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Microemulsion Polymerization Modeling Based on the Experimental Conversion Trend and its Derivative

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Summary: In this work, the microemulsion polymerization modeling problem is addressed with an integrodifferential approach. The procedure was applied to experimental data, previously presented, on the microemulsion polymerization of hexyl methacrylate (C_6MA) and styrene (STY). It was found that: (i) the nucleation rate is not linear with time, as assumed before, (ii) a vitreous effect is observed even in reactions where the polymer's glass transition temperature is lower than the reaction temperature, (iii) radical entry to polymer particles and coagulation among particles are negligible, (iv) the rate decrease interval is also caused by a reduction of active sites, (v) a mechanism in which micelles provide monomer to living particles was detected, and (vi) a simple three-parameter mechanistic model was obtained, capable of describing the studied systems.

Keywords: kinetics; mechanism; microemulsion polymerization; modeling

Introduction

The field of microemulsion polymerization is a prototypical example exhibiting well the general problematic situation of parameter estimation and model discrimination 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,[1] in many cases, wrong parameter-model pairs have become fitting devices of experimental data, and many necessary basic kinetic and thermodynamic parameters are still lacking. Hitherto, the model assessment and parameter fitting studies on microemulsion polymerization have been performed within an integral regression framework, in which a candidate model is proposed, the constancy of some adjustable parameters is *a priori* assumed, and then the parameters are adjusted so that the model solution (i.e., integration) fits the experimental data in a suitable (typically weighted least squares) sense. In some studies,[2–4] conversion measurement trend derivatives against time have been performed to show tendencies and delimit the presence of two intervals in microemulsion polymerization, in contraposition to the three intervals of emulsion polymerization.[5] Here, microemulsion polymerization experimental data of C_6MA and STY, presented previously,[3] are examined under a integrodifferential estimation method employed[6–9] to address the model assessment, discrimination, and parameter estimation[6–9] that exploits the information contained in the measurement trend derivatives.

Model Development

The main assumptions constructing the model that are validated in this work, are: (i) a 0-1 compartmentalized system describes the conversion (x) evolution,[5] (ii) the experimental monomer partitioning function $C_m(1-x)^b$, with C_m and b

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reported,[3] depicts the monomer concentration in the particles, (iii) the initial number of micelles (N_{mo}) can be measured as described by Full[10] *et al.*, (iv) the radical entry [to particles (ρ) and to micelles (ρ_m)] and exit k (from particles) rate coefficients are first order, with respect to the corresponding micelles (N_m) or particles (N_1, N_2) concentration.[5] The following events are considered: (i) swollen micelles can provide monomer (k_m) to polymerizing particles, (ii) coagulation could exist (k_c) among polymer particles, and c) the radical capture rates by micelles and polymer particles may be different. The model is given by the following set of ordinary differential equations, with conversion measurements (y):

$$\frac{dx}{dt} = K(1-x)^b N_1;$$

$$K = \frac{k_p C_m}{M_0 N_{av}} \quad (1a); \quad y = x \tag{1b}$$

$$\frac{dN_m}{dt} = -\rho_m N_m - k_m N_m N_1 \tag{2}$$

$$\frac{dN_1}{dt} = \rho(N_0 - N_1) - kN_1 + \rho_m N_m - 2k_c N_1^2 \tag{3}$$

$$\frac{dN_0}{dt} = \rho(N_1 - N_0) + kN_1 + k_c(N_1^2 - N_0^2 - N_0 N_1) \tag{4}$$

I.C. $x(0) = N_0(0) = N_1(0) = 0$ and
$N_m(0) = N_{mo}$

The known parameters[3] are: the propagation rate constant k_p (L mole^{-1}s^{-1}), the partition coefficients C_m (mole L^{-1}) and $b(-)$, the initial monomer charge M_0 (mole L^{-1}) and Avogadro's number N_{av}. Unknown in the model are: the first order exit from particles k (s^{-1}) rate constant, the second order coagulation between particles k_c (L mole^{-1}s^{-1}) rate constant, the second order monomer feeding from micelles to particles k_m (L mole^{-1}s^{-1}) rate constant, the initial micellar concentration N_{mo} (L^{-1}), and the first order radical entry to particles ρ and to micelles ρ_m (s^{-1}). The reader can realize that, in the preceding equation set, the radical balance in the aqueous phase is not consider because with this approach it is not required, opposed to previous works.[11]

Proposed Approach

In order to obtain a smooth continuous representation, from the conversion experimental data, an *ad hoc* function[6–9] is constructed (here the integral or regression method is applied). From that function it is possible to obtain its derivative (differential method). Equation 1, can be rewritten as:

$$N_{1e} = \frac{\frac{dy}{dt}}{K(1-y)^b} \tag{1c}$$

Equation (1c) says that, if K and b are known,[3] from the experimental conversion (y) and its derivative (dy/dt), the active particles evolution (N_{1e}) can be inferred, without a radical balance in the water phase, and its functionality does not need to be assumed, as done before.[11–15] Therefore, N_{1e} can be used to compare its behavior with previous proposals, but also be utilized as an additional measurement to estimate the parameters that appear in Equation (2) to (4). It can be seen that N_1 appears, repeatedly in these equations and that fact will robustify the solution. Finally, if a difference between the model active particles (N_1) and the inferred N_{1e} evolutions appears, a possible cause could be due to a vitreous effect [The parameters contained in K (equation 1) are measured independently, but k_p is assumed to be constant]. This variation could be analyzed (differential and integral methods) as follows:

$$k_p(x) = k_p \frac{N_{1e}}{N_1} \tag{5}$$

Next, the results using conversion against time data at different initiator concentrations, reported previously,[3] are analyzed whit this approach. Two examples were chosen: hexyl methacrylate (C_6MA) with a value of its polymer T_G being inferior (−20 °C) to the reaction temperature (60 °C) and styrene (STY) whose polymer's T_G (106 °C) is higher than the reaction temperature. The known parameters were taken elsewhere.[3] And a value of initial micelles was taken[10] to be $N_{mo} = 1 \times 10^{21}$ (L^{-1}) for all studied cases; however, the effect of this assumption is discussed herein.

Results and Discussion

The proposed approach application, assuming a constant k_p, yields the kinetic parameters (equation 2–4) shown in Table 1 (C_6MA) and 2 (STY), where the initial value of the micellar concentration (N_{mo}) effect is also presented.

It is clear that only the entry rate to micelles (ρ_m) is affected by varying N_{mo}. The other two parameters (k and k_m) are not affected with a two-fold change in N_{mo}. In these tables the coagulation (not considered in previous works) and entry to particles do not appear because the values obtained were close to zero, implying that these events can be disregarded.

The finding of negligible entry to particles agrees with previous reports.[6,12] Also, it can be seen that, as expected, the entry and exit rate coefficients increase with increasing initiator concentration. Figure 1 shows that for both studied systems, the model predictions explain almost perfectly the conversion evolution. In the insert, the active particles evolution comparison between the inferred (symbols) and the model (continuous line) is presented against time. It is evident that N_1 does not follow a linear behavior with time, as assumed before.[3,11,12] The model describes adequately the active particles evolution (bell shaped form) and also the time where the maximum occurs is also correctly described.

The application of equation 5 yields the results presented in Figure 2 where a vitreous affect is evident and it appears even for C_6MA whose polymer's T_G is much lower than the reaction temperature. This effect appears sooner the lower the initiator concentration, which promotes a higher molecular weight.

For the STY case, whose polymer's T_G is higher than the reaction temperature, a pronounced vitreous effect is present,

Table 1.
Obtained parameters and the effect of N_{mo} on them for C_6MA.

Initiator conc. (mM)	N_{mo}	ρ_m	k	k_m/N_{av}
	L^{-1}	s^{-1}	s^{-1}	$L\ mol^{-1}\ s^{-1}$
Io = 0.015	1×10^{20}	8.95×10^{-6}	2.14×10^{-3}	1.73×10^{-20}
Io = 0.015	1×10^{21}	8.95×10^{-7}	2.14×10^{-3}	1.74×10^{-20}
Io = 0.015	1×10^{22}	8.95×10^{-8}	2.14×10^{-3}	1.74×10^{-20}
Io = 0.044	1×10^{20}	2.66×10^{-5}	2.73×10^{-3}	9.05×10^{-21}
Io = 0.044	1×10^{21}	2.66×10^{-6}	2.73×10^{-3}	9.12×10^{-21}
Io = 0.044	1×10^{22}	2.66×10^{-7}	2.73×10^{-3}	9.12×10^{-21}

Table 2.
Obtained parameters and the effect of N_{mo} on them for STY.

Initiator conc. (mM)	N_{mo}	ρ_m	k	$k_{m/}\ N_{av}$
	L^{-1}	s^{-1}	s^{-1}	$L\ mol^{-1}\ s^{-1}$
Io = 0.061	1×10^{20}	3.43×10^{-5}	6.05×10^{-3}	5.45×10^{-21}
Io = 0.061	1×10^{21}	3.42×10^{-6}	6.07×10^{-3}	5.52×10^{-21}
Io = 0.061	1×10^{22}	3.42×10^{-7}	6.07×10^{-3}	5.53×10^{-21}
Io = 0.240	1×10^{20}	1.01×10^{-4}	8.62×10^{-3}	8.97×10^{-21}
Io = 0.240	1×10^{21}	1.01×10^{-5}	8.64×10^{-3}	9.12×10^{-21}
Io = 0.240	1×10^{22}	1.01×10^{-6}	8.64×10^{-3}	9.13×10^{-21}
Io = 0.490	1×10^{20}	2.30×10^{-4}	2.09×10^{-2}	5.96×10^{-21}
Io = 0.490	1×10^{21}	2.29×10^{-5}	2.08×10^{-2}	6.33×10^{-21}
Io = 0.490	1×10^{22}	2.29×10^{-6}	2.08×10^{-2}	6.37×10^{-21}

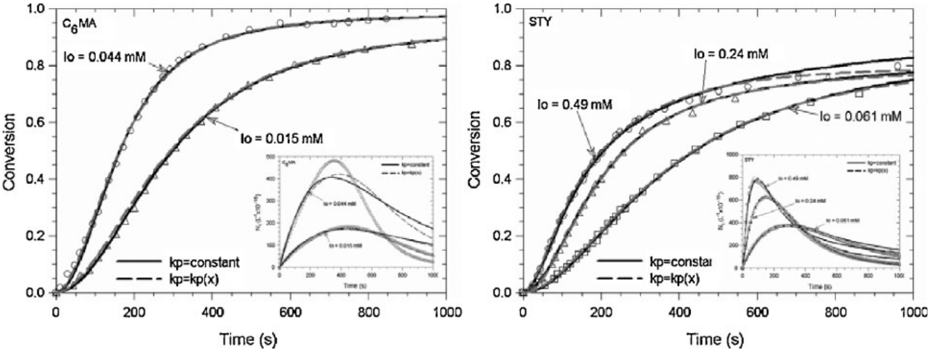

Figure 1.
Conversion (x) evolution with time. Continuous line model k_p constant, dotted line model $k_p = k_p(x)$, experimental data[3] symbols. Insert: Active particles (N_1) evolution with time. Inferred from the conversion and derivative (Symbols). Model with k_p constant (Continuous line), model with $k_p = k_p(x)$ (Dotted line).

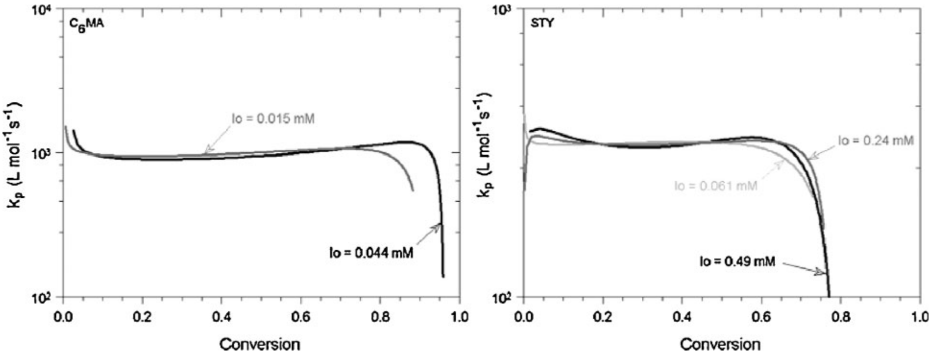

Figure 2.
Propagation rate "constant" evolution with conversion.

earlier in conversion (c.a. 70%). Applying the Fox equation and taking a T_G for the monomer[16] of 185 K, the resulting polymer weight fraction for the reaction temperature is about 89%, therefore the vitreous effect is present at a lower conversion than the one predicted by the Fox equation. Here also, the lower the initiator concentration, the sooner the appearance of the diffusion limitation effect.

Conclusions

The problem of modeling and assessment in microemulsion polymerization 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. This active particles functional dependence was used as an inferred measurement which permitted the estimation of five parameters (ρ_m, k, k_m, ρ, k_c), 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 previously. It was confirmed that entry to particles is negligible ($\rho \sim 0$), agreeing with previous works, and that particle coagulation, not treated before, was not important ($k_c \sim 0$). A vitreous effect, triggered earlier at lower initiator concentrations, appeared even in polymers whose T_G is lower than the reaction temperature. To find evidence on possible causes for this vitreous/diffusive effect, future work could be performed, analyzing the addition of transfer agents or solvents and correlating the molecular weight with the appearance of this phenomenon. Also, as a second step in the developing of this work, the events occurring in the aqueous phase will be evaluated.

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