

## Microemulsion copolymerization modeling study via a combined integral-differential experimental data processing approach.

F. López-Serrano,<sup>1</sup> E. Mendizábal,<sup>2</sup> J. E. Puig<sup>2</sup> and J. Álvarez<sup>3</sup>.

<sup>1</sup>Universidad Nacional Autónoma de México.

<sup>2</sup>Universidad de Guadalajara.

<sup>3</sup>Universidad Autónoma Metropolitana-Iztapalapa

[lopezserrano@correo.unam.mx](mailto:lopezserrano@correo.unam.mx)<sup>1</sup>:

### 1. Abstract

On the basis of a combined integral-differential data processing approach, the styrene/acrylonitrile microemulsion copolymerization system is studied with a three-state (conversion, active particles and micelles) and four-parameter model (entrance and exit of radicals to and from particles, monomer transport from micelles to growing particles and initial micelle number) in conjunction with experimental conversion measurements. The resulting model accurately describes the S-shaped experimental overall conversion evolutions and particle size, as well as the active particles' bell-shaped form behavior. This last finding is contrary to previous assumptions in which active particle behavior was believed to grow linearly with time. As expected, the entry and exit rate coefficients increase with initiator concentration. The monomer transport from micelles decreased with initiator concentration and the initial micelles concentration value only impacts the entry rate. For the systems studied no vitreous effect was detected, even at high conversions.

### 2. Introduction

Microemulsion polymerization (ME) is a process in which materials with small particle sizes (10-50 nm) and high molecular weights ( $< 10^6$  Da) are obtained with high reaction rates. In the literature, few models for microemulsion copolymerization have been reported. Sanghvi et al. [1] reported a simple model that can only predict the kinetics at low conversions, Ovando-Medina et al. [2] proposed a model which is capable of predicting copolymerization kinetics; however, it is complicated. Several assumptions are involved and many parameters are required. A simple mechanistic three-parameter copolymerization model is presented here as an extension to our model for ME homopolymerization [3].

### 3. The Model

Not assuming *a priori* that the particle generation rate is constant [1,4] and using the monomer partition expression reported before [1, 4], the conversion evolution can be expressed as:

$$\dot{x} = K (1-x) N_1(t), K = (k_p C_m) / (M_o N_{av}); \quad x(0) = x_o \quad (1)$$

PRE

where  $x$  is the conversion,  $N_I$  the active particles ( $L^{-1}$ ),  $k_p$  ( $L \text{ mol}^{-1} \text{ s}^{-1}$ ) is the propagation rate constant,  $C_m$  ( $\text{mol L}^{-1}$ ) is an experimentally measured parameter [1, 4],  $M_o$  ( $\text{mol L}^{-1}$ ) is the initial monomer charge and  $N_{av}$  is Avogadro's number, the values for  $K$  can be found elsewhere [1]. Eq 1 can be rewritten as:

$$N_{Ia}(t) = \dot{y} / [K (1-y)] \quad (2)$$

where  $y$  is the smoothed [3] conversion data trend and  $\dot{y}$  its derivative. Therefore, the active particles evolution  $N_{Ia}(t)$ , in principle, can be estimated from the conversion experimental data. In case this solution exists, the  $N_{Ia}$  dependency is used as an additional measurement and the equation-set describing the process is completed as follows:

$$\dot{N}_m = -\rho_m N_m - k_m N_m N_I; \quad N_m(0) = N_{m0} \quad (3)$$

$$\dot{N}_I = \rho_m N_m - k N_I; \quad N_I(0) = 0 \quad (4)$$

where  $N_m$  ( $L^{-1}$ ) is the micelles concentration, and  $N_I$  ( $L^{-1}$ ) the active particle number evolutions described before [3]. The estimated parameters are the entry to micelles  $\rho_m$  ( $s^{-1}$ ), exit from particles  $k$  ( $s^{-1}$ ) and monomer transport from micelles to particles  $k_m$  ( $L \text{ mol}^{-1} \text{ s}^{-1}$ ) rate coefficients.

### 3. Results

The proposed model was applied to styrene-acrylonitrile ME polymerization data reported previously [1]. Figure 1 presents the inferred  $N_{Ia}$  (Eq 2) and model predictions of  $N_I$  evolutions against time. It can be seen that the model describes qualitatively well the bell shaped form of the curves and this behavior is opposed to a linear form used before [1,4,5].

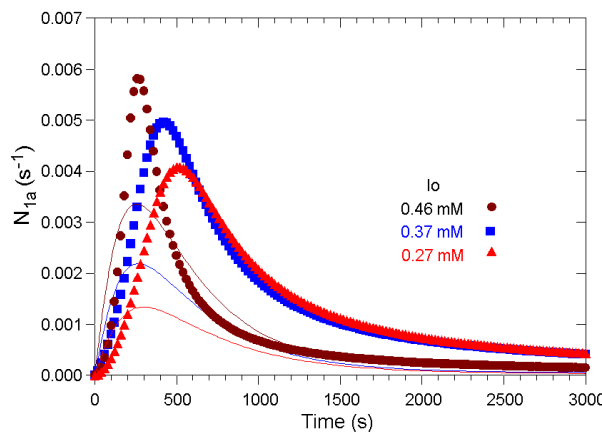


Figure. 1.  $N_{Ia}$  evolution against time ( $I_o$  is the initiator concentration), model (continuous lines) and inferred (Eq 2) from the conversion derivative (symbols).

Figure 2 depicts the monomer conversion evolution where the S-shaped experimental curves are adequately described. Some differences in the model predictions can be observed at low and intermediate conversions. The model can be improved, not assuming a constant value of the propagation rate.

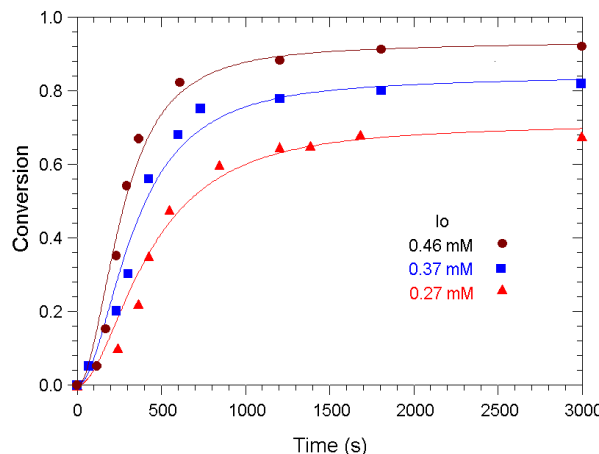


Fig.2. Overall conversion evolution against time of acrylonitrile-styrene, model (Eq 1) (continuous lines) and experimental data (symbols) [1].

The evolution of the average particle size with time is depicted in Fig. 3. The shape describes very well the experimental behavior (not shown) and also the obtained values are close to the reported ones [1].

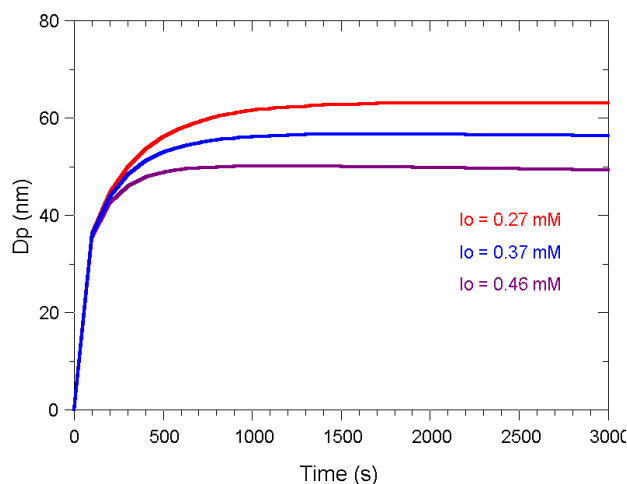


Fig.3. Particle diameter ( $D_p$ ) time evolutions.

Table 1. Parameter values obtained assuming  $N_{m0} = 1 \times 10^{21} (L^{-1})$

$I_0$ (mM) → Parameters ↓	0.27	0.37	0.46
$k$ (s <sup>-1</sup> ) / std. dev.	$2.35 \times 10^{-3} / 5.05 \times 10^{-4}$	$2.63 \times 10^{-3} / 4.59 \times 10^{-4}$	$2.97 \times 10^{-3} / 5.20 \times 10^{-4}$
$\rho_m$ (s <sup>-1</sup> ) / std. dev.	$1.15 \times 10^{-6} / 3.14 \times 10^{-8}$	$2.06 \times 10^{-6} / 5.07 \times 10^{-8}$	$3.37 \times 10^{-6} / 9.12 \times 10^{-8}$
$k_m$ (Lmol <sup>-1</sup> s <sup>-1</sup> ) /std.dev.	$3.42 \times 10^{-20} / 7.67 \times 10^{-21}$	$2.29 \times 10^{-20} / 3.99 \times 10^{-21}$	$1.48 \times 10^{-20} / 2.38 \times 10^{-21}$

Table 1 presents the obtained values for the parameters appearing in Eq set 1, 3 and 4. As expected,  $k$  and  $\rho_m$  increase with initiator concentration and  $k_m$  decreases. Table 2 shows the impact of  $N_{m0}$  varied within the reported experimental values. In this table (for  $I_0 = 0.37$  mM) it appears that the only parameter that is affected, as expected analyzing the Eq set, is  $\rho_m$ . This behavior is similar for the other two initiator concentrations.

Table 2. Effect of  $N_{m0}$  over the obtained parameters

$I_0$ (mM) → Parameters ↓	0.37	0.37	0.37
$k$ (s <sup>-1</sup> )	$2.63 \times 10^{-3}$	$2.63 \times 10^{-3}$	$2.63 \times 10^{-3}$
$\rho_m$ (s <sup>-1</sup> )	$2.06 \times 10^{-5}$	$2.06 \times 10^{-6}$	$2.06 \times 10^{-7}$
$k_m$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$2.29 \times 10^{-20}$	$2.29 \times 10^{-20}$	$2.29 \times 10^{-20}$
$N_{m0}$ (L <sup>-1</sup> )	$1.00 \times 10^{20}$	$1.00 \times 10^{21}$	$1.00 \times 10^{22}$

#### 4. Conclusions

The problem of modeling and assessment in microemulsion copolymerization was studied by applying the integral and differential methods. The differential estimation consideration allowed the obtainment of the active particles' evolution, whose dependence was not linear with time, as opposed to previous works [1,4,5]. This active particles' functional dependence was used as an inferred measurement which permitted the estimation of three parameters ( $\rho_m$ ,  $k$ ,  $k_m$ ), that could not have been obtained with the integral method alone. A mechanism that explained the feeding of monomer from micelles to growing particles was found ( $k_m \neq 0$ ), not mentioned in previous works. It was assumed that entry to particles is negligible ( $\rho \sim 0$ ), agreeing with previous works [5].

**Acknowledgments:** Funds for this work were provided by UNAM (PAPIIT IN101806 and PAPIIT 539030) and are gratefully acknowledged.

#### 5. References.

- [1] Sanghvi P. G., N. K. Pokhriyal, P. A. Hassan, S. Devi, *Polym Int*, 2000, **49**, 1417-1425
- [2] Ovando-Medina V.M., E. Mendizábal, R D. Peralta, *Pol Bull*, 2005, **54**, 129-140
- [3] López-Serrano, F., J. E. López-Aguilar, E. Mendizábal, J. E. Puig, J. Álvarez. *Macromol Symp*, 2008, **271**, 94-98
- [4] Co C. C., de Vries, R., E. W. Kaler, *Macromol*, 2001, **34**, 3224-3232
- [5] Nomura M., K. Suzuki, *Ind. Eng. Chem. Res.* 2005, **44**, 2561-2567.