

# Kinetic modeling of styrene emulsion polymerization: a step toward prediction.

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## 1. Abstract

Emulsion polymerization is a complex process in which interrelated chemical and physicochemical phenomena evolve simultaneously. This has led to mathematical models of different degrees of simplification, predictability and usage of adjustable parameters. In this work, a mathematical model reported by one of the authors is modified such that some adjustable parameters are avoided. This was done by taking into account advances in colloid science, free-radical chemistry, as well as by modelling the mass transfer of monomer from the droplets to the growing polymer latex particles. Comparison of model predictions against experimental data is shown and the effect of such modifications on the predictability of the model is discussed.

## 2. Introduction

Emulsion polymerization is a very important industrial process involved in the production of synthetic rubber, paintings and coatings, additives for concrete, products for biomedical use, etc. The number of applications of this process could still increase in the near future due to the convenience for using it to perform controlled/living radical polymerizations [1]. However, in spite of this growing interest and that emulsion polymerization has been studied from decades ago, it still exist some aspects of their kinetics that are not completely understood. Thus, the usage of adjustable parameters and simplifications are unavoidable leading to kinetic models of different degrees of predictability.

In this work, a kinetic model proposed by one of the authors [1,2] is modified such that some key aspects of the kinetics like initiator decomposition, swelling of polymer latex particles and monomer transport from droplets to particles, are treated with more detail leading to an improvement of the model predictability. The general features of this latter are discussed next making emphasis on the key aspects referred above.

### 3. Kinetic model. Main characteristics y results

- The population balance equations (PBEs) that describe the particle size distribution (PSD) have two internal coordinates: the number of radicals within particles ( $n$ ) and the size of these. The free-radical capture, desorption and termination rate coefficients as well as the growth rate coefficient used in the PBEs are size dependent. This allows one to take into account the compartmentalization effect on the PSD. According to the model this effect can be manifested as bimodal PSDs in batch emulsion polymerizations [3] whose peak of small particles (radius  $r < 10$  nm), has been confirmed by asymmetrical flow field-flow fractionation (AF<sup>4</sup>) [4], although it seems not to be detected by the usual techniques.

- Aqueous phase kinetics is taken into account including the initiator decomposition induced by surfactant molecules free in the aqueous phase [5]. The initiator decomposition rate coefficient ( $k_d$ ) for potassium persulfate (KPS) is given by

$$k_d = k_1 + (2k_1k_2 / k_4)S_{free} / Mw_{SDS} \quad (1)$$

$k_1$  is the rate coefficient in the absence of SDS.  $S_{free}$  is the mass concentration of SDS molecules free in the aqueous phase.  $Mw_{SDS}$  is the molecular mass of SDS. The ratio  $k_2/k_4$  refers to rate coefficients of intermediate reactions; for more details see reference [5]. Equation (1) implies that the generation rate of radicals ( $Ri$ ) not only depends on the initiator concentration ( $I$ ) but also on  $S_{free}$ . Accordingly,  $Ri$  should be practically constant if micelles exist ( $S_{free} = CMC$ ) and can diminish during interval II because more and more surfactant is adsorbed onto the growing surface area of the particles. Another implication is that, in polymerizations performed below CMC, the lower the value of the initial surfactant concentration ( $S_0$ ) the lower the value of  $Ri$  even if the initial initiator concentration ( $I_0$ ) is kept constant.

- Coagulation rate coefficients are calculated by applying DLVO theory. The repulsive energy term is estimated through the extended Hogg-Healy-Fuerstenau (HHF) equation for moderate surface potential [6]. These coefficients are included in the PBEs.
- Homogeneous and micellar nucleation are in competition. This latter can occur by capture of desorbed (monomeric) or initiator derived radicals in micelles.
- The effect of the hydrophobic part of the surfactant molecules on swelling is considered. Tauer et al. [7], have reported evidences suggesting that the hydrophobic tail of surfactants may increase the swelling of polymer latex particles. The authors have also found experimental evidences that confirm this notion [8]. It is well known

that the presence of linear low molecular mass hydrocarbons (e.g. dodecane) promotes superswelling of polymer particles [9]. Therefore, besides of reducing the interfacial tension, it is expected that the presence of surfactant may be affecting the swelling of particles especially for low particle sizes for which the volume fraction of surfactant is very significant. Thus, in the present work the hydrophobic part of surfactant molecules is considered as a third component in the equilibrium swelling calculations. For this purpose a modified version [7] of the Morton-Kaizerman-Altier (MKA) [10] equation is used. In Figure 1, the volume fraction of monomer calculated using this equation is compared against swelling experiments reported by Tauer et al. The polystyrene particles used in these experiments were synthesized using certain amounts of sulfonated monomer and subject to a post-reaction cleaning procedure to avoid the presence of surfactant molecules. Continuous and dotted lines correspond to calculations performed considering and without considering the contribution of the surfactant to the particle volume, respectively. The thickest line corresponds to the original MKA equation for complete surfactant coverage ( $\theta$ ). In both cases the effect of the surfactant  $\theta$  on the interfacial tension is considered. It can be observed that the greater the surface charge density (i.e.  $\theta$ ) the greater the difference between both kind of lines indicating how the presence of the hydrophobic tail enhanced the swelling of the particles. It can also be observed that the original MKA equation overestimates the volume fraction of monomer ( $\phi_m$ ).

- Monomer transport from droplets to polymer particles is considered. For this purpose the average droplet size in a stirred tank is estimated through a semi-empirical correlation [11] which is function of parameters that have to do with the hydrodynamics of the reactor.
- The propagation rate coefficient of monomeric radicals ( $Kp_I$ ) is a very important parameter in the model because determines the probability that this specie desorbs to the aqueous phase or remain in a given particle. There are not consistency in the values reported in the literature, its value lies between  $Kp_I=4Kp$  up to  $Kp_I=100Kp$  where  $Kp$  is the propagation rate coefficient of long chain radicals. By using desorption rate coefficients reported in the literature, it was determined in this work that  $Kp_I \sim 15Kp$ , value that is very close to that reported by Heuts and Russel [12].

As an example of the model predictability, in figure 2 the model results are compared against experimental data [13] of two styrene emulsion polymerizations effected at the

same conditions except for the agitation speed that in one case was 400 rpm and in the other 200 rpm. According to the model results, at 200 rpm eventually the mass transport of monomer from droplets to particles is not enough to maintain the polymer particles saturated. This is caused by the decrease of the interfacial area of monomer droplets which in turn is caused by the increment of the interfacial tension during interval II.

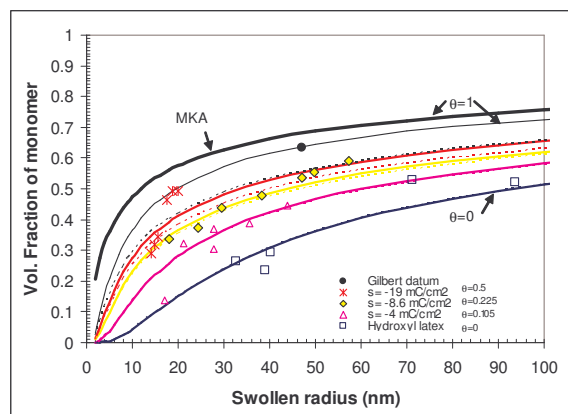


Figure 1. Comparison of the corrected MKA equation predictions against experimental data [7]. The original MKA equation is also plotted (upper line).

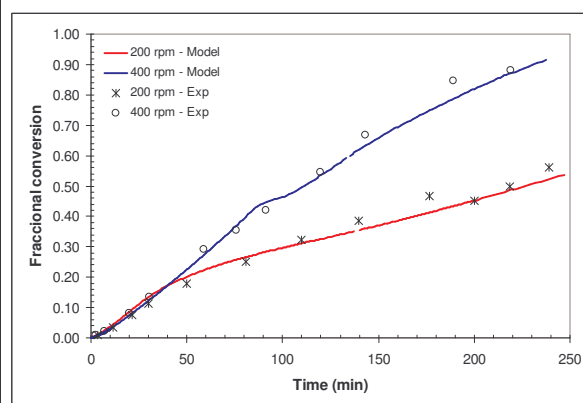


Figure 2. Conversion versus time curves for styrene emulsion polymerization effected at different agitation speeds. Experimental data taken from [13].

#### 4. Concluding remarks

The predictability in emulsion polymerization modeling is still a challenge because the usage of adjustable parameters is unavoidable and because of the adoption of mechanistic simplifications proposed decades ago. Improvements in the prediction capability of kinetic models can be made if advances in fields related to this process are incorporated to the kinetic models and if instead of disregard effects *a priori*, a more complete kinetic scheme is considered provided most of the parameters involved can be estimated.

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