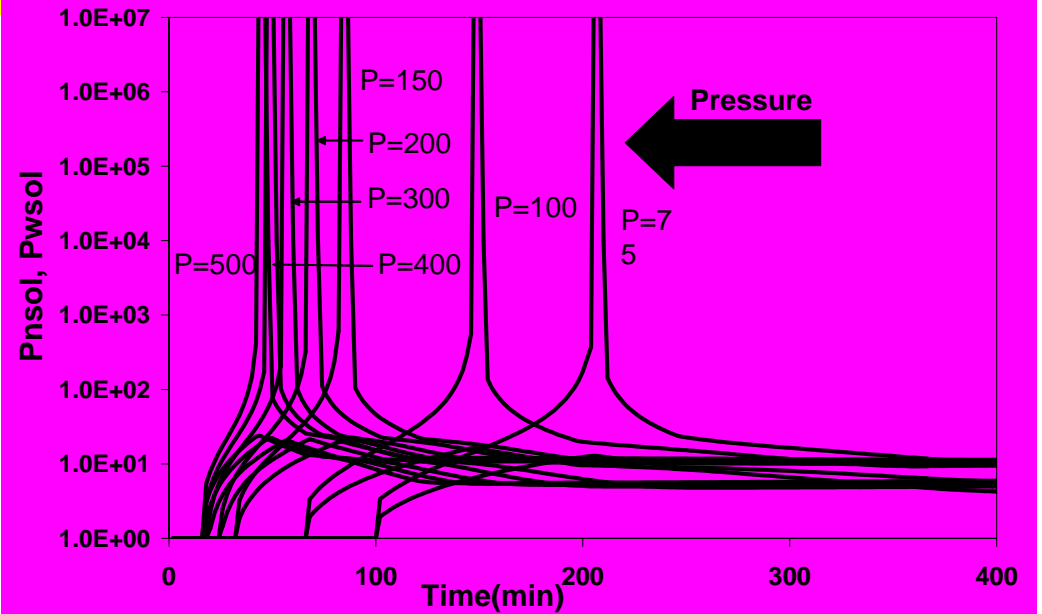
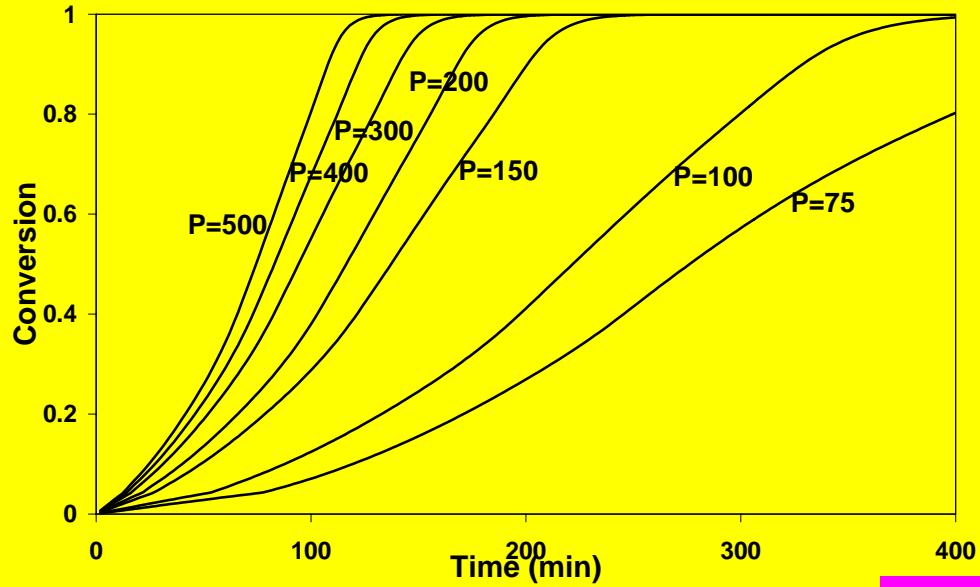
PEP



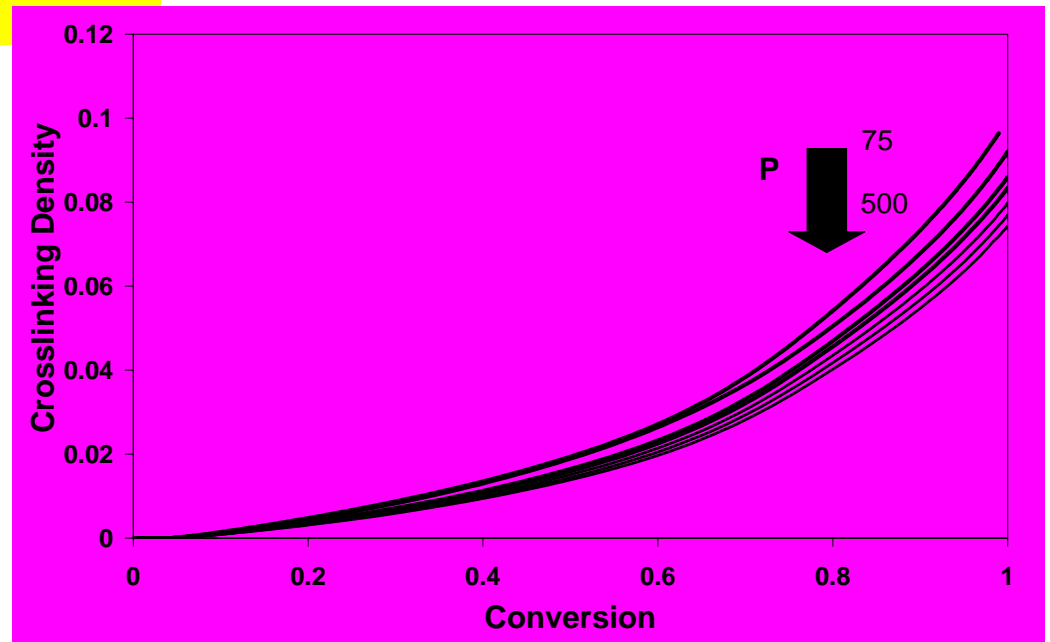
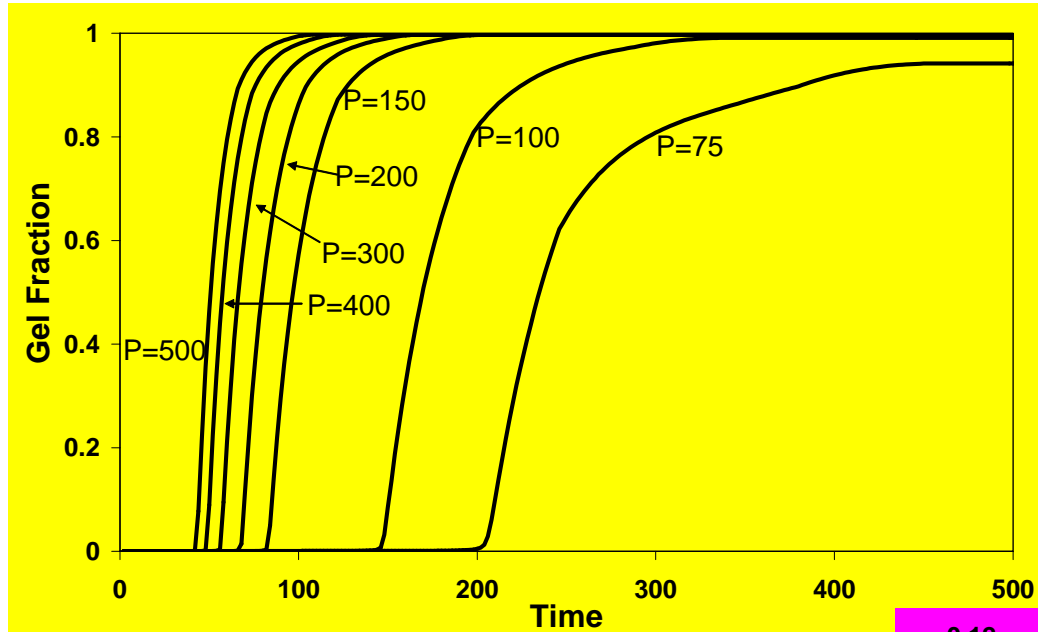
Reference System (Cooper et al.)

- Commercial DVB (80% DVB, roughly 20% EVB)
- $P = 310 \text{ bar}$
- $T = 65 \text{ }^{\circ}\text{C}$
- $[\text{AIBN}] = 0.0974 \text{ M}$
- $[\text{M}]_0 = 1.6025 \text{ M}$
- $V = 10 \text{ mL}$

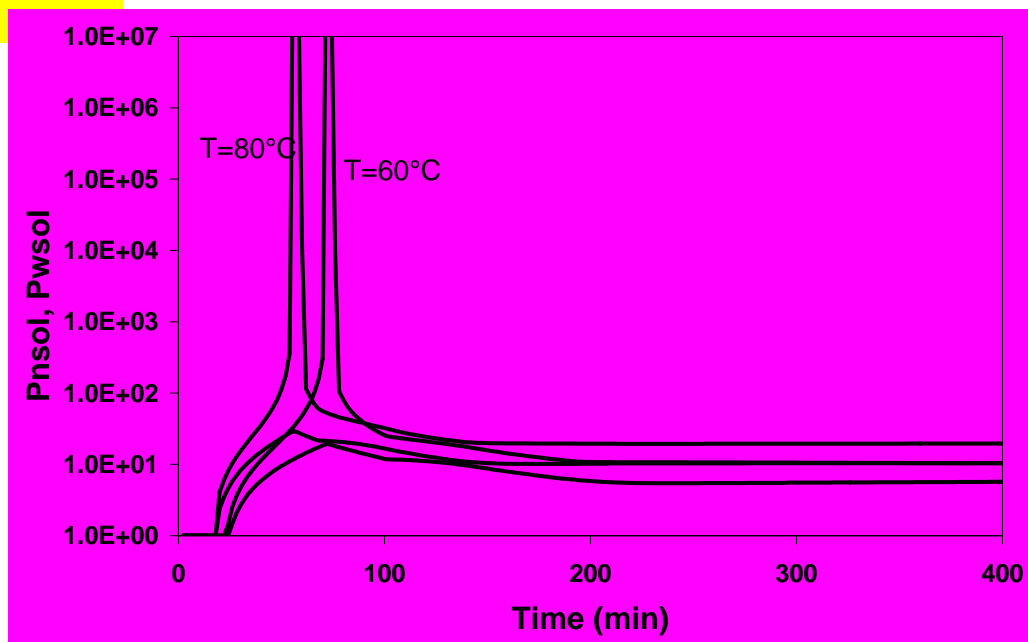
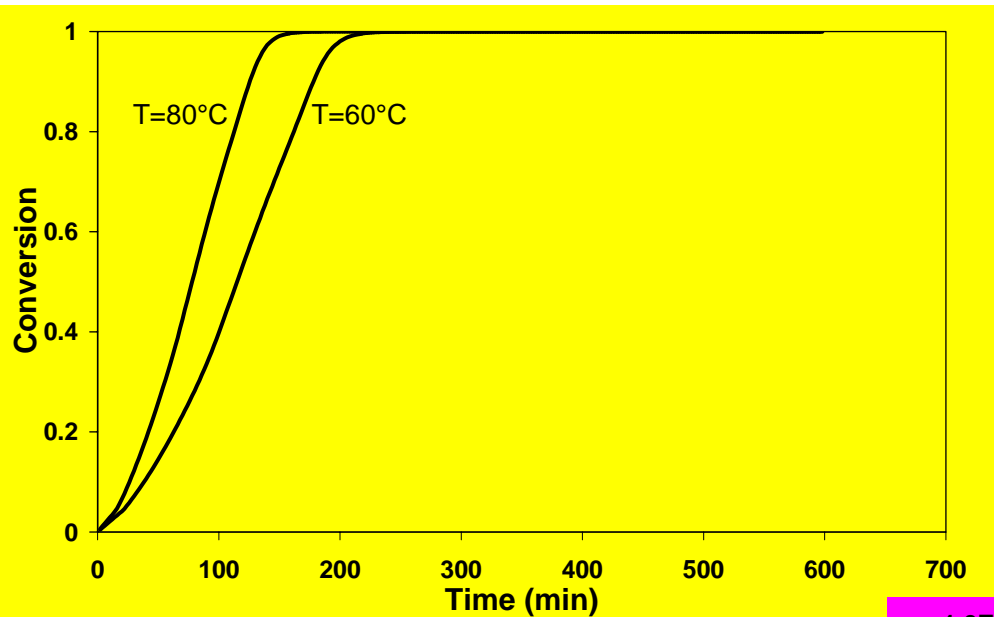
Effect of Pressure



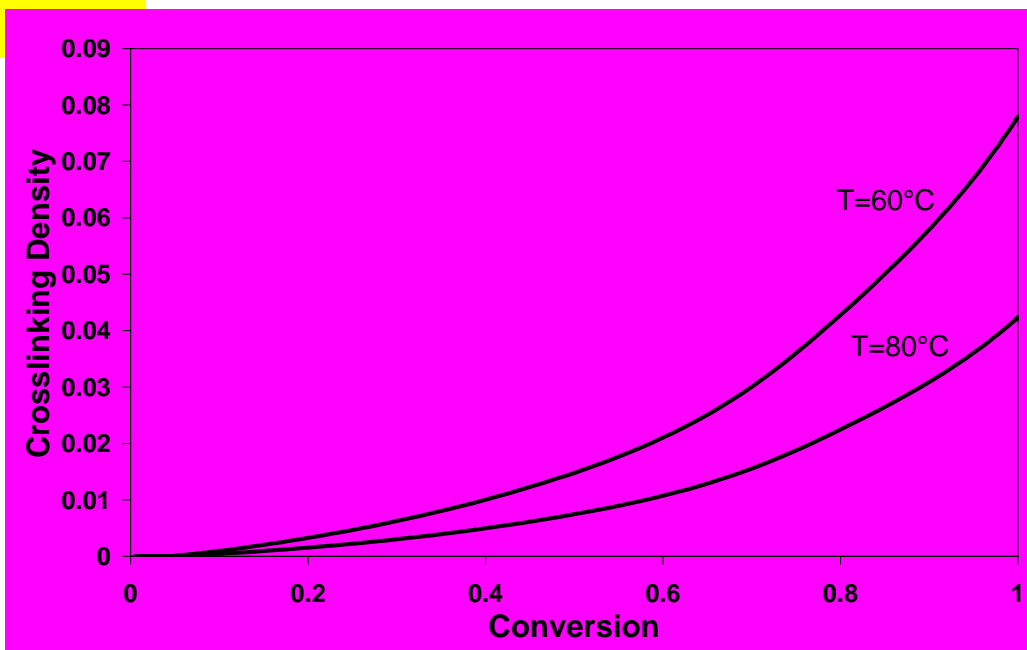
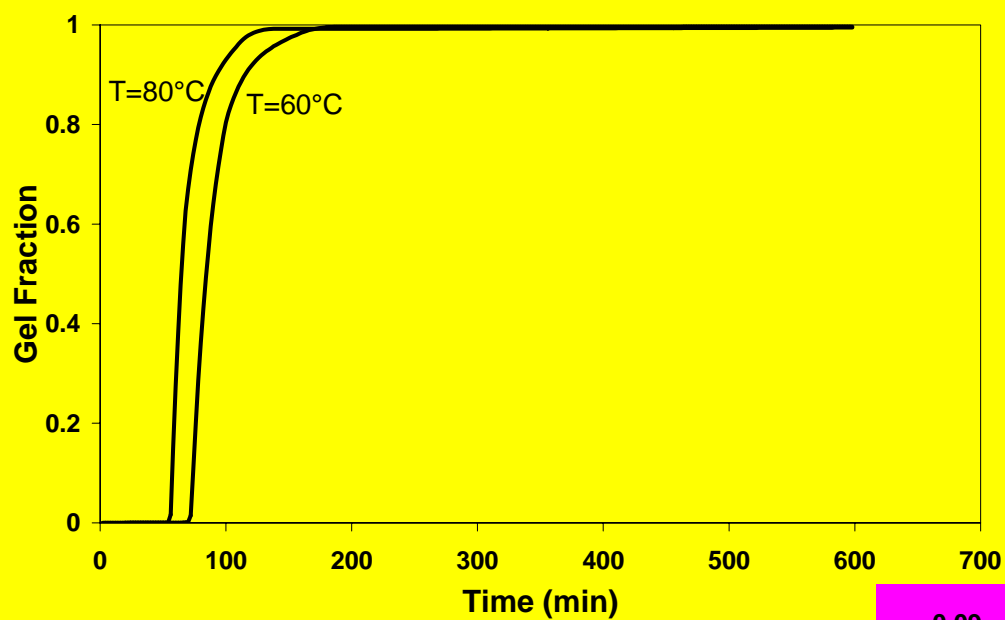
Effect of Pressure



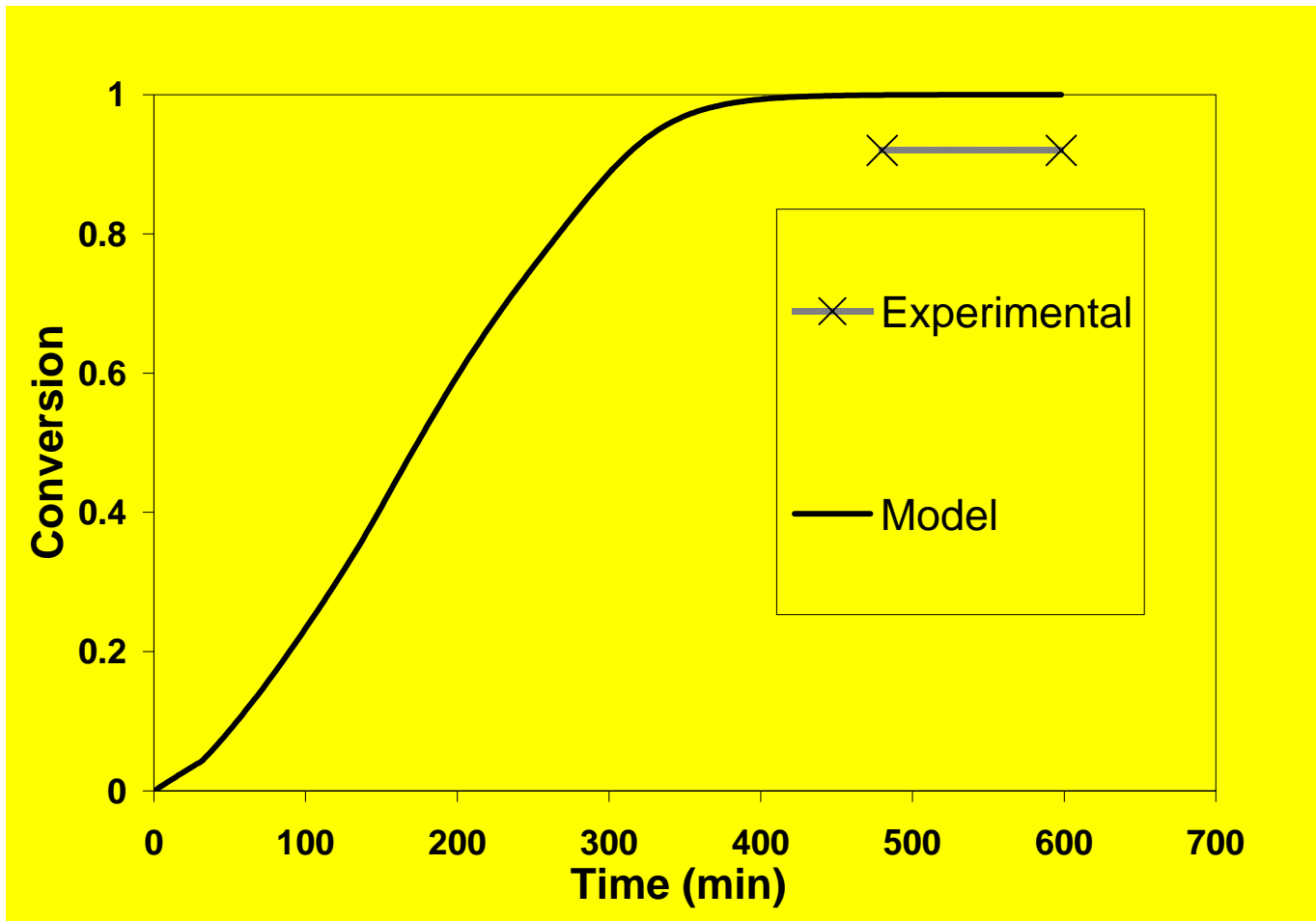
Effect of Temperature



Effect of Temperature



Comparison *versus* Experimental Data



Effect of Other Parameters

Physical Parameters

- Initial monomer concentration
- Initial initiator concentration
- Crosslinker initial concentration
- Free volume parameter, A_2

Kinetic parameters

- Propagation
- Termination
- Propagation through pendant double bonds
- Primary cyclization

Homogeneous Homopolymerization of FOA

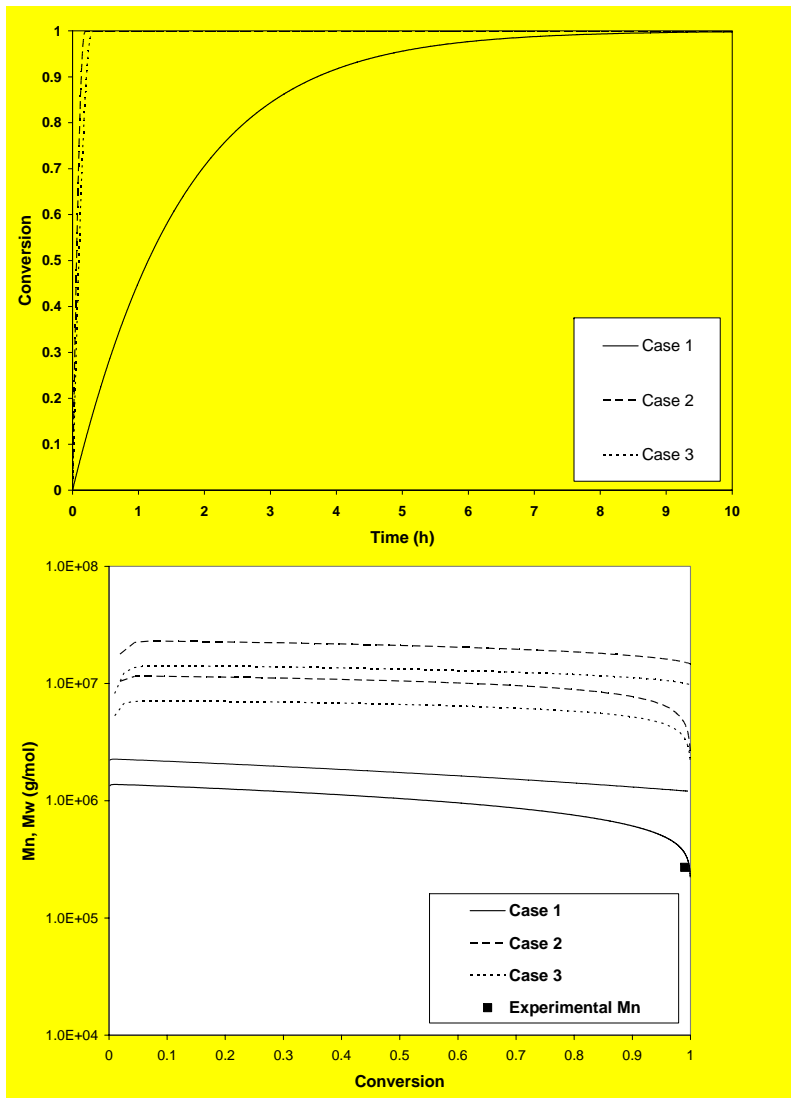


Table 6. Physical and Kinetic Parameters for the Free-Radical Homopolymerization of FOA in scCO₂

Parameter, units	Value, Case 1	Value, Case 2	Value, Case 3	Reference
k_p , L mol ⁻¹ s ⁻¹	7400 ^a	7400 ^a	2960 ^b	38
k_d , s ⁻¹	3.4×10^{-6}	3.4×10^{-6}	3.4×10^{-6}	9
k_{fm} , L mol ⁻¹ s ⁻¹	1.14×10^{-2}	1.14×10^{-2}	1.14×10^{-2}	26
k_t , L mol ⁻¹ s ⁻¹	1.8×10^{8c}	740 ^d	740 ^d	26, 38
f	0.83	0.83	0.83	9

^a k_p for TFE at 40° C; ^b k_p for TFE at 40° C, corrected by pressure (taken as 40% of the value at normal conditions); ^c k_t for Styrene; ^dValue for TFE at 40° C, corrected by pressure (taken as ten times the value at normal conditions).

Effect of k_p and k_t on polymerization rate and molecular weight development in FOA polymerization in scCO₂, at P= 207 bar and T= 60 °C

Heterogeneous Copolymerization of TFE/VAc in scCO₂

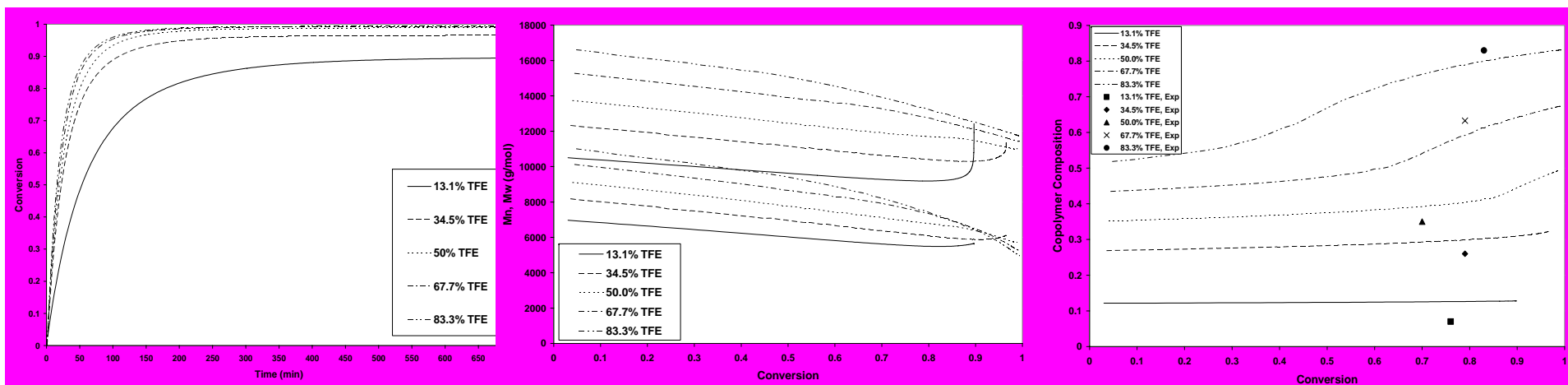


Table 7. Kinetic Parameters for the Free-Radical Copolymerization of TFE/VAc in scCO₂

Parameter	Value	Reference
f_0 , dimensionless	0.7	10
k_d , s ⁻¹	$k_d = 1.053 \times 10^{15} \exp\left(-\frac{30660}{RT}\right)$	28
k_{11} L mol ⁻¹ s ⁻¹	3258	37
k_{22} L mol ⁻¹ s ⁻¹	2968	36
k_{f1} , L mol ⁻¹ s ⁻¹	$0.18k_{11}$	28
k_{fm} , L mol ⁻¹ s ⁻¹	$k_{fm} = 2.31 \times 10^6 \exp\left(-\frac{12671}{RT}\right)$	28
k_{fp} , L mol ⁻¹ s ⁻¹	0.0	28
k_t , L mol ⁻¹ s ⁻¹	5.8×10^9	36
k_{f1}, k_{f2} , L mol ⁻¹ s ⁻¹	$0.0133 k_{11}$	28
r_1 , dimensionless	$\left(\frac{k_{11}}{k_{12}}\right) = 1.03$	21
r_2 , dimensionless	$\left(\frac{k_{22}}{k_{21}}\right) = 0.051$	21

Conclusions (Conventional FRP in scCO₂)

- Detailed kinetic model for the copolymerization with crosslinking successfully developed
- Gelation point can be drastically delayed/accelerated (up to 100 min!!) with P changes with no significant network property modification
- By specifying appropriate process conditions, our model can handle linear homopolymerization & copolymerization, homogeneous & heterogeneous

Controlled-Radical Polymerization

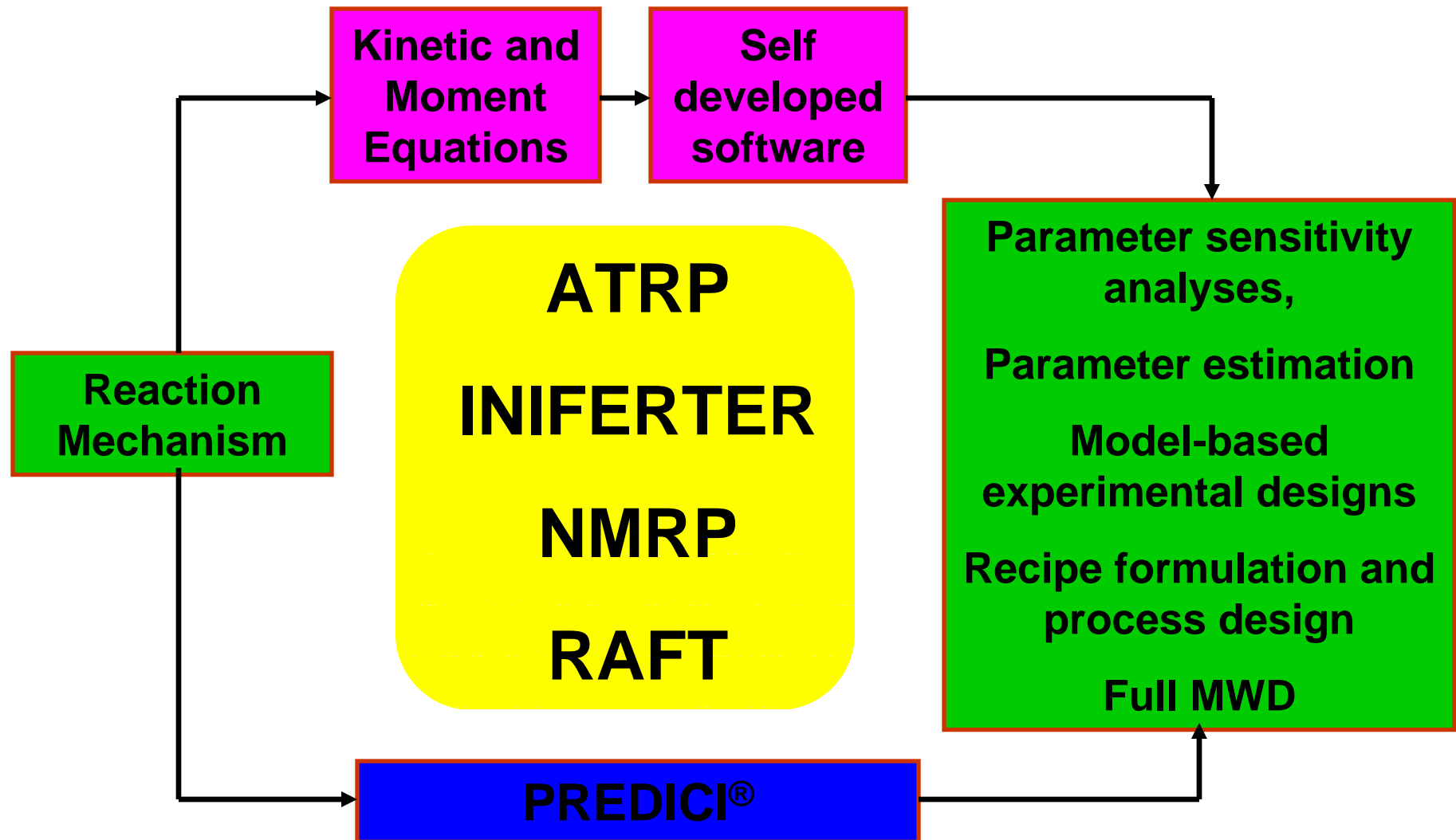
- Living polymerization: absence of termination reactions; possibility of production of polymers with controlled structure; commercial route: anionic polymerization; expensive, compared to free-radical technology
- Free-radical processes: robust to impurities; inexpensive; poor control of microstructure
- Controlled radical polymerization (CRP): free-radical technology with quasi-living behavior
- CRP Processes: INIFERTER, ATRP, NMRP, RAFT



Specific CRP Reactions

Description	RAFT	NMRP
Chemical Initiation	$I \xrightarrow{k_d} 2R_{in}^\bullet$	$I \xrightarrow{k_d} 2R_{in}^\bullet$
Generation of Controller		$N_{OE} \xrightleftharpoons[k_{d2}]{k_{a2}} R_{noe}^\bullet + \bullet ON_x$
Rxn Between Controller and a Polymer Radical	$RM_n^\bullet + AB \xrightleftharpoons[k_{-a}]{k_a} RM_n \dot{A} B \xrightleftharpoons[k_{-b}]{k_b} RM_n A + B^\bullet$	$RM_n^\bullet + \bullet ON_x \xrightleftharpoons[k_a]{k_d} RM_n O_{NX}$
Living/Dormant Equilibrium	$RM_n^\bullet + RM_m A \xrightleftharpoons[k_{-a}]{k_a} RM_n \dot{A} RM_m \xrightleftharpoons[k_a]{k_{-a}} RM_m^\bullet + RM_n A$	$RM_n^\bullet + RM_m O_{NX} \xrightleftharpoons[k_b]{k_f} RM_m^\bullet + RM_n O_{NX}$
Other Reactions	$RM_p \dot{A} RM_q + RM_r^\bullet \xrightarrow{k_{tir}} RM_p(A) \begin{matrix} RM_q \\ RM_r \end{matrix}$	

Modelling Approach



Experimental Approach

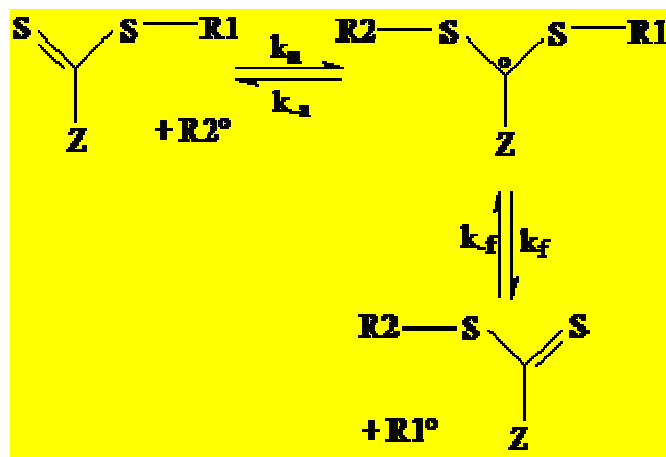
NMRP

- Comparison of Polymerization Methods (Schlenk, Vials, Ampoules)
- Experiments at high conversions using Predici as design tool
- Experimental simulation of high conversions using anionic synthesized prepolymer or GPC standard
- Promotion of high viscosity using small amounts of DVB (Sty/DVB copolym.)
- Measurement of radical concentrations using ESR
- Semi-batch policies
- NMRP in sc-CO₂?
- NMRP in miniemulsion?

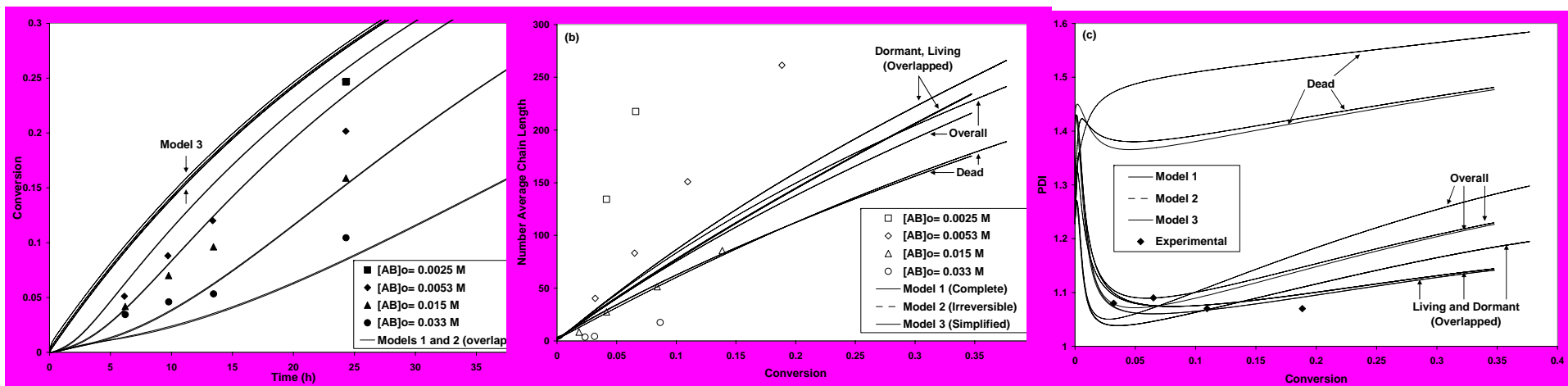
RAFT

- Synthesis of the best reported controllers
- Synthesis of new controllers using Predici as design tool
- Evaluation of controllers in the full conversion range
- Synthesis of block copolymers
- Semi-batch policies
- RAFT in sc-CO₂?
- RAFT in miniemulsion?
- Viny/divinyl copolymerization with RAFT?

RAFT Main Reaction



RAFT: Low Pressure (Exp. Data from Davis et al., JPS-PC, 2001)



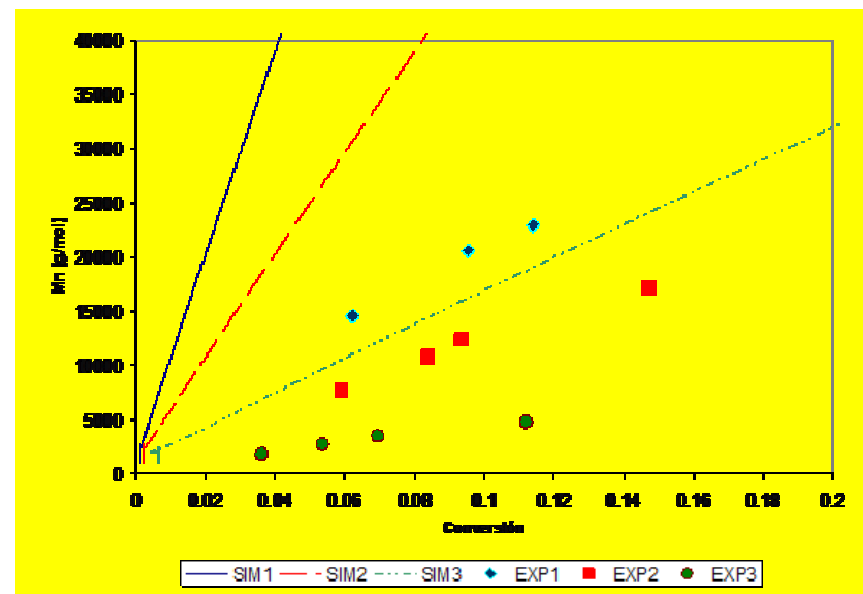
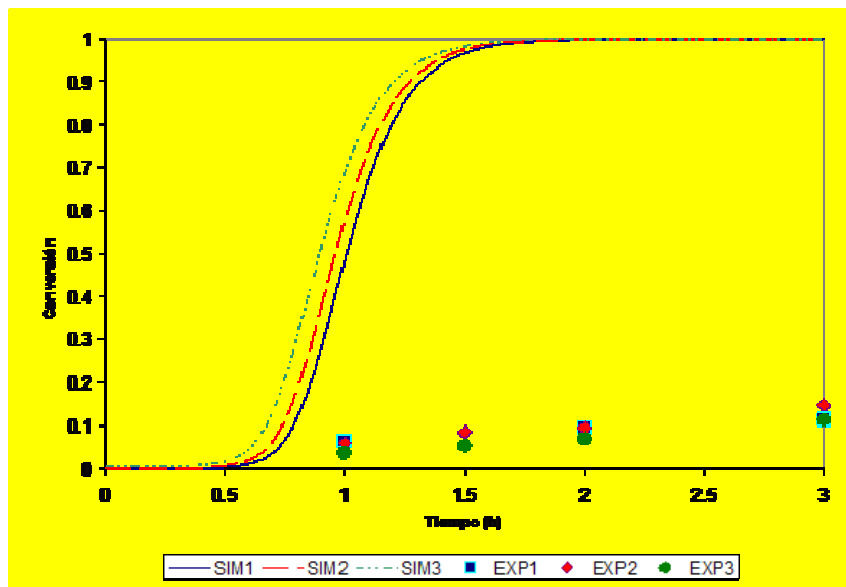
- Iniciación
- ⊕ I[•] → R[•], k_d
- ⊕ R[•] + M → P(1), k_i
- Propagación
- ⊕ P(s) + M → P(s+1), k_p
- Adición primaria
- ⊕ P(s) + AR → PAR(s), k_a
- Fragmentación primaria
- ⊕ PAR(s) → PA(s) + R[•], k_f
- Adición
- ⊕ P(s) + PA(r) → D(s) + DA(r), k_a
- Fragmentación
- ⊕ D(s) → P(s), k_f
- ⊕ D(s) → PA(s), k_f
- ⊕ DA(s) → P(s), k_f
- ⊕ DA(s) → PA(s), k_f
- Aducto de tres brazos
- ⊕ D(s) + P(r) → T1(s) + T3(r), k_t
- ⊕ DA(s) + P(r) → T2(s) + T3(r), k_t
- ⊕ D(s) → T1(s), k_t
- ⊕ DA(s) → T2(s), k_t
- Terminación
- ⊕ P(s) + P(r) → Q(s+r), k_t, P(s) + P(r) → Q(s) + Q(r), k_t

Figure 7. Comparison of model predictions obtained with models 1, 2 and 3, and experimental data (25) of conversion vs. time for the RAFT polymerization of styrene with cumyl dithiobenzoate and AIBN at 60°C. The polymerization conditions and kinetic parameters are: $[M]_0 = 5 \text{ mol L}^{-1}$, $[I]_0 = 3.5 \times 10^{-3} \text{ mol L}^{-1}$, $k_d = 9.53 \times 10^{-6} \text{ s}^{-1}$, $f = 0.64$, $k_i = k_p = 339 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{td} = 0$, $k_{tc} = 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{tir} = 0$, $k_a = k_b = 5.4 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{add} = k_{bd} = 3.5 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$, and $k_b = k_a = k_{bd} = k_{add} = 3.3 \times 10^{-2} \text{ s}^{-1}$. All other rate constants are set equal to zero.

Pallares et al., J. Macromol. Sci., A: Pure Appl. Chem., in press, 2006

RAFT in scCO₂ (Exp. Data from Arita et al., 2005)

- Preliminary Results of Dispersion Polymerization using Predici
- Styrene Polymerization at 80 °C and 300 bar with Cumil Ditiobenzoate as RAFT agent, and AIBN as initiator, $[I]_0=2.6e-3$ M, $[M]_0=6.49$ M, $[RAFT]= (0.35, 0.7 \text{ and } 2.1) \times 10^{-2}$ M



Present Research Lines

- Polymer Network Formation via free-radical copolymerization with crosslinking and nonlinear step growth polymerization.
- Dispersed phase polymerization (suspension, dispersion and emulsion).
- “Living”/Controlled free radical polymerization (CRP).
- **Polymerization and processing in supercritical carbon dioxide.**
- Microwave activated polymerizations.
- Non ideal mixing in stirred tank reactors.
- Reactive processing.



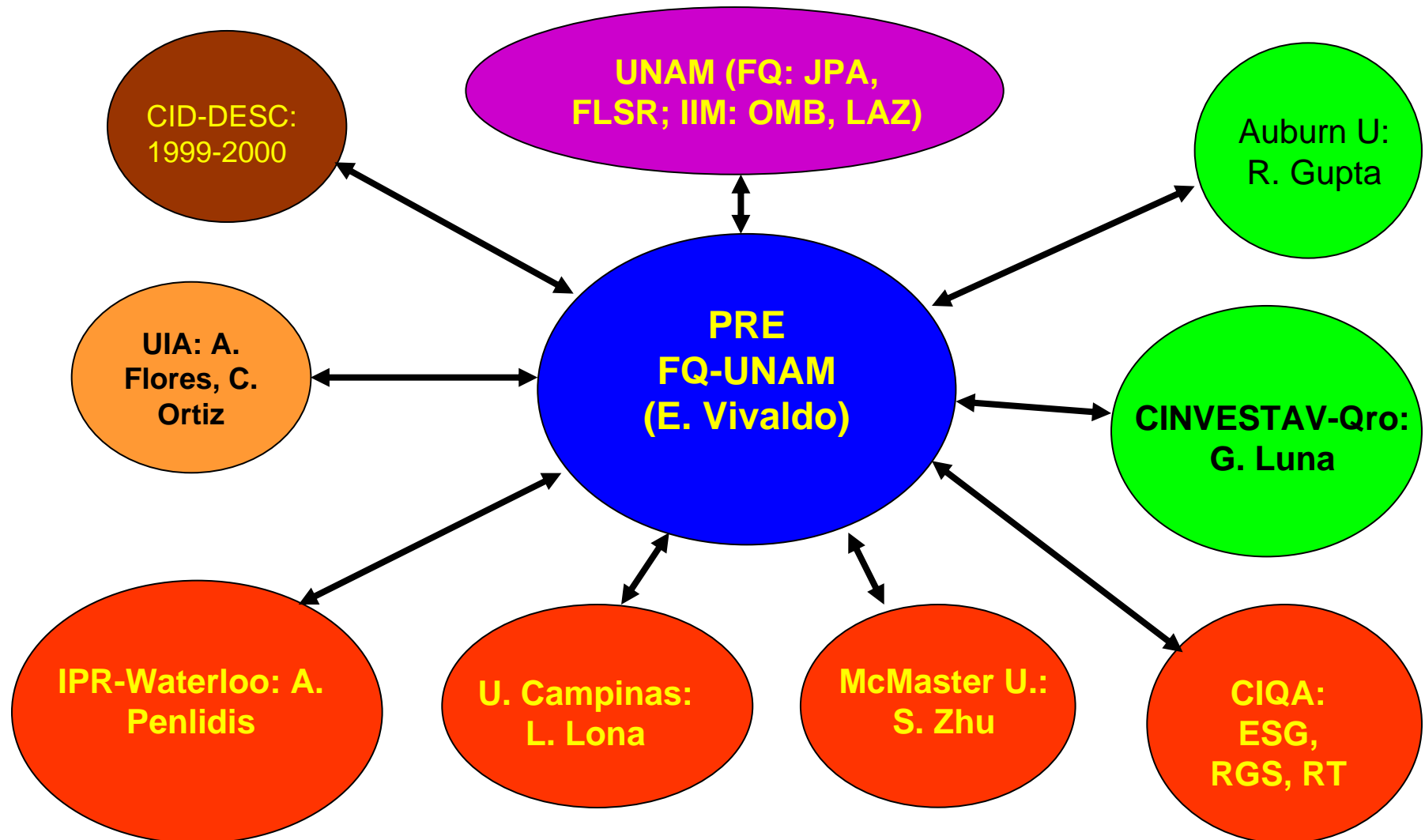
Infrastructure at UNAM



- **COMPUTING:**
- 4 personal computers (PCs) for simulation work.
- 2 portable computers (laptops).
- Self developed and commercial polymerization packages (Predici[®], Parsival[®], Emulpoly, Watpoly), with teaching and research licenses.
- **POLYMERIZATION AND CHARACTERIZATION:**
- GPC Waters, with RI, viscosity and UV detectors
- Particle size analyzer (0.02 a 2000 micras), Malvern Mastersizer 2000
- 2 liter Parr reactor with PID temperature controller, lateral windows, display for other variables (e.g., agitation), and fittings
- 600 mL Parr Reactor for high pressure applications (up to 5000 psia) with PID temperature controller.
- High pressure, low volume cell with dual syringe ISCO pumps
- Conventional glassware and chemical equipments (vacumm pump and oven, friedge for flammables, recirculators with temperature control, etc.)
- Access to NMR, IR, DSC X-Ray, etc., at the analytical central facilities (USAI) of FQ-UNAM



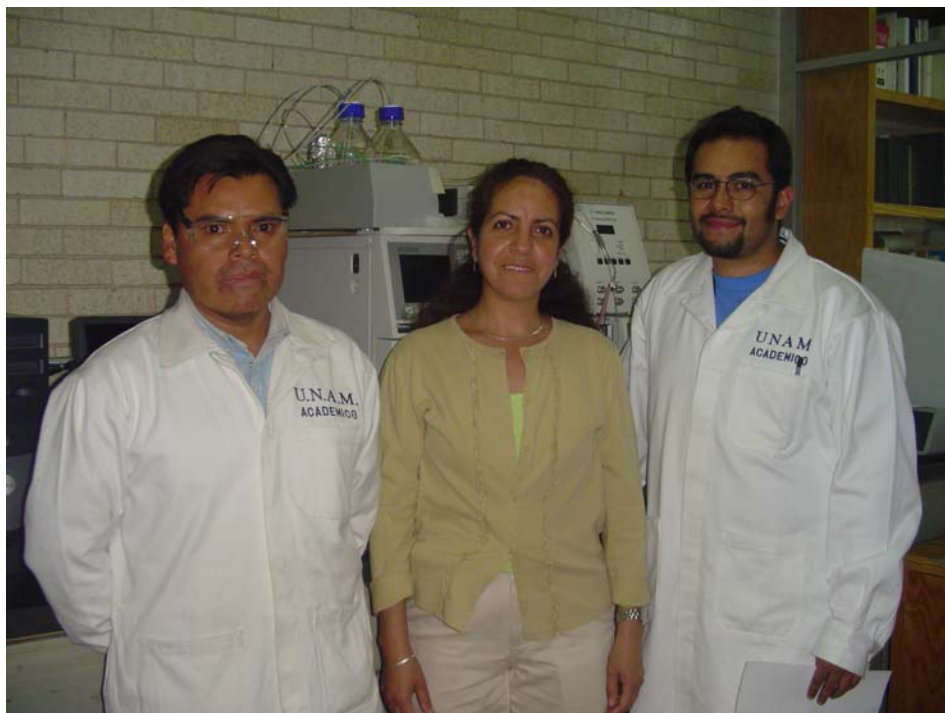
How have we managed to obtain good results in non optimal conditions?



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Present Research Group



Pedro García (Experimental Polym. In $sc\text{-CO}_2$); Martha Roa (Experimental NMRP); Gabriel Jaramillo (Modeling and Experimental RAFT Polym.), and Iraís Quintero (Modeling of Polymerization and Processing in $sc\text{-CO}_2$)



Guillermo Soriano (CIQA): Synthesis of RAFT controllers