



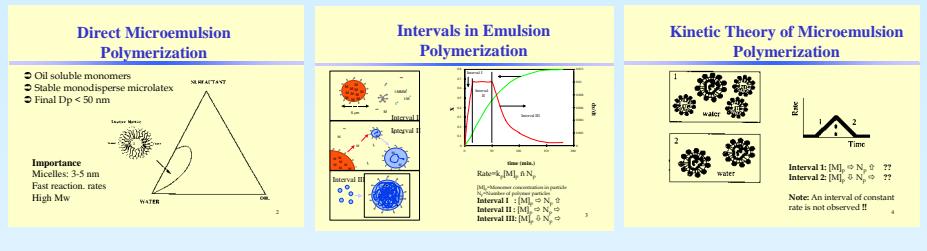
MODEL DISCRIMINATION IN MICROEMULSION POLYMERIZATION



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Emulsion and Micremulsion Differences



Integrodifferential Approach

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

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

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

$$M_p = C_m(1-x)^b$$

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

$$A = \frac{k_p C_m \rho}{M_o}$$

Analytic solution

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

x = fractional conversion
 $\rho = k_p$ - rate of initiation.
 k_p = propagation rate constant
 M_p = monomer conc. inside parts.
 M_o = initial monomer concentration

Integrodifferential Estimation

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

Provided that $b \neq 1$. This Eq has two parameters; A and b, then if we have the conversion (y_o) and its derivative measurements (y'_o) against time, then we have:

$$y_i = A(1-y_o)^b t$$

Solution:

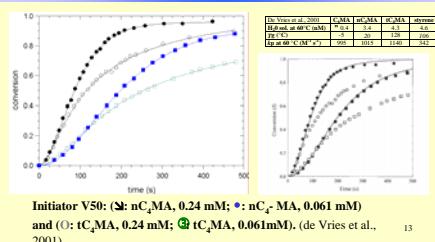
$$A = \frac{2(1-y_o)^{1-b} - 1}{(b-1)t^2}$$

$$b = \frac{\ln\left(\frac{y_i}{At}\right)}{\ln(1-y_o)}$$

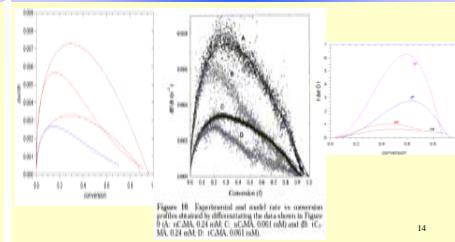
The solution exists always for $b \neq 1$ and $t \neq 0$, $y_o \neq 1$ and $y'_o \neq 0$.

Results

Conversion Curves



Conversion Derivative and Observability



Parameter Estimates $A = k_p \frac{C_m}{M_0} (M_p/M_0)^b$; $M_p = C_m(1-x)^b$

Initiator V50: (Δ : nC₄MA, 0.24 mM; \bullet : nC₄MA, 0.061 mM) and (\circ : tC₄MA, 0.24 mM; \square : tC₄MA, 0.061 mM).

$b = 1.4$ (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 tC₄MA 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.

Micremulsion Models

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

$$\frac{dN}{dt} = k_p [M]_o N^b$$

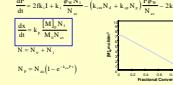
$$\frac{dN}{dt} = k_{tr} N_i$$

$$\frac{dP}{dt} = 2k_t N_i + k_{tr} N_i - (k_{in} N_d + k_{in} N_c) \frac{dN}{dt}$$

$$\frac{dx}{dt} = \frac{[M]_o N^b}{M_o}$$

$$N = N_d + N_c + N_i$$

$$N_d = N_d(1 - e^{-k_{in} t})$$



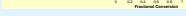
Model by Morgan, et al. (1997). C₆MA Pseudomassic

$$\frac{dx}{dt} = \frac{[M]_o N^b}{M_o}$$

$$N^b = \rho_w N$$

$$N = N_d + N_c + N_i$$

$$N_d = N_d(1 - e^{-k_{in} t})$$



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

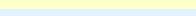
$$\frac{dx}{dt} = \frac{[M]_o N^b}{M_o}$$

$$\frac{dx}{dt} = \frac{[M]_o N^b}{M_o}$$

$$N^b = \rho_w N$$

$$N = N_d + N_c + N_i$$

$$N_d = N_d(1 - e^{-k_{in} t})$$



Approaches to Model Microemulsion Polymerization

Guo, et al (1992) PS	Morgan, et al (1997) PS	Mendizábal, et al (1997) PS
[M]_o	Cot(1-s)	Cot(1-s)
Particle generation	N _p = N _p (1-exp(-kt))	Micelle formation
rate of capture of monomers (order)	Monomer	N _m = K ₁
capture coefficient	second	first
rate of capture of monomers (order)	second	first
rate of desorption (order)	second	second
desorption	second	second
System	Compartmentalized	Pseudo-bulk (neglects water phase)
Describes	Conversion, particle generation	Conversion, particle generation, conversion

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 bulk vs compartmentalized systems
- Order of magnitude difference between capture coefficients per particle/drop
- Redundant equations non steady state on N_i and N_d (Guo and Mendizábal)

Compartmentalized	Conversion	Total No. Particles
$\frac{dx}{dt} = \frac{k_p M_o \bar{n} N_d}{M_o}$	$\frac{dN_d}{dt} = \rho_w N_d$	$\frac{dN_d}{dt} = \rho_w N_d$
$\frac{dx}{dt} = \frac{k_p M_o N^b}{M_o}$	$\frac{dN^b}{dt} = \rho_w N^b$	$\frac{dN^b}{dt} = \rho_w N^b$

Both models are analogous !

Conversion

Total No. Particles

$\frac{dx}{dt} = \frac{k_p M_o \bar{n} N_d}{M_o}$

$\frac{dx}{dt} = \frac{k_p M_o N^b}{M_o}$

$\frac{dN^b}{dt} = \rho_w N^b$

$\frac{dN_d}{dt} = \rho_w N_d$

$\frac{dN_d}{dt} = \rho_w N_d$

$\frac{dN^b}{dt} = \rho_w N^b$

$\frac{dN_d}{dt} = \rho_w N_d$

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