



# MODEL DISCRIMINATION IN MICROEMULSION POLYMERIZATION



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## Emulsion and Micremulsion Differences

### Direct Microemulsion Polymerization

- Oil soluble monomers
- Stable monodisperse microlatex
- Final Dp < 50 nm

**Importance**  
 Micelles: 3-5 nm  
 Fast reaction rates  
 High Mw

### Intervals in Emulsion Polymerization

Interval I:  $[M] \neq N_p \neq \emptyset$   
 Interval II:  $[M] = N_p = \emptyset$   
 Interval III:  $[M] \neq N_p = \emptyset$

### Kinetic Theory of Microemulsion Polymerization

Interval I:  $[M] \neq N_p \neq \emptyset$   
 Interval 2:  $[M] \neq N_p \neq \emptyset$

Note: An interval of constant rate is not observed !!

## Micremulsion Models

### Model by Guo, et al. (1992). Styrene

$$\frac{dN_p}{dt} = k_p(N_p - N) + k_{tr}N_p$$

$$\frac{dN_m}{dt} = k_{tr}N_p - k_{tm}N_m$$

$$\frac{dN_c}{dt} = k_{tr}N_p - k_{tc}N_c$$

$$\frac{dN_s}{dt} = k_{tr}N_p - k_{ts}N_s$$

### Model by Morgan, et al. (1997). C<sub>6</sub>MA Pseudomassic

$$\frac{d[M]}{dt} = -k_p \frac{[M]N_p}{M_0}$$

$$[M] = C_m(1-x)$$

### Model by Mendizábal, et al. (1997). Styrene

$$\frac{dN_p}{dt} = k_p(N_p - N) + k_{tr}N_p$$

$$\frac{dN_m}{dt} = k_{tr}N_p - k_{tm}N_m$$

$$\frac{dN_c}{dt} = k_{tr}N_p - k_{tc}N_c$$

$$\frac{dN_s}{dt} = k_{tr}N_p - k_{ts}N_s$$

## Integrodifferential Approach

### Proposal

- Take advantage of the integral method robustness and the differential one discrimination capability (López-Serrano et al., 2004, AIChE and IECR)
- First step. Smooth experimental data
- Second step verify unicity in the solution and interval zones
- Third step. Analyse constancy of the parametes and compare the with original modeling/thermodynamic hypotheses.
- Corroborate or modify model (based on first principles)

### Pseudomassic Model

(de Vries et al. Macromolecules, 2001, 34, 3233)

$$\frac{dx}{dt} = k_p \frac{M_0 \rho}{M_0} = k_p C_m(1-x)^b$$

$$\frac{dx}{dt} = A(1-x)^b t$$

Analytic solution

$$x = 1 - \left[ 1 - \frac{(1-b)A t^{\frac{1}{1-b}}}{2} \right]^{\frac{1}{1-b}}$$

x = fractional conversion  
 p = k<sub>p</sub> = rate of initiation  
 K<sub>p</sub> = propagation rate constant  
 M<sub>0</sub> = monomer conc. inside parts.  
 M<sub>i</sub> = initial monomer concentration

### Integrodifferential Estimation

Provided that b ≠ 1. This Eq has two parameters; A and b, then if we have the conversion (y<sub>i</sub>) and its derivative measurements (y<sub>i</sub>') against time, then we have:

$$y_i = 1 - \left[ 1 - \frac{(1-b)A t^{\frac{1}{1-b}}}{2} \right]^{\frac{1}{1-b}}$$

Solution:

$$A = \frac{2(1-y_i)^{1+b} - 1}{(b-1)t^2} \quad b = \frac{\ln\left(\frac{y_i'}{A t}\right)}{\ln(1-y_i)}$$

The solution exists always for b ≠ 1 and det O ≠ 0, t ≠ 0, y<sub>i</sub> ≠ 1 and y<sub>i</sub>' ≠ 0

## Approaches to Model Microemulsion Polymerization

	Guo et al. (1992)	Morgan et al. (1997)	Mendizábal et al. (1997)
Imp	Cell-A	Cell-A	Micellar + compartmentalized
Particle generation	N <sub>p</sub> = N <sub>0</sub> (exp(kt)) Micellar	N <sub>p</sub> = K <sub>1</sub> Micellar	Micellar and homogeneous (N <sub>p</sub> , N <sub>0</sub> ) (time = 1000s)
Capture coefficients	k <sub>tr</sub> > k <sub>tm</sub> second	k <sub>tr</sub> = k <sub>tm</sub> first	k <sub>tr</sub> > k <sub>tm</sub> second
rate of capture of particles (total)	second	first	second
rate of capture of micelles	second	second	first
rate of desorption (total)	second	second	first
System	Compartmentalized	Pseudo-hull, (neglect water phase termination)	Compartmentalized
Describes	Conversion, particle generation	Conversion, termination	Conversion, particle generation, molecular weight

## Modeling Contradictions

- Monomer inside particles
- Mass balance of monomer in droplets (micelles)
- Nucleation along the whole reaction
- First and second order capture and exit rate constants
- Pseudo-hull vs compartmentalized systems
- Order of magnitude difference between capture coefficients particles vs droplets
- Redundant equations non steady state on N<sub>i</sub> and N<sub>c</sub> (Guo and Mendizábal)

**Compartmentalized**

$$\frac{dx}{dt} = k_p \frac{M_0 \rho}{M_0}$$

**Pseudomassic**

$$\frac{dx}{dt} = k_p \frac{M_0 \rho}{M_0}$$

**Total No. Particles**

$$\frac{dN_p}{dt} = \rho_p N_p$$

Both models are analogous !

## Results

### Conversion Curves

Initiator V50: (▲) nC<sub>6</sub>MA, 0.24 mM; (●) nC<sub>7</sub>MA, 0.061 mM and (○) tC<sub>6</sub>MA, 0.24 mM; (◐) tC<sub>6</sub>MA, 0.061mM. (de Vries et al., 2001)

### Conversion Derivative and Observability

### Parameter Estimates

$$A = k_p \left( \frac{C_m}{M_0} \right); \quad M_p = C_m(1-x)^b$$

Initiator V50: (▲) nC<sub>6</sub>MA, 0.24 mM; (●) nC<sub>7</sub>MA, 0.061 mM and (○) tC<sub>6</sub>MA, 0.24 mM; (◐) tC<sub>6</sub>MA, 0.061mM. b = 1.4 (de Vries et al., 2001)

## Conclusions

- An Integro-Differential Approach has been presented. The observability notion was incorporated (unicity).
- With only conversion measurements it is not possible to determine if microemulsion polymerization is compartmentalized or pseudomassic.
- For tC<sub>6</sub>MA the parameter b seemed to be higher than the one reported before (de Vries et al., 2001).
- New experiments should be designed under a differential structure with a more dense mesh of data (more discrimination capability than integral method). Study measurement propagation error on estimates.
- This method allows to obtain the parameters functional dependencies in terms of the system states and have a better model assessment.