

Kinetics Modeling of Microemulsion Copolymerization

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INTRODUCTION

Microemulsion polymerization is a complex heterogeneous process where monomer and free radical transport between the aqueous and organic phases take place. Compared with other heterogeneous polymerization processes (suspension, emulsion) microemulsion polymerization is a more complicated system. The polymerization rate is controlled by the monomer partitioning between the phases, particle nucleation and adsorption and desorption of radicals. In this work, we propose a simple mathematical model to simulate the kinetics of microemulsion copolymerization of a monomer with relatively high water solubility and another with low water solubility such as vinyl acetate and butyl acrylate, respectively.

MODEL DEVELOPMENT

The model consists of a system of differential and algebraic equations based on mass and population balances and the following assumptions:

1. The reactor is perfectly mixed.
2. Polymer particles contain only one radical in propagation (zero-one kinetics).
3. The particles are generated by micellar and homogeneous nucleation.
4. The noninitiated microemulsion droplets serve as monomer reservoir.
5. The main loci of polymerization are the polymer particles.
6. Terminal kinetics model (Mayo-Lewis) is valid.

Physical picture.

The important physical and chemical processes in microemulsion polymerization include radical generation in aqueous phase, chain propagation and termination. The following events can also occur in the water phase: radical capture by swollen monomer micelles and particles and radical desorption from the polymer particles. There are two main mechanisms of particle nucleation: micellar and homogeneous. If a micelle captures a radical, this becomes an active particle (micellar nucleation). Hansen and Ugelstad (1978) stated that particles could be generated by oligomeric radicals precipitated in the water phase which are stabilized by surfactant molecular (homogeneous particle nucleation). A kinetic mechanism similar to the one presented by Mendizabal et al. (1998) was used for the mathematical model. The mechanism includes but is not restricted to the following events.

- a) Initiation.
- b) Propagation in the water phase.
- c) Termination in the water phase.
- d) Radical desorption from the polymer particles.
- e) Radical capture by the microemulsion droplets.

- f) Radical capture by the polymer particles.
- g) Dead particles generated by encounter of two radicals in the aqueous phase.
- h) Oligomeric radicals precipitated in the water phase (homogeneous nucleation).

In the polymer particles, the following events can take place:

- i) Propagation.
- j) Termination in the polymer phase.
- k) Termination by chain transfer to monomer.

Balance equations of the model subjected to these assumptions are as follows.

Global polymer particle generation rate

$$\frac{dN}{dt} = \frac{dN_m}{dt} + \frac{dN_H}{dt} + \psi_0 \quad (1)$$

where N_m , N_H and ψ_0 are given by (all symbols are described in the nomenclature)

$$\frac{dN_m}{dt} = \rho_m N_d = \left(k_{cmA} \sum_{i=1}^c P_{iA} + k_{cmB} \sum_{i=1}^c P_{iB} \right) N_d \quad (2)$$

$$\begin{aligned} \frac{dN_H}{dt} &= (k_{pwAA} P_{cA} M_{Aa} + k_{pwAB} P_{cA} M_{Ba} + k_{pwBA} P_{cB} M_{Aa} + k_{pwBB} P_{cB} M_{Ba}) N_{AV} \\ &= [P_{cA} (k_{pwAA} M_{Aa} + k_{pwAB} M_{Ba}) + P_{cB} (k_{pwBA} M_{Aa} + k_{pwBB} M_{Ba})] N_{AV} \end{aligned} \quad (3)$$

$$\psi_0 = \left(k_{twAA} \sum_{i=1}^c P_{iA} \sum_{j=c-i+1}^c P_{jA} + k_{twAB} \sum_{i=1}^c P_{iA} \sum_{j=c-i+1}^c P_{jB} + k_{twBB} \sum_{i=1}^c P_{iB} \sum_{j=c-i+1}^c P_{jB} \right) N_{AV} \quad (4)$$

Polymer particle, which are assumed to contain one growing radical, can be represented as follows:

$$\frac{dN_1}{dt} = -(k_{dA} + k_{dB}) N_1 + (N_0 - N_1) (k_{cpA} P_A + k_{cpB} P_B) + \frac{dN_H}{dt} + \frac{dN_m}{dt} \quad (5)$$

The rate of primary radical generation is

$$\frac{dR^*}{dt} = 2fk_I I \quad (6)$$

Mass balance for radicals containing one monomer unit in the water phase is given by

$$\begin{aligned} \frac{dP_{1i}}{dt} &= (2fk_I I) + \left(k_{di} \frac{N_1}{N_{AV}} \right) - \left(\frac{k_{cmi} N_d + k_{cpi} N}{N_{AV}} \right) P_{1i} - (k_{pwii} M_{ia} + k_{pwij} M_{ja}) P_{1i} \\ &\quad - 2(k_{twii} P_{1i} P_i + k_{twij} P_{1i} P_j) \end{aligned} \quad (7)$$

$$\text{where } P_i = \sum_{n=1}^c P_{ni}$$

Mass balance for radicals containing n monomer units in the water phase is given by

$$\begin{aligned} \frac{dP_{ni}}{dt} = & (k_{pwii}M_{ia}P_{n-i} + k_{pwji}M_{ia}P_{n-1j}) - (k_{cmi}N_d + k_{cpi}N)\frac{P_{nj}}{N_{AV}} \\ & - (k_{pwii}M_{ia}P_{ni} + k_{pwijB}M_{ja}P_{ni}) - 2(k_{twii}P_{ni}P_i + k_{twij}P_{ni}P_j), \quad 2 \leq n \leq c \end{aligned} \quad (8)$$

The reaction rate of each monomer is given by:

$$\frac{dx_i}{dt} = \frac{(k_{pii}N_1M_{ip} + k_{pji}N_1M_{ip})/N_{AV} + (k_{pwii}M_{ia}P_i + k_{pwji}M_{ia}P_j)}{M_{i0}} \quad (9)$$

where $i, j = A, B$ and $i \neq j$

and the rate of disappearance of microemulsion droplets is

$$-\frac{dN_d}{dt} = \rho_m N_d \quad (10)$$

this equation is valid as long as the monomer concentration in the microemulsion droplets are greater than zero.

Kinetic data used in simulation and the model parameters were obtained from the literature (Delgado, 1986) and sorption and desorption rate parameters were estimated.

Monomer Partition in microemulsion copolymerization.

The monomer partitioning was calculated with similar equations used by Guo, et al. (1992), in terms of the three domains in thermodynamic equilibrium (organic phase, water phase and polymer phase) and material balances for each component.

RESULTS AND DISCUSSION

A simulation using the model was made for the monomer mixture of vinyl acetate and butyl acrylate (Vac:BuA, 85:15 w/w) for a monomer contents of 4.25% and 3.25% w/w with respect to the total reaction mixture. The initiator was KPS 1% with respect to the total monomers. The normal microemulsions were stabilized with a mixture of sodium dodecyl sulfate (SDS) and bis 2-ethylhexyl sodium sulfosuccinate (AOT), (3:1 w/w). Figure 1 shows conversion of each monomer as a function of time. This figure shows a fast consumption of BuA at the beginning of the reaction and the polymer is richer in this monomer; when BuA has been depleted, the global rate of polymerization are controlled by the consumption of VAc. Figure 2 compares the experimental and the predicted curve of global conversion versus time for 4.25 and 3.25% monomer contents with respect to the total mixture of reaction at 60 °C. At high conversions the model deviates from the experimental data, because the propagation rate constant can decrease at high conversion. Parameter sensibility analysis and others predictions of the model, such as particle diameter and particle number will be discussed in the presentation.

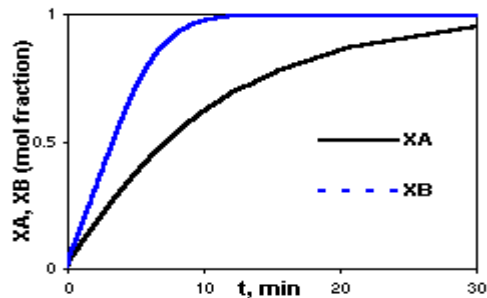


Fig. 1. Individual monomer conversions, BuA and VAc, calculated by simulation of microemulsion copolymerization at 60 °C with 4.25% of monomer with respect to the total mixture reaction. Initiator: KPS 1% with respect to the total monomer content. Surfactant to water ratio was 5/95 in the parent microemulsion.

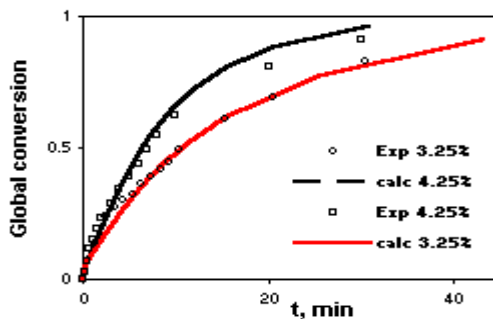


Fig. 2. Global conversions of the microemulsion copolymerization of VAc and BuA (85:15 w/w) with 4.25 and 3.25% of monomer with respect to the total mixture reaction at 60 °C. Initiator: KPS 1% with respect to the total monomer content. Surfactant to water ratio was 5/95 in the parent microemulsion.

NOMENCLATURE

f	Initiator efficiency
I	Initiator concentration
N	Total particle number
t	Time
x_i	Conversion of monomer i
k_{cmi}	Constant for type i radical capture by microemulsion droplets
k_{cpi}	Constant for type i radical capture by polymer particles
k_{di}	Desorption constant of type i radical from polymer particles
k_I	Initiator decomposition constant
k_{pij}	Propagation rate constant into the particles
k_{pwij}	Propagation rate constant in the aqueous phase
k_{twij}	Termination rate constant in the aqueous phase
A, B	Monomer type 1 and 2, respectively
P_{ci}	Critical size radical concentration in the aqueous phase

N_1, N_0	Particle number with one or zero radical in propagation, respectively
N_{AV}	avogadro's number
ψ_0	Particle number generated by encounter of two radicals in the aqueous phase
N_m, N_H	Particle number generated by micellar and homogeneous nucleation
M_{ia}	Monomer concentration in the aqueous phase
M_{ip}	Monomer concentration in the particle phase
N_d	Number of microemulsion droplets
P_i	Radical concentration in the aqueous phase
c	Critical monomer units for precipitation of oligomeric radicals in aqueous phase
R^*	Primary radicals concentration
M_{i0}	Initial amount of monomer in the system
ρ_m	Radical entry rate coefficient into the microemulsion droplets

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