

MATHEMATICAL MODELING OF THE MICROEMULSION POLYMERIZATION USING EXPERIMENTAL MEASUREMENTS AND ITS DERIVATIVES.

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1. Abstract.

In this work the microemulsion polymerization kinetics are analyzed for the hexyl methacrylate (C_6MA), n-butyl methacrylate (nC_4MA) and styrene (STY) systems at 60 °C, applying an integrodifferential approach. A five-parameter model [radical entry to micelles (ρ_m) and particles (ρ), monomer and surfactant transfer to particles from micelles (k_m), radical desorption (k_d) and coagulation between particles (k_c)] was assessed for different initiator concentrations. With the proposed approach and the experimental conversion data, and its derivative, it was found that: (i) the model's conversion prediction agrees in an excellent fashion with experimental data, (ii) the radical generation does not follow a linear behaviour with time, opposed to previous assumptions, (iii) there is no coagulation between particles, (iv) no radical entrance to particles was found, (v) a diffusive effect on the propagation constant was detected even for low- T_g polymers and (vi) the particle diameter estimation agrees with reported experimental data. These findings are put into perspective with the ones from other authors.

2. Introduction.

The microemulsion polymerization (MEP) is a process in which several physical and chemical phenomena, like equilibrium between phases and complex chemical reactions, take place. Due to this fact, MEP modelling is one case in chemical engineering where the parameter estimation and the modelling assessment present a challenge. There are several controversies in MEP modelling [2-4 and references therein]. Here, a kinetics-based integrodifferential approach to model the MEP [2-4], is presented. This technique allows to obtain additional information from the available experimental data, and its derivative. The procedure is applied to experimental data, previously reported by de Vries et al. [1] on the microemulsion polymerization at 60 °C of C_6MA , nC_4MA , and STY.

3. The model

The following assumptions are performed to develop the model: (i) there is a 0-1 compartmentalized behaviour, (ii) the monomer concentration in the particles is given by the partition

function reported by de Vries et al. [1], (iii) the initial number of swollen micelles can be measured [5], (iv) the radical entry (to particle and micelle) and desorption (from particles) rates are described by first-order mechanisms with respect to the corresponding (micelles or particles) concentration, (v) swollen micelles can provide monomer to polymerizing particles, (vi) there may be polymer particle-particle coagulation, and (vii) the radical capture rates by micelles and polymer particles may be different. The resulting equation set is shown next:

$$\frac{dx}{dt} = A (1-x)^b; \quad A = \frac{k_p C_{mo} N_1}{M_0 N_A}; \quad x(0) = 0 \quad (1)$$

$$\frac{dN_m}{dt} = -\rho_m N_m - k_m N_m N_1; \quad N_m(0) = N_{m0} \quad (2)$$

$$\frac{dN_1}{dt} = \rho(N_0 - N_1) - k_d N_1 + \rho_m N_m - 2k_c N_1^2; \quad N_1(0) = 0 \quad (3)$$

$$\frac{dN_0}{dt} = \rho(N_1 - N_0) + k_d N_1 + k_c(N_1^2 - N_0^2 - N_1 N_0); \quad N_1(0) = 0 \quad (4)$$

Here, x is the conversion, t is the reaction time (s), k_p is the propagation constant ($\text{L mol}^{-1} \text{s}^{-1}$), C_m is the monomer concentration inside the particles (mol L^{-1}), N_1 is the number density of particles with one radical (L^{-1}), N_0 is the number density of particles with no radicals (L^{-1}), N_m is the number density of micelles (L^{-1}), M_0 is the monomer initial concentration in the reactor (mol L^{-1}), N_A is Avogadro's number, b is a parameter characterizing the monomer partitioning and C_{mo} is the monomer initial concentration in the particles (mol L^{-1}). The last two were determined experimentally [1]. In this model, micellar nucleation is considered, ρ_m (s^{-1}); the exit of the radical from a particle gives termination, k_d (s^{-1}); there is monomer and surfactant feed from micelles to particles, k_m ($\text{L mol}^{-1} \text{s}^{-1}$); entry to particles is allowed, ρ (s^{-1}); and particle coagulation is considered formally, k_c ($\text{L mol}^{-1} \text{s}^{-1}$).

4. Integrodifferential approach.

The details of the procedure are stated elsewhere [3]. Here it suffices to obtain an additional measurement. All the quantities in A (Eq 1) are known [1]. And, N_1 that can be inferred from the smoothed experimental conversion (y) and its derivative as follows:

$$A = \frac{dy/dt}{(1-y)^b} \quad (5)$$

Therefore, this additional (to the conversion) measurement (N_1) is used in the evaluation of the parameters in the model (Eqs 1-4). Furthermore, if a model mismatch exists, the only parameter that could change in A is k_p , due to a vitreous effect in the reaction loci, this is also evaluated by comparing:

$$k_p(x) = \frac{N_{1\text{exp}}}{N_{1\text{model}}} k_p \quad (6)$$

4. Results.

The model describes the MEP conversion curves of C_6MA , nC_4MA and STY in an excellent fashion as seen in the in Fig. 1 (upper curves). Also, the bell-shaped N_1 evolution form is described (lower curves of Figure 1). This behaviour is opposite to the one previously assumed [1]. The parameters obtained in solving the system are listed in Table 1.

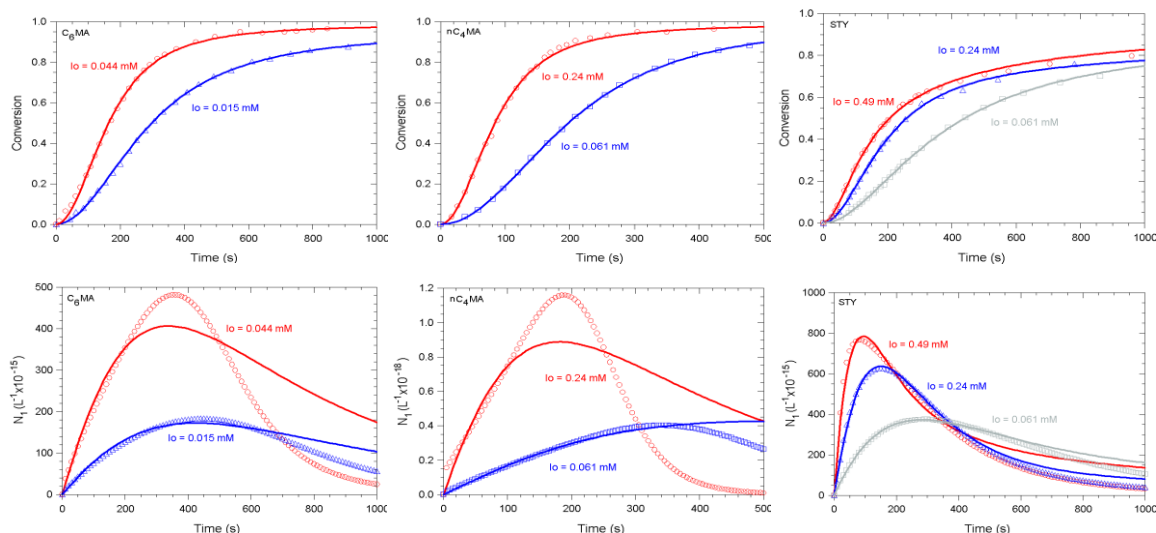


Figure 1. Conversion and N_1 versus time for the analyzed systems (lines-model, symbols-experimental data).

As seen in Figure 1, the model slightly over predicts the N_1 evolution. As established in Eq 6 the corrected k_p values are presented in Fig. 2. It is observed that there is a pronounced vitreous effect at the end of the reaction even for systems with low- T_g .

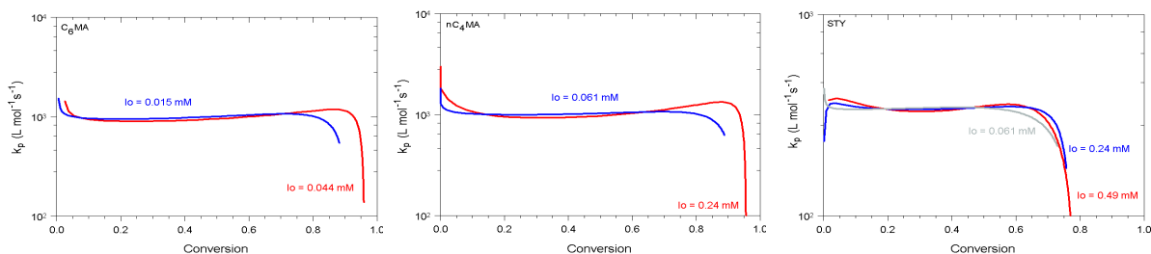


Figure 2. k_p versus conversion for the analyzed systems.

Finally, the predicted particle size value (not shown) for the C₆MA, depending the initiator concentration, is between 39-50 nm, close to reported (46-52 nm) values. For the nC₄MA system with the initiator concentration of 0.061 mM (43 nm), that is slightly larger than the reported experimental value (34 nm) and for STY we have 25 nm (29 nm experimental value) [6].

Table 1. Parameters obtained for the analyzed systems.

Parameters / I ₀ (mM) – Monómer	ρ_m (s ⁻¹)	k_d (s ⁻¹)	k_m (L mol ⁻¹ s ⁻¹)	k_c (L mol ⁻¹ s ⁻¹)	ρ (s ⁻¹)
0.015 - C₆MA	8.95x10 ⁻⁷	2.14x10 ⁻³	10478.28	0	0
0.044 - C₆MA	2.66x10 ⁻⁶	2.73x10 ⁻³	5492.06	0	0
0.061 - nC₄MA	1.81x10 ⁻³	6.82x10 ⁻⁴	7166.18	0	0
0.240 - nC₄MA	1.07x10 ⁻⁵	4.57x10 ⁻³	5233.12	0	0
0.061 - STY	3.42x10 ⁻⁶	6.07x10 ⁻³	3324.14	0	0
0.240 - STY	1.01x10 ⁻⁵	8.64x10 ⁻³	5492.06	0	0
0.490 - STY	2.29x10 ⁻⁵	2.08x10 ⁻²	3811.93	0	0

5. Conclusions.

An integrodifferential approach was applied successfully to three MEP systems. The conversion prediction is in excellent agreement with experimental data. The model also describes the bell-shaped form of N₁ (not *a priori* assumed) giving a non linear radical generation with time opposed to previous works and the deviation at high conversion can be explained due to a vitreous effect on k_p . This effect was found even in the low-T_g systems, being more important for STY. Also a dependence with the initiator concentration was observed, as expected, the lower the initiator concentration, the higher the molecular weight increase and, with this the chemical species diffusion in the reaction loci is prevented. Here also, we found that: radical entry to particles was negligible [2-4] and the coagulation between particles (no treated before) was not found during the reaction. In general, k_d is three orders of magnitude larger than ρ_m and both increase with initiator concentration, as expected.

6. References.

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