

## MODELING CONTROVERSIES IN MICROEMULSION POLYMERIZATION

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**Abstract-** Here, the previously presented integrodifferential approach to estimate parameters and to evaluate modeling consistency is now applied to the microemulsion polymerization (MEP) system. Two monomers, n-butylmethacrylate (n-C<sub>4</sub>MA) and tert-butylmethacrylate (t-C<sub>4</sub>MA) with T<sub>g</sub>s of 20 and 128 °C, respectively, at two initiator concentrations (0.24 and 0.61M) each, reported in the literature are evaluated. Using the pseudomassic model for MEP the two parameters appearing in the model, one (A) containing the propagation rate constant and the other (b) considering thermodynamic monomer partition, are estimated. The system's observability determinant is used as a guide to evaluate the rich-in-information zone. Using only conversion measurements it is not possible to determine if the MEP follows a compartmentalized or pseudomassic scheme. For the t-C<sub>4</sub>MA system the parameter b was higher than the one reported before.

### Introduction

Parameter estimation, model discrimination, and experimental design are three related subjects with important applications and implications in basic research and in process analysis, design, scale-up, monitoring, optimization, and control. Batch, semi-batch, or transitions of continuous processes and transient experiments are represented by differential equations with some parameters that must be fitted from experimental data, and where models have to be discriminated. In Chemical Engineering the parameter estimation and model discrimination problems have been mostly addressed with deterministic or statistical nonlinear regression methods (Esposito and Floudas). The field of emulsion polymerization is a prototypical example exhibiting well the general situation of the parameter estimation and model discrimination problems in chemical engineering. Complex multiphase reaction kinetic schemes and thermodynamic equilibria are present, and many related parameters are involved. According to van Herk and German (1998), in many cases wrong parameter-model pairs have become fitting devices of experimental data, and many basic kinetic and thermodynamic parameters needed are still lacking. For instance, it is generally accepted that the experimental determination of the entry-exit coefficient rate pair in the interval-II emulsion polymerization is a key point in the understanding the emulsion polymerization mechanism. Here, the previously presented integrodifferential approach (Lopez-Serrano et al., 2004) to estimate parameters and to evaluate modeling consistency is now applied to the microemulsion polymerization (MEP) system. Two monomers, n-butylmethacrylate (n-C<sub>4</sub>MA) and tert-butylmethacrylate (t-C<sub>4</sub>MA) with T<sub>g</sub> of 20 and 128 °C, respectively, at two initiator concentrations (0.24 and 0.61M) each, reported in the literature (De Vries et al., 2001) are evaluated. Using the pseudomassic model for MEP the two parameters appearing in the model, one (A) containing the propagation rate constant and the other (b) considering thermodynamic monomer partition, are estimated.

### Previous work.

Table 1, presents the assumptions made by several models reported in the literature. Here it is evident that not only differences exist among the models, but also, important contradictions do exist. The first controversy refers to monomer concentration inside the particle. The monomer concentration value in a particle, surrounded by monomer droplets, is the result that the system minimizes its free energy: to reach equilibrium between to opposed forces to reduce the free surface energy (which acts to maintain the particles as small as possible and to diminish monomer concentration in the particle) and the other which reduces the free energy of mixing of monomer /polymer (this pushes the particle to swell to the maximum value of pure monomer). This equilibrium is given by Morton's equation (1954). Morton's equation predicts that monomer concentration increases as the radio increases, also, during the first polymerization stage, the particle radius should increase with conversion, which contradicts Guo et al., (1992) and Morton et al., (1997) proposal. These latter authors say that monomer concentration decreases linearly with conversion.

Another inconsistency is found with the capture of radicals coefficient, Guo et al., (1992) and Mendizábal et al., (1998) propose that the capture of radicals coefficient by particles is much larger than the one of capture by micelles (up to two orders of magnitude). However Morgan et al., assume that no difference exists among them. Guo et al. (1992), as well as Morgan et al. (1997), propose that neither the micelles nor the droplets disappear during the polymerization, however, Mendizábal et al., (1998) explain that the maximum reaction rate occurs when the droplets in the microemulsion disappear.

The only work that proposes homogeneous nucleation is the one by Mendizábal et al., however, this model requires propagation rate constant values, in the water phase, two orders of magnitude higher than the ones reported in conventional emulsion, mass or solution polymerizations.

Also discrepancies exist among the capture of radicals coefficient's orders, varying between one and two. Another contradiction is that Guo et al., and Mendizábal et al., Propose a compartmentalized system, while Morgan et al., assume that the system is pseudomassic, neglecting free radicals termination in the water phase. In the only topic that all these authors seem to agree is in the radicals rate of exit order.

**Table 1. Assumptions and predictions of several microemulsion polymerization models reported before.**

	<b>Guo et al. (1992) Polystyrene</b>	<b>Morgan et al. (1997) C<sub>6</sub>MA</b>	<b>Mendizábal et al. (1998) several monomers</b>
<b>Monomer in particles</b>	Co(1-x)	Co(1-x)	Morton's Eq.
<b>Particle Generation d</b>	$N_p = N_{do}(1 - \exp(-k t))$ Micellar	Radicals $N^* = K t$ Micellar	Micellar and homogeneous ( $N_o, N_i$ ) ( $k_{pw} = 100 k_p$ )
<b>Capture Coefficients</b>	$K_{cp} > k_{cm}$	$k_{cp} = k_{cm}$	$k_{cp} > k_{cm}$
<b>Order of capture of radicals by particles</b>	Second	First	Second
<b>Order of capture of radicals by micelles</b>	Second	First	Second
<b>Desorption orden</b>	Second	Second	Second
<b>System</b>	Compartmentalized	Pseudomassic (Neglects water phase termination)	Compartmentalized
<b>Describes</b>	Conversion, particle generation	Conversion, rate of reaction	Conversion, particle generation, molecular weight

In Table 2, the comparison of the two main models is presented, here it can be seen that with only conversion measurements, no discrimination can be done, for instance in the case of conversion the two rate equations are the same. Actually when comparing the rate equations in any Polymer Textbook, the total radical concentration (in mass or solution free radical polymerization) equals  $\tilde{n}N_T/N_{av}$ , where  $\tilde{n}$  is the average number of radicals inside the particles,  $N_T$  is the total number of particles and  $N_{av}$  is Avogadro's number. In the particles or radicals evolution case, it is a well-known fact that the number of micelles;  $N_m$ , is several orders of magnitude higher than the particle number, therefore it remains approximately constant, when compared to the total number of particles, therefore with the rate expression for the number of particles (or radicals) for the compartmentalized (or pseudomassic) model, the rate equations are also equivalent. As seen in Table 2.

Table 2. Compartmentalized and Pseudomassic models

Model	Conversion	Total No. Particles
Compartmentalized	$\frac{dx}{dt} = \frac{k_p M_p \tilde{n} N_T}{M_o N_{av}}$	$\frac{dN_T}{dt} = \rho_m N_m$
Pseudomassic	$\frac{dx}{dt} = \frac{k_p M_p N^*}{M_o}$	$\frac{dN^*}{dt} = \rho_0$

### Pseudomassic model

Due to the fact that no discrimination between the pseudomassic or the compartmentalized models can be performed only with conversion data, we proceed to study a pseudomassic model reported previously (Vries, 2001). This scheme is rather simple and to model the conversion (x) evolution the following equation has been used:

$$\frac{dx}{dt} = A(1-x)^b t \quad (1); \quad \text{here } A = \frac{k_p C_m \rho}{M_o} \quad (2)$$

the parameter b corresponds to a monomer thermodynamic partition between the micelle and the particle domains,  $k_p$  is the propagation rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ ),  $C_m$  is the monomer concentration inside the reacting particles,  $M_o$  is the initial monomer concentration ( $\text{mol L}^{-1}$ ) and  $\rho$  is the initiation rate given by:

$$\rho = 2 k_d I \quad (3)$$

where  $k_d$  ( $\text{s}^{-1}$ ) is the initiator dissociation rate constant and  $I$  ( $\text{mol L}^{-1}$ ) its concentration.

### Differential Estimation

Eq 1 analytic solution is:

$$x = 1 - \left[ 1 - \frac{(1-b)At^2}{2} \right]^{\frac{1}{1-b}} \quad (4)$$

Provided that  $b \neq 1$ . Eq 4 has two parameters; A and b, then if we have the conversion ( $y_o$ ) and its derivative measurements ( $y_1$ ) against time, then eqs 4 and 1 can be rewritten as:

$$y_o = 1 - \left[ 1 - \frac{(1-b)At^2}{2} \right]^{\frac{1}{1-b}} \quad (5) \quad y_1 = A(1-y_o)^b t \quad (6)$$

Here we have two Eqs (5 and 6) and two unknowns (A, b). The system of Eqs 5 and 6 has a solution if  $\det O \neq 0$  where  $\det O$  is given by:

$$\det O = \begin{bmatrix} \partial_A z_1 & \partial_b z_1 \\ \partial_A z_2 & \partial_b z_2 \end{bmatrix} \neq 0, \text{ where } z_1 = x \text{ and } z_2 = \frac{dx}{dt}$$

after simple algebraic manipulations the solution for the two parameters is:

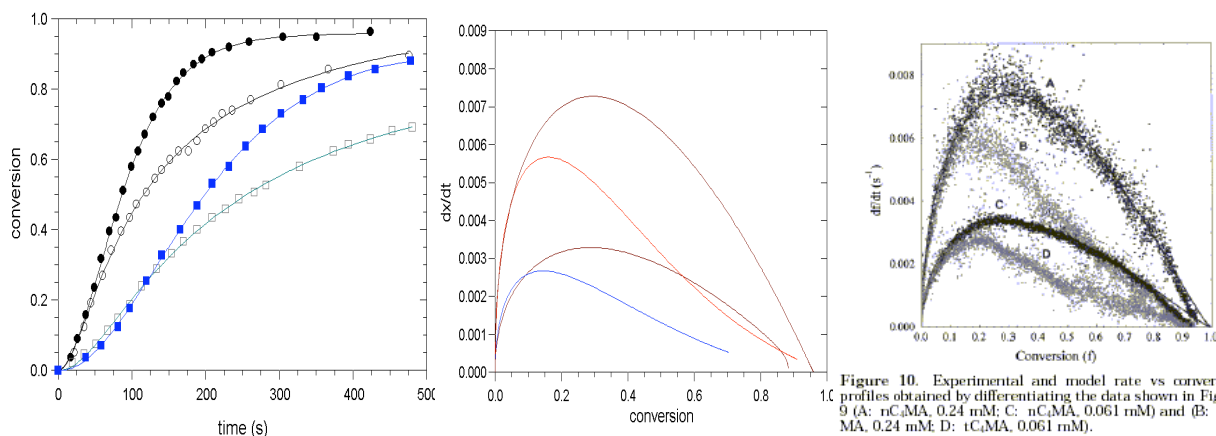
$$A = \frac{2(1-y_o)^{1-b} - 1}{(b-1)t^2} \quad (8) \text{ and } b = \frac{\ln\left(\frac{y_1}{At}\right)}{\ln(1-y_o)} \quad (9)$$

The solution exists always A and b when  $\det O \neq 0$  and  $b \neq 1$ ,  $y_1 \neq 0$  and  $y_o \neq 1$  and  $t \neq 0$ .

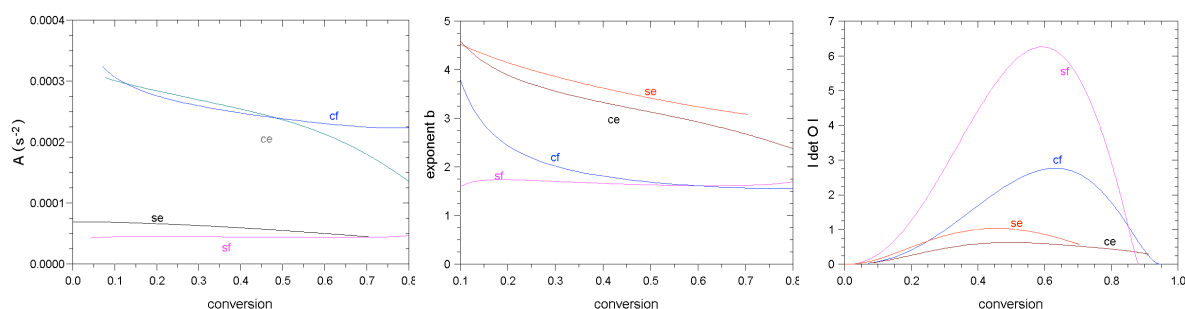
## Results and Discussion

Figure 1 (left) shows the fittings performed to the conversion data (Lopez-Serrano et al., 2004). The Figure in the center corresponds to the obtained filtered derivative (Lopez-Serrano et al., 2004) from the conversion data, and the Figure on the right is the reported derivative experimental data (Vries et al., 2001).

Figure 2 present the A (left) and b (center) estimates as well as the observability matrix determinant absolute value (right). In general the lumped parameter A, which contains the propagation rate constant (see Eq 2), shows a nearly constant or decreasing behavior. Regarding the parameter b, only in one case (nC<sub>4</sub>MA; 0.061 mM initiator a constant behavior (center graph, curve sf) was found, in all the other experiments b shows a decay with conversion. The values found for the parameter b are greater than the ones reported by Vries et al., 2001, claiming a constant value of 1.4 for all these cases.



**Figure 1. Left curve:** Conversion-time experimental data (Vries et al., 1999). nC<sub>4</sub>MA/DTAB and tC<sub>4</sub>-MA /DTAB. (●)nC<sub>4</sub>MA 0.24 mM, (■) nC<sub>4</sub>MA 0.061 mM initiator and (○) tC<sub>4</sub>-MA 0.24 mM and (□) 0.61 mM initiator conc. **Central curve:** derivative in this work. **Right curve:** Experimental derivative reported previously (Vries et al., 2001).



**Figure 2.** Estimates for  $A$  (Left curve),  $b$  (Center curve) and the absolute value for  $\det O$  (Right curve), respectively; for systems  $nC_4MA/DTAB$  and  $tC_4MA/DTAB$ . (cf)  $nC_4MA$  0.24 mM, (sf)  $nC_4MA$  0.061 mM initiator and (ce)  $tC_4MA$  0.24 mM and (se) 0.61 initiator concentration.

## Conclusions

An integrodifferential approach has been presented to estimate with unicity, that is obtaining a unique solution, two parameters one lumped ( $A$ ) containing, among others, the propagation rate constant and the other ( $b$ ) considering thermodynamic monomer partition. The observability notion was incorporated (unicity). With only conversion measurements it is not possible to determine if microemulsion polymerization is compartmentalized or pseudomassic because both models are similar. For  $tC_4MA$  the parameter  $b$  appeared to be higher than the one reported before. New experiments should be designed under a differential structure with a more dense data mesh (more discrimination capability than integral method). This method allows to obtain the parameters functional dependencies in terms of the system states and achieve a better modeling assessment.

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