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Francisco Lopez Serrano

Abstract

Presentation

Poster

Determination of Styrene-Methyl Methacrylate Reactivity Ratios Dependencies on Feed Composition.

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Introduction

Generally, in nonlinear regression with constant parameter fitting, the information derived from the measurement derivative is not exploited [1,2] and there are multiple fittings with some models [3, 4] and it is not clear if this is due to the model or the fitting. In standard regression, a candidate model is evaluated [5,6] where the parameters constancy is assumed, the regression is applied and the model adequacy is judged by the size of its prediction errors; the choice of the number of parameters is guided by the specific candidate model [3, 4], physical insight and some dosage of trial and error. To improve the parameter model approach, recently [7] the employment of differential estimation has been proposed to address polymerization kinetics problems. The idea is to split the problem in two parts and to exploit the measurements derivatives information, in order to improve the capability and systematization of the modeling task. In the first step, the measurements and its derivatives are used with mass balances without *a priori* kinetic assumptions to draw the parameters shape against feed composition. In the second step, based on the results of step one, and on a sound theoretical or physicochemical insight, a parameter or parameter groupings fitting versus feed composition is performed according to the standard curve fitting procedure. The differential method is a well-known tool in nonlinear estimation theory, as well as in reaction kinetics via the so-called differential method [8] in batch and continuous reactor experiments. Here this approach will be employed to assess the reactivity ratios dependency on feed composition without *a priori* kinetic assumptions and in a second step, a fit can be performed according to the functionalities of existing models. The proposed approach is tested with the ultimate model (eq 1) and data previously presented in the literature for the copolymerization of styrene and methyl methacrylate [11, 12].

Constant parameter approach

In the ultimate model [5], the copolymer equation is:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

and the average propagation rate constant is:

$$\langle k_p \rangle = \frac{r_1^2 f_1^2 + 2f_1 f_2 + r_2^2 f_2^2}{r_1^2 f_1 / k_{11} + r_2^2 f_2 / k_{22}} \quad (2)$$

where F_1 and f_1 are the monomer compositions in the polymer and monomer feed, respectively, $r_i = k_{ii}/k_{ij}$ ($i = 1, 2$) are the reactivity ratios and k_{ii} and k_{ij} are the homopolymerization and cross propagation rate constants, respectively. Eqs 1 and 2 can also represent the penultimate model; in this case replace k_{ii} by k_{ii}^p and r_i by r_i^p as follows:

$$r_i^p = r_i \left(\frac{r_i f_i + f_j}{r_i f_i + f_j} \right) \quad (3)$$

$$k_{ii}^p = k_{ii} \left(\frac{r_i f_i + f_j}{r_i f_i + f_j / s_i} \right) \quad (4)$$

As it can be seen in eqs 1 and 2, four parameters appear for the ultimate model: two reactivity ratios (r_i) and two homopolymerization rate constants (k_{ii}). However, in the penultimate model, eight parameters appear: four monomer reactivity ratios ($r_i = k_{ii}/k_{ij}$), $r_i^p = k_{ii}^p/k_{ij}$), two homopolymerization rate constants (k_{ii}) and two radical reactivity ratios ($s_i = k_{ii}^p/k_{ii}$). The homopolymerization (k_{ii} , k_{ij}) rate constants can be determined from independent experiments; therefore, in the ultimate model two parameters are left to be determined and six in the penultimate model. In this last model six parameters are still too many to be determined from polymer composition (F_1) and the propagation

rate constant (k_p) versus monomer feed composition (f_1). Comparing the ultimate and the penultimate models, it can be realized that the four parameters appearing in the ultimate model, can be treated as functions. It can be seen (eq 3) that r_i^p is a function of f_i with two parameters r_i and s_i and k_{ii}^p is also a function of f_i , where r_i and s_i are the parameters. Therefore, in principle, if r_i^p are allowed to vary against monomer feed (f_i) the penultimate model (eq 3) functional form can be tested, otherwise the ratios r_i^p will remain constant indicating the ultimate model validity. The same applies to eq 4, allowing also, in principle, the determination of the corresponding parameters.

The differential estimation approach.

Let us apply the differential method and take the derivative [9, 10, 15] of F_1 with respect to f_1 in eq 1 to obtain:

$$\dot{F}_1 = \frac{1 - f_1 + 2f_1(r_1 - 1)r_2 + f_1^2(r_1 + r_2 - 2r_1r_2)}{(r_2 + f_1(2 - 2r_2 + f_1(r_1 + r_2 - 2)))^2} \quad (5)$$

Mathematically speaking, this equation is a notion of "instantaneous" or differential observability [9, 10] in the sense that r_1 and r_2 can be uniquely determined from the composition measurements and their derivatives. This corresponds to the so-called differential estimation method to determine reaction rates [8]. Eq 1 represents the mass balance and eq 5 is the rate of monomer incorporation to the polymer. To determine whether eqs 1 and 5 are independent and where, the observability matrix (Jacobian) determinant is calculated yielding [15]:

$$\det O = \frac{(f_1 - 1)^2 f_1^2}{(r_2 + f_1(2 - 2r_2 + f_1(r_1 + r_2 - 2)))^3} \quad (6)$$

Eq 6 indicates that the system has no solution only when f_1 is zero or one and that elsewhere r_1 and r_2 can be uniquely determined from the

data of F_1 and \dot{F}_1 versus f_1 . Therefore, the left hand side of eqs 1 and 5 and also f_1 are known from experimental data (fit a function to the F_1 versus f_1 data take this function derivative to obtain \dot{F}_1). This procedure yields two equations (eqs 1 and 5) with two unknowns (r_1 and r_2) that allow the calculation of each reactivity ratios at every composition as follows [15]:

$$r_1 = \frac{(f_1 - 1)(F_o - 2F_o^2 + (f_1 - 1)f_1 F_p)}{f_1(-2(F_o - 1)F_o + (f_1 - 1)f_1 F_p)} \quad (7)$$

$$r_2 = \frac{f_1((3 - 2F_o)F_o - 1 + (f_1 - 1)f_1 F_p)}{f_1(-2(F_o - 1)F_o + (f_1 - 1)f_1 F_p)} \quad (8)$$

Here, F_o is the interpolated value of F_1 , and F_p its derivative at every feed composition f_1 .

Results and discussion

Composition and propagation rate data for the copolymerization of styrene and methyl methacrylate at 40°C were taken from the literature [11, 12]. Figure 1 shows the composition data fitted with four sets of penultimate reactivity ratios (Table 1). Two of the sets have been reported previously [3] indicating multiplicity of solutions; this is corroborated in Fig. 1 where no distinction can be made from the four sets. Figures 2 and 3 present the estimation of r_1 and r_2 , for each of the four fits, respectively. In these two figures, the continuous lines represent the penultimate model fit (eq 3) and it can be seen that none of the fits accurately describes this model. Another interesting fact is that all the fits coincide for $0.2 < f_1 < 0.84$ in the case of r_1 and about $0 < f_1 < 0.8$ for the r_2 estimate. This is confirmed verifying the value of the observability matrix determinant (eq 6) and also is corroborated for the values given by Tidwell and Mortimer [13] assuming the reactivity ratios constancy.

Table 1. Multiplicity of solutions when fitting the data of Fig. 1 with the penultimate model.

	Set a (this work)	Set b (this work)	Set 1 ref. [3]	Set 2 ref. [3]
r_1	0.6475	0.829	0.646	0.727
r_2'	0.3324	10.634	0.400	4.581
r_1'	0.3264	3.848	0.386	2.886
r_2	0.4994	0.5106	0.483	0.489

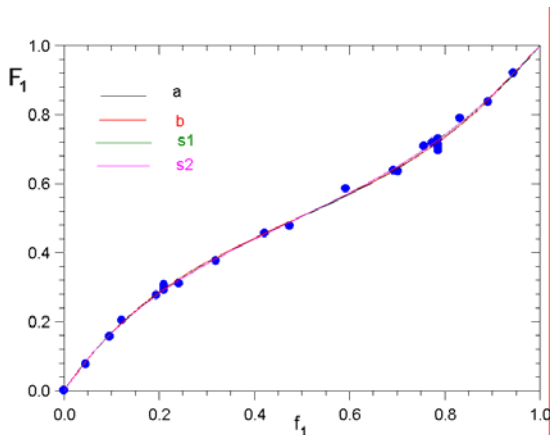


Figure 1. Composition curve, data taken from the literature [11, 12]. The continuous lines represent the fit using the penultimate model and parameters presented in Table 1.

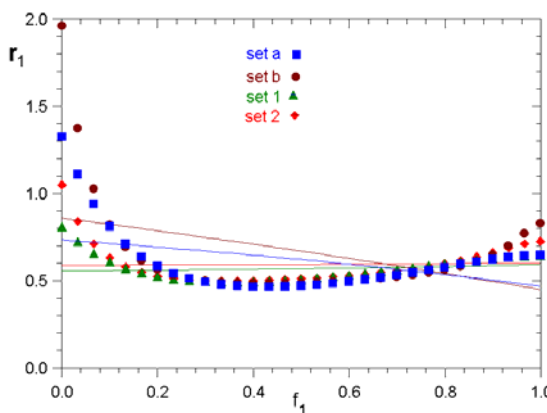


Figure 2. The symbols represent the estimation of r_1 (eq 7) using the four fits presented in Table 1. The continuous lines represent the penultimate model fit (eq 3).

An empirical fit of the estimates was applied to the four sets presented in Table 1. The fit has the following form:

$$r_1 = k_a + k_b f_1 + k_c \exp(k_d f_1) \quad (9)$$

where, k_a , k_b , k_c and k_d are fitting parameters. Eq 9, resembles the form presented previously [14]:

$$\log r_{12} = \log r_{1S} + u_2 \sigma_1 + v_2 \quad (10)$$

Here r_{1S} is the reactivity ratio of monomer 1 with styrene, u_2 represents the polarity of monomer 2, σ_1 represents the polarity of the polymer radical derived from monomer 1 and v_2 represents the intrinsic reactivity of monomer 2.

The same procedure was applied to the k_p versus f_1 data [11] and the k_{11} and k_{22} estimates using eq 2 and its derivative are presented in Figure 4. Non constant behavior is observed here.

Conclusions

A differential approach with an observability notion was applied to the styrene methyl methacrylate data finding that the penultimate model, even fitting adequately the data but with multiplicity, cannot explain the copolymerization behavior. With the differential approach presented here, where the searched

parameters were obtained with unicity, a different dependency of the reactivity ratios was found, as compared by the one postulated by the penultimate model. Also the differential approach shows a more accurate capability of model discrimination.

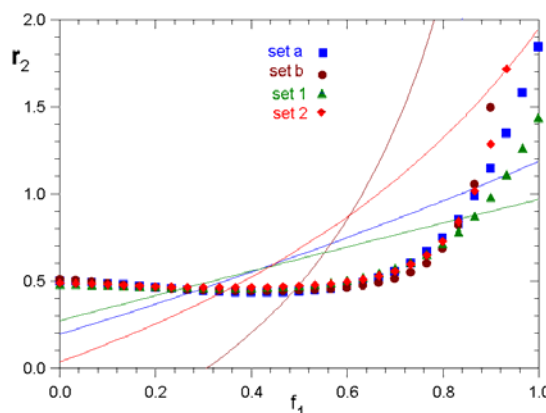


Figure 3. The symbols represent the estimation of r_2 (eq 8) using the four fits presented in Table 1. The continuous lines represent the penultimate model fit (eq 3).

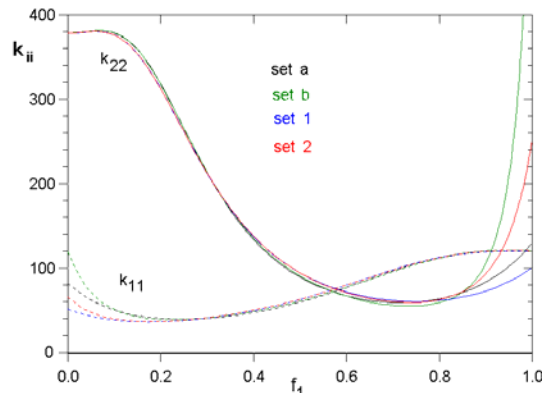


Figure 4. Estimates of k_{11} and k_{22} obtained from eq 2 and its derivative and the values of r_1 and r_2 presented in Figs. 2 and 3. The experimental k_p data was taken from the literature [11].

References

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Determination of Styrene/Methyl Methacrylate Reactivity Ratios Dependencies on Feed Composition

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Motivation

“The elucidation of the mechanism of free radical copolymerization remains an open problem” (Keleman and Klumperman, *Macromolecules*, 2004, 37, 9338)

“... It is concluded that the ‘explicit’ or complete penultimate model should be regarded as the base model for the majority of copolymerization reactions” (Coote and Davis, *Prog. Polym. Sci.* 1999, 24, 1217)

“In conclusion, the triad sequence distributions measured in the work for the styrene-MMA system allow us to state with more authority that there is no penultimate unit effect on polymer chain structure.” (Maxwell et al., *Macromolecules*, 1993, 26, 1956)

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Contents

- Copolymerization
- Previous Approaches
- Differential and Integral Methods Comparison
- Integro-Differential Estimation Proposal
- Reactivity Ratios (parameters) Estimation and Modeling Assessment. Sty-MMA
- Conclusions

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Importance of Copolymerization

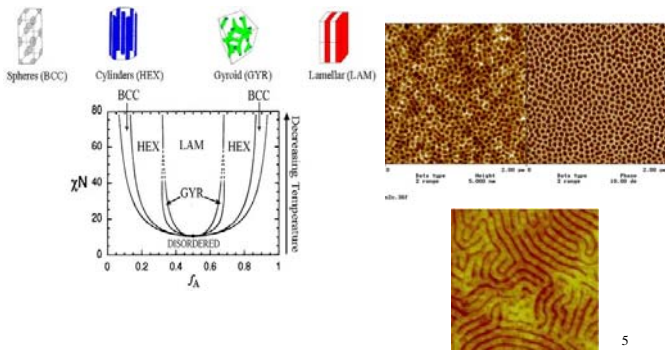
- Statistical or random
~ABAABBABAAABABB~
- Alternating
~ABABABABABABABA~
- Block
~AAAABBBBBBBBAAAA~



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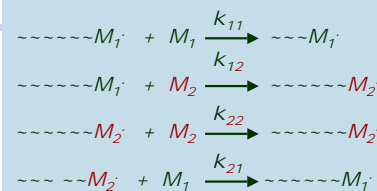
Structure and Morphology



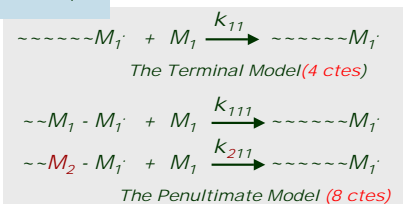
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The Kinetics of Free Radical Copolymerization



Note that we are actually making an assumption; that the rate constants depend only on the nature of the terminal group.





The Copolymer Equation which is a differential equation; r_1 and r_2 are the reactivity ratios

$$\begin{aligned} -\frac{d[M_1]}{dt} &= k_{11}[M_1 \cdot][M_1] + k_{21}[M_2 \cdot][M_1] \\ -\frac{d[M_2]}{dt} &= k_{22}[M_2 \cdot][M_2] + k_{12}[M_1 \cdot][M_2] \end{aligned}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1] \frac{[M_1 \cdot]}{[M_2 \cdot]} + k_{21}[M_1]}{k_{22}[M_2] + k_{12}[M_2] \frac{[M_1 \cdot]}{[M_2 \cdot]}}$$

$$-\frac{d[M_1 \cdot]}{dt} = -k_{12}[M_1 \cdot][M_2] + k_{21}[M_2 \cdot][M_1] = 0$$

$$\frac{[M_1 \cdot]}{[M_2 \cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]}$$

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{r_2 \frac{[M_2]}{[M_1]} + 1}$$

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The Copolymer Equation; Alternative Forms

$$y = \frac{d[M_1]}{d[M_2]} \quad x = \frac{[M_1]}{[M_2]}$$

$$y = \frac{1 + r_1 x}{1 + \frac{r_2}{x}}$$

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]}$$

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2}$$

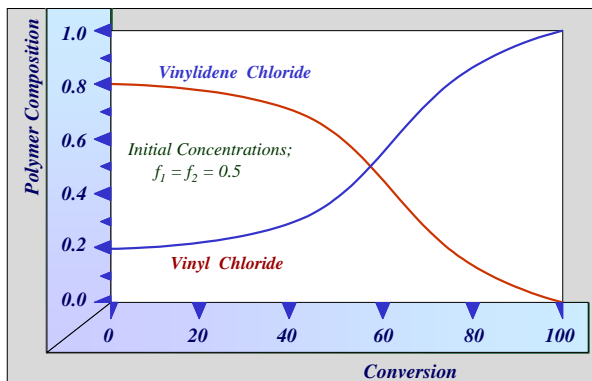
Instantaneous compositions

 f_1 is the monomer composition in the feed F_1 is the monomer composition in the copolymer

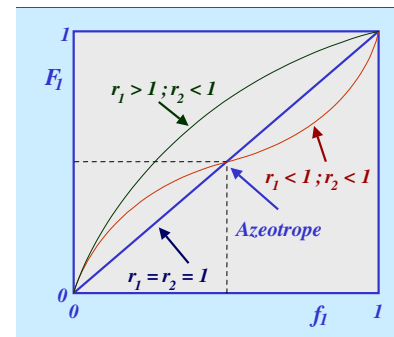
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Composition Drift



The Instantaneous Copolymer Composition



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Reactivity Ratios Determination

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{r_2 \frac{[M_2]}{[M_1]} + 1}$$

$$y = \frac{d[M_1]}{d[M_2]} \quad x = \frac{[M_1]}{[M_2]}$$

$$y = \frac{1 + r_1 x}{1 + \frac{r_2}{x}}$$

Older Methodologies

- Prepare a number of copolymers as a function of monomer composition.
- Measure the resulting copolymer composition and obtain the reactivity ratios using various plots.

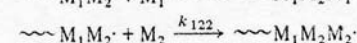
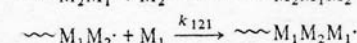
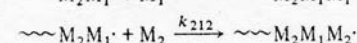
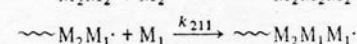
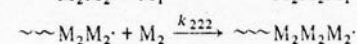
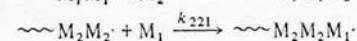
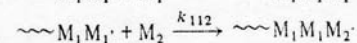
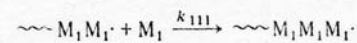
Newer Methodologies

- Measure sequence distributions using nmr and/or $\langle k_p \rangle$ with pulsed experiments.

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Penultimate Effect Model



$$r_1 = \frac{k_{111}}{k_{112}} \quad r_1' = \frac{k_{211}}{k_{212}}$$

$$r_2 = \frac{k_{222}}{k_{221}} \quad r_2' = \frac{k_{122}}{k_{121}}$$

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Penultimate Model

(4 parameters, 8 rate constants)

$$\frac{dM_1}{dM_2} = \frac{1 + r_{21} \frac{M_1 r_{11} M_1 + M_2}{M_2 r_{21} M_1 + M_2}}{1 + r_{12} \frac{M_2 r_{22} M_2 + M_1}{M_1 r_{12} M_2 + M_1}}$$

$$r_{11} = k_{111}/k_{112}, r_{21} = k_{211}/k_{212}$$

$$r_{22} = k_{222}/k_{221} \text{ y } r_{12} = k_{122}/k_{121}$$

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Previous Approaches with Integral Method

• Linear

- Mayo and Lewis, *J. Am. Chem. Soc.*, **1944**, 66, 1994
- Fineman and Ross, *J. Polym. Sci.*, **1950**, 5, 259)
- Kelen and Tudos, *J. Macromol. Sci. Chem.*, **1975**, A9, 1)

• Nonlinear (Error in Variables Method)

- Rossignoli, P.J. and T. A. Duever, *Polym. React. Eng. J.*, **1995**, 3, 361
- Polic *et al.*, *J. Pol. Sci., Part A. Pol. Chem.*, **1998**, 36, 813
- Hagiopol and Frangu, *J. Macromol. Sci.*, **2003**, A40, No 6, 571

All assume constant reactivity ratios !

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Ultimate vs Penultimate Model

r_i 's in the penultimate model can be seen as functions

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} < k_p > = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{r_1 f_1 / k_{11} + r_2 f_2 / k_{22}}$$

$$r_i^p = r_i \left(\frac{r_i f_i + f_j}{r_i f_i + f_j} \right) \quad k_{iii}^p = k_{iii} \left(\frac{r_i f_i + f_j}{r_i f_i + f_j / s_i} \right)$$

Penultimate Model

- 4 monomer reactivity ratios ($r_i = k_{iii}/k_{ijj}$, $r_i' = k_{iii}/k_{ijj}$) [i, j = 1, 2]
- 2 homopolymerization constants (k_{iii}), and
- 2 radical reactividad ratios ($s_i = k_{iii}/k_{iii}$).

The homopolymerization "constants" (k_{ii} , k_{ij}) can be determined from independent experiments; therefore, the Ultimate Model has 2 parameters to be determined, 4 in the Restricted Penultimate and 6 in the Penultimate Model.



The Bootstrap Model

Harwood, H. J. *Makromol. Chem., Macromol. Symp.* **1987**, 10/11, 331

M_{it} is considered the true monomer concentration in the reaction site and M_i is the overall monomer concentration. The partition coefficient; K is defined as:

$$\frac{M_{it}}{M_{2t}} = K \frac{M_1}{M_2} \quad F_1 = \frac{r_{1p} f_1^2 + f_1 f_2}{r_{1p} f_1^2 + 2f_1 f_2 + r_{2p} f_2^2}$$

$$< k_p > = \frac{f_1 (K(2 + f_1(r_{1p} - 2)) + r_{1p}(1 - f_1)) + r_{2p} K(f_1 - 1)^2}{(1 + f_1(K - 1))(r_{1p} f_1 / k_{11} + r_{2p} K(1 - f_1) / k_{22}}$$

$r_{1p} = r_1 K$ and $r_{2p} = r_2 / K$. Notice that the composition equation is identical to the one of the Ultimate Model. If k_i are known this model has 3 parameters.

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Facts !!!

- The Ultimate Model (2-4p) for some systems cannot predict the $<k_p>$ behavior. To remedy this problem the Penultimate (6-8p), the Restricted Penultimate (4-6p) and the Bootstrap (3-5p) Models have been used.
- The Penultimate model presents multiplicity of solutions.
- The Bootstrap model presents two feasible solutions. $\rightarrow \rightarrow$ It is not possible to discriminate between the Ultimate-Penultimate-Bootstrap models $\leftarrow \leftarrow$
- The integral method has always been used in which it is assumed that the parameters are constant.

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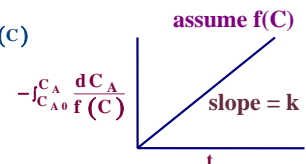
Integral and Differential Methods

I. Integral Method

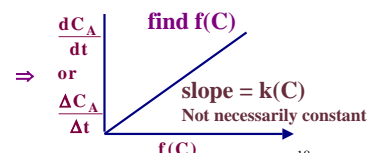
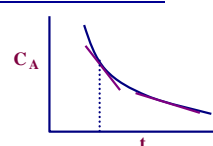
$$-r_A = -\frac{dC_A}{dt} = kf(C)$$

$$\frac{-dC_A}{f(C)} = k dt$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{f(C)} = kt$$



II. Differential Method



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Integral and Differential Methods Comparison

Integral Method (IM)	Differential Method (DM)
Very robust	Less robust
Few experimental data required	Many experimental data required
Unicity verified <i>a posteriori</i>	Unicity verified <i>a priori</i> or in parallel
Observability not verified generally	Verification of observability
Requires an initial estimate of the parameters	Does not require an initial estimate of the parameters
Does not require data smoothing	Requires data smoothing
Assumes constancy in the parameters (minimizes error between model and the measurement)	Variable parameters with the independent variable (system of algebraic equations)
Contains information from past and present	Contains information at the moment

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Methodology: Take advantage of both methods

- Fit experimental data (smoothing). Take advantage of IM robustness.
- From conservation balances write rate equations (model). DM
- Determine by means of the observability matrix the parameters to be determined (unicity) and the more robust experimental zone (less error propagation)
- Find functional dependencies of the parameters in terms of the system states. DM
----- This presentation ends here -----
- Use global regression with empirical fits for a better description (with IM)
- Based on first principles corroborate/modify the model



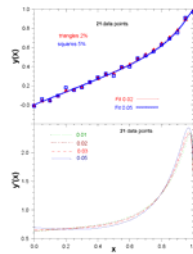
Proposed Approach: Integro-Differential Method.

Two equations (F_1, \dot{F}_1), two unknowns (r_1, r_2)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$\dot{F}_1 = \frac{f_2 + 2f_1(r_1 - 1)r_2 + f_1^2(r_1 + r_2 - 2r_1 r_2)}{(r_2 + f_1(2 - 2r_2 + f_1(r_1 + r_2 - 2)))^2}$$

$$\det O = \frac{(f_1 - 1)^2 f_1^2}{(r_2 + f_1(2 - 2r_2 + f_1(r_1 + r_2 - 2)))^3}$$



Has no solution in the neighborhood of $f_1 = 0$ and $f_1 = 1$

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Solution. Dependence of r_1 y r_2 on f_1

$$\hat{r}_1 = \frac{(f_1 - 1)(F_o - 2F_o^2 + (f_1 - 1)f_1 F_p)}{f_1(-2(F_o - 1)F_o + (f_1 - 1)f_1 F_p)}$$

$$\hat{r}_2 = \frac{f_1((3 - 2F_o)F_o - 1 + (f_1 - 1)f_1 F_p)}{f_1(-2(F_o - 1)F_o + (f_1 - 1)f_1 F_p)}$$

F_o is the experimental copolymer composition (F_1) measurement and F_p its derivative (\dot{F}_1)

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Example MMA-STY (40°C)

Composition, triads and propagation rate constant data

Experimental data were taken from:

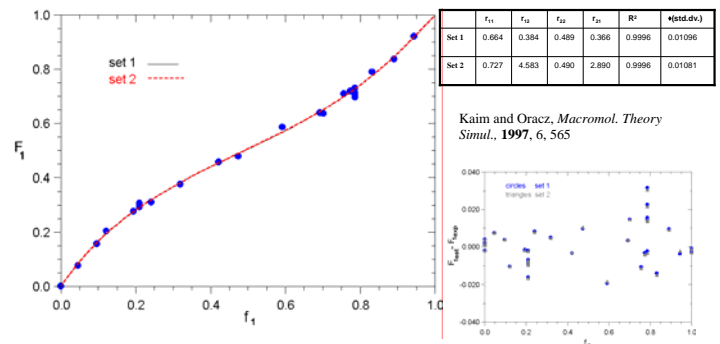
Maxwell, I. A., A. M. Aerdt and A. German. Free Radical Copolymerization: An NMR Investigation of Current Kinetic Models, *Macromolecules*, **1993**, 26, 1956

Fukuda, T., Y-D Ma and H. Inagaki, Free Radical Copolymerization. 3. Determination of Rate Constants of Propagation and Termination for the Styrene/Methyl Methacrylate System. A Critical Test of Terminal-Model Kinetics, *Macromolecules*, **1985**, 18, 17

23

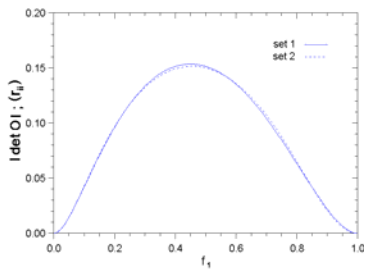


Penultimate Model Data Interpolation (Sty-MMA)





Observability Matrix Determinant

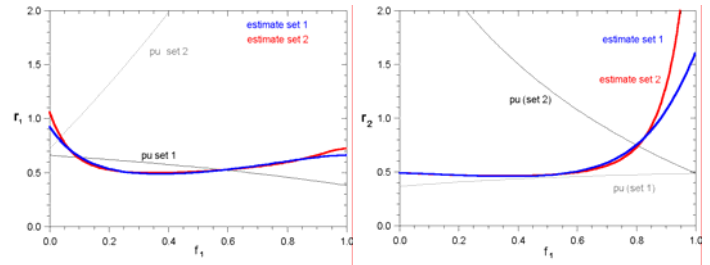


$$\det O = \frac{(f_1 - 1)^2 f_1^2}{(r_2 + f_1(2 - 2r_2 + f_1(r_1 + r_2 - 2)))^3}$$

Has no solution in the neighborhood of $f_1 = 0$ and $f_1 = 1$ 25



Reactivity Ratios Feed Composition Dependencies (ID Approach; thick lines, Penultimate Model; thin lines)



	r_{11}	r_{12}	r_{21}	r_{22}	R^2	$\chi^2(\text{std.dev.})$
Set 1	0.664	0.384	0.489	0.366	0.9996	0.01096
Set 2	0.727	4.583	0.490	2.890	0.9996	0.01081

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Conclusions (up to this point)

- Set 1 (with Penultimate Model), Reactivity Ratios dependencies on feed composition are more similar to the ID approach ones.
- In the Observable zone the ID approach, with either Set 1 or Set 2 (Penultimate Model used as a smoothing/fitting tool) the two RRs dependencies are not distinguishable.

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Error Propagation Assessment. Standard Deviation σ

(Mikhail & Ackermann, Observations and Least Squares, H&R, 1976)

$$\Sigma = \mathbf{A} \mathbf{R} \mathbf{A}^T$$

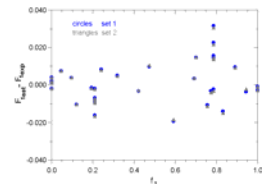
\mathbf{A} is the Observability Matrix inverse

$$\mathbf{R} = \begin{bmatrix} \sigma_{xx}^2 & 0 \\ 0 & 2\sigma_{xx}^2 \end{bmatrix}$$

\mathbf{R} contains the square of the standard deviation obtained from the F_1 vs f_1 fit

$$\Sigma = \begin{bmatrix} s_{xx} & s_{xy} \\ s_{yx} & s_{yy} \end{bmatrix}$$

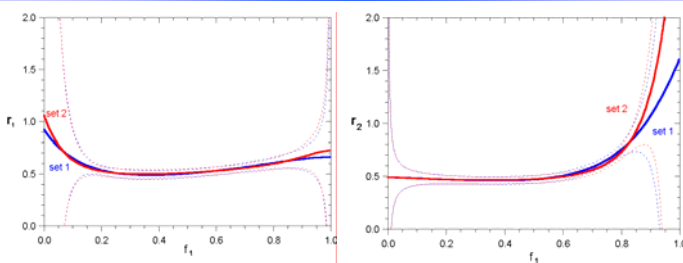
Σ contains the square of the standard deviation propagated from the F_1 vs f_1 measurements and its derivative towards r_1 and r_2 .



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Error Propagation Assessment. Standard Deviation σ (thin lines)



Coincides with Tidwell and Mortimer's assuming constant reactivity ratios (J. Polym. Sci., 1965, A-3, (1), 369)

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Triad Predictions

Maxwell et al., Macromolecules 1993, 26, 1956

Table II
Assignments to Peak Areas (Indicated by Chemical Shift) of the Aromatic C1 Region (Styrene-Centered Triads) in the ¹³C NMR Spectra of Styrene-MMA Statistical Copolymers¹¹

X ¹¹	Y ¹¹	Z ¹¹
147.5-146.8 ppm	146.8-146.15 ppm	145.15-143.5 ppm
$(1 - \sigma_{ms})^2 F_{ms}$	$(1 - \sigma_{ms})^2 F_{ms}$	$(1 - \sigma_{ms}) \sigma_{ms} F_{ms}$
	$2\sigma_{ms}(1 - \sigma_{ms})^2 F_{ms}$	$\sigma_{ms}^2 F_{ms}$
	$\sigma_{ms}^2 F_{ms}$	$\sigma_{ms}^2 F_{ms}$
	$(1 - \sigma_{ms})(1 - \sigma_{ms}) F_{ms}$	
	$\sigma_{ms}(1 - \sigma_{ms}) F_{ms}$	
	$2\sigma_{ms}(1 - \sigma_{ms}) F_{ms}$	

Table III
Assignments to Peak Areas (Indicated by Chemical Shift) of the α -Methyl Region (MMA-Centered Triads) in the ¹³C NMR Spectra of Styrene-MMA Statistical Copolymers¹¹

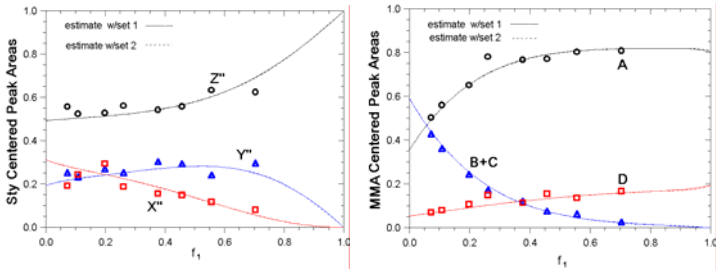
A	B	C	D
23-21.2 ppm	21.2-19.8 ppm	19.8-17.8 ppm	17.8-16.5 ppm
$\sigma_{ms}^2 F_{ms}$	$\sigma_{ms}(1 - \sigma_{ms}) F_{ms}$	$2\sigma_{ms}(1 - \sigma_{ms}) F_{ms}$	$(1 - \sigma_{ms})^2 F_{ms}$
$\sigma_{ms}^2 F_{ms}$	$2\sigma_{ms}(1 - \sigma_{ms}) F_{ms}$	$(1 - \sigma_{ms})(1 - \sigma_{ms}) F_{ms}$	
$\sigma_{ms}^2 F_{ms}$	$(1 - \sigma_{ms})^2 F_{ms}$	$(1 - \sigma_{ms})(1 - \sigma_{ms}) F_{ms}$	
	$(1 - \sigma_{ms})^2 F_{ms}$		

¹¹ This peak shows resonance splitting and appears in both the B and C peak areas.

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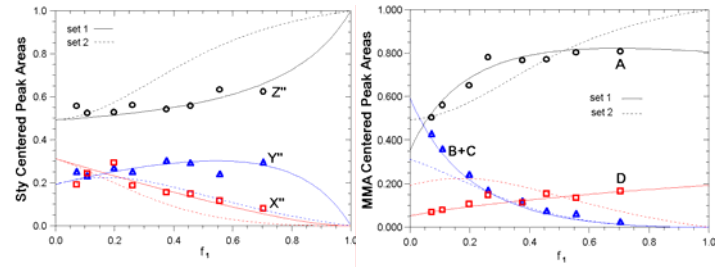
Differential Estimation Areas Prediction



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Penultimate Model Areas Prediction



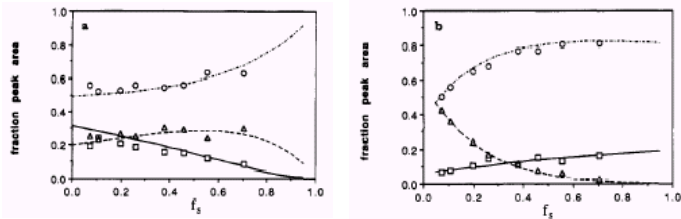
	r_{11}	r_{12}	r_{21}	r_{22}	R^2	$w(\text{std.dev.})$
Set 1	0.664	0.384	0.489	0.366	0.9996	0.01096
Set 2	0.727	4.583	0.490	2.890	0.9996	0.01081

Kaim and Oracz, *Macromol. Theory Simul.*, 1997, 6, 565

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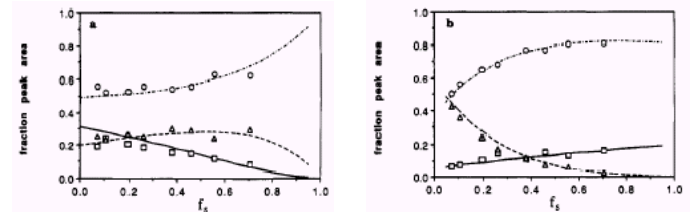
Ultimate Model Predictions ($r_s = 0.48$; $r_m = 0.42$) Maxwell et al., *Macromolecules* 1993, 26, 1956



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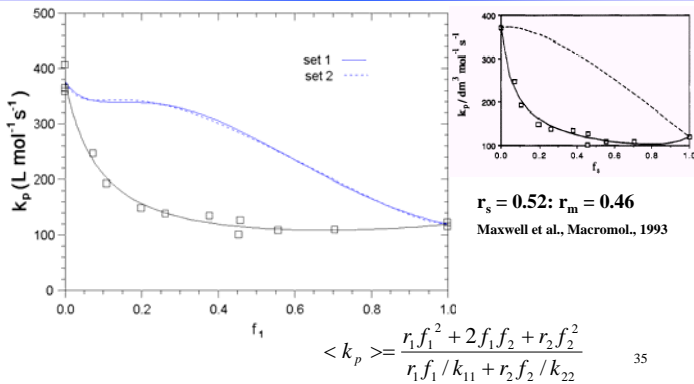
Ultimate Model Fits ($r_s = 0.51$; $r_m = 0.52$) Maxwell et al., *Macromolecules* 1993, 26, 1956



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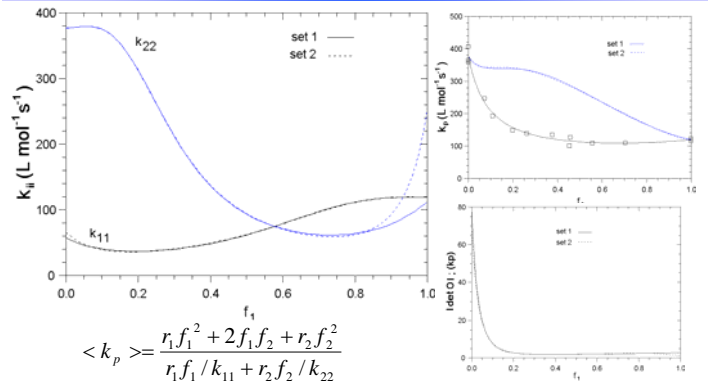
Terminal Model k_p Predictions



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k_{11} and k_{22} Feed Composition Dependencies. Proceed as before





Error Propagation Assessment. Standard Deviation σ

(Mikhail & Ackermann, Observations and Least Squares, H&R, 1976)

$$\Sigma = \mathbf{A} \mathbf{R} \mathbf{A}^T$$

\mathbf{A} is the Observability Matrix inverse for the F_1 and F_1 vs f_1 system

$$\mathbf{Q} = \begin{bmatrix} q_{xx} & 0 \\ 0 & q_{yy} \end{bmatrix}$$

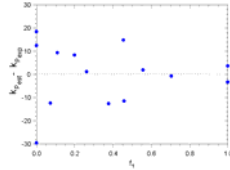
\mathbf{Q} contains the square of the standard deviation obtained from the k_p vs f_1 fit

$$\Xi = \mathbf{B} (\mathbf{Q} + \Sigma) \mathbf{B}^T$$

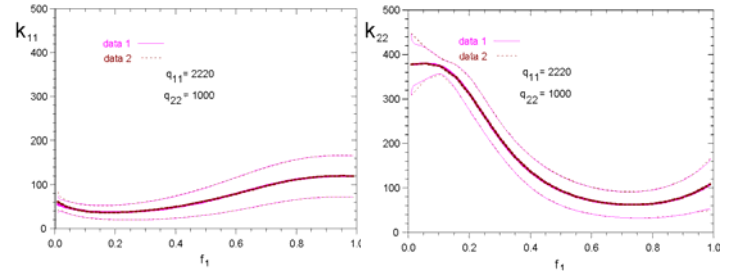
\mathbf{B} is the Observability matrix inverse for the k_p and k_p vs f_1 system

Σ contains the square of the standard deviation propagated from the F_1 vs f_1 measurements and its derivative.

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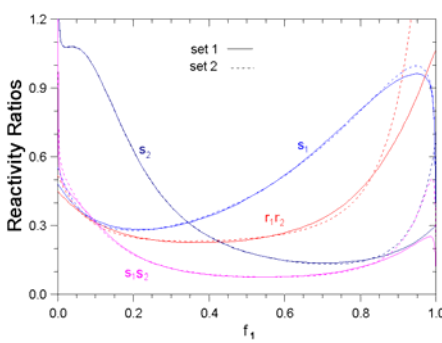
Error Propagation Assessment. Standard Deviation σ (thin lines)



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Reactivity Ratios Feed Composition Dependencies (r_i and s_i ; $i = 1, 2$)



$$\langle k_p \rangle = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{r_1 f_1 / k_{11} + r_2 f_2 / k_{22}}$$

$$k_{ii}^p = k_{iii} \left(\frac{r_i f_i + f_j}{r_i f_i + f_j / s_i} \right)$$

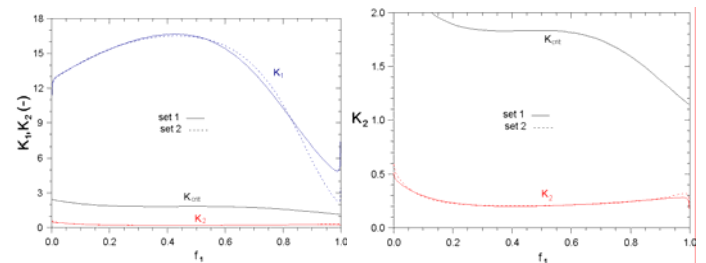
Penultimate Model
radical reactivity ratios

$$s_i = k_{ji} / k_{iii}$$

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Bootstrap Model: Partition Coefficient (K) Feed Composition Dependency



$$\langle k_p \rangle = \frac{f_1 (K(2 + f_1(r_{1p} - 2)) + r_{1p}(1 - f_1)) + r_{2p} K (f_1 - 1)^2}{(1 + f_1(K - 1))(r_{1p} f_1 / k_{11} + r_{2p} K (1 - f_1) / k_{22})}$$

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Conclusions

- An Integro-Differential Approach has been presented.
- No modeling *a priori* assumptions were made on reactivity ratios (i.e., constancy).
- A comonomer effect (not reported before) can be detected. A slight solvent effect on the reactivity ratios was observed (reported earlier).
- The observability notion was incorporated (unicity).
- Neither the ultimate nor the penultimate models were adequate (consistent) in terms of parameter constancy.
- One of the Bootstrap Model solutions seems to be the most consistent, based on parameter constancy.
- New experiments should be designed under a differential structure with a more dense mesh of data (more discrimination capability than integral method).
- This method allows us to obtain functional dependencies in terms of the system states.

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Future Work

- Study the problem of individual parameter **error-propagation-estimation-robustness**
- Evaluation of several reacting systems (at present the method is being tested in other systems).
- From **First Principles** explain the **parameters evolutions**
- Apply to other polymerization systems

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The End

Thank you for your attention!



MODEL DISCRIMINATION IN MICROEMULSION POLYMERIZATION



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 *Universidad Nacional Autónoma de México. ^oUniversidad de Guadalajara. [#]Universidad Autónoma Metropolitana-Iztapalapa. MÉXICO

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

Rate: $k_p[M] \cdot N_p$

Interval I: $[M] \approx N_p \approx ??$
 Interval II: $[M] \approx N_p \approx ??$
 Interval III: $[M] \approx N_p \approx ??$

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

Kinetic Theory of Microemulsion Polymerization

Interval I: $[M] \approx N_p \approx ??$
 Interval II: $[M] \approx N_p \approx ??$

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

Micremulsion Models

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

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

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

$$\frac{dM}{dt} = -k_p N_p M$$

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

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

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

$$\frac{dM}{dt} = -k_p N_p M$$

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

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

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

$$\frac{dM}{dt} = -k_p N_p M$$

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 parametres 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)

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

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

Analytic solution

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

x = fractional conversion
 p = k_p = rate of initiation
 K_p = propagation rate constant
 M₀ = monomer conc. inside parts.
 M_p = initial monomer concentration

Integrodifferential Estimation

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

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

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_i ≠ 1 and y_i' ≠ 0

Approaches to Model Microemulsion Polymerization

	Guo et al. (1992)	Morgan et al. (1997)	Mendizábal et al. (1997)
Imp	Cell-A	Cell-A	Micellar + constant
Particle generation	N _p = N _c (exp(kt)) Micellar	N _p = K ₁ Micellar	Micellar and homogeneous (N _p , N _c) (time = 1000s)
Capture coefficients	k ₁₀ > k ₁₁ second	k ₁₀ = k ₁₁ first	k ₁₀ > k ₁₁ 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	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_i and N_c (Guo and Mendizábal)

Compartmentalized

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

Pseudomassic

$$\frac{dx}{dt} = k_p \frac{M_p N_p^0}{M_0}$$

Total No. Particles

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

Both models are analogous !

Results

Conversion Curves

Initiator V50: (▲) nC₆MA, 0.24 mM; (●) nC₇MA, 0.061 mM and (○) tC₆MA, 0.24 mM; (◐) tC₆MA, 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: (▲) nC₆MA, 0.24 mM; (●) nC₇MA, 0.061 mM and (○) tC₆MA, 0.24 mM; (◐) tC₆MA, 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 tC₆MA 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.