

# Modeling and Sensitivity Analysis for Molecular Weight Distribution in an Emulsion VAc/BuA Copolymerization Reactor

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This study addresses the modeling of molecular properties in a semibatch emulsion vinyl acetate/butyl acrylate copolymerization reactor. Among the molecular properties of the copolymer, molecular weight distribution (MWD) plays a key role in the determination of final properties of the latex (Elizalde *et al.*, 2002). For example, good adhesive properties are achieved when the product is in a proper balance of high and low molecular weight polymer (sometimes, a bimodal distribution is required). Hence, it is well motivated to compare the properties of product by a blending process with that by the in-reaction produced MWD (to form the whole MWD during the process).

The model is developed applying the two tier method developed in our group for particle size distribution (Immanuel and Doyle, 2003). It is assumed that the element for the particle size is a batch reactor where the generation of living radicals by the entry of oligomers, the loss of monomeric radical by the desorption to the aqueous phase, and polymerization

**Table 1.** Polymerization kinetic scheme in the particle phase

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Entry	$P_{l,i}^w \xrightarrow{e_i^l} R_{n,i} \cdot \quad i = 1, 2, \quad l = 0, 1, \dots, j_{cr} - 1$
Propagation	$R_{n,i} \cdot + M_j \xrightarrow{k_{pij}} R_{n+1,j} \cdot \quad i, j = 1, 2$
Termination	$R_{n,i} \cdot + R_{m,j} \cdot \xrightarrow{k_{tdij}} P_n + P_m$
	$R_{n,i} \cdot + R_{m,j} \cdot \xrightarrow{k_{tcij}} P_{n+m}$
Chain transfer to monomer	$R_{n,i} \cdot + M_j \xrightarrow{k_{trij}} P_n + R_{0,j} \cdot$
Chain transfer to chain transfer agent (CTA)	$R_{n,i} \cdot + D \xrightarrow{k_{trid}} P_n + R_{0,j} \cdot$
Desorption	$R_{0,i} \cdot \xrightarrow{k_{dMi}} P_{0,i}^w$

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reactions listed in Table 1 occur. On the basis of the copolymerization reaction mechanism, rate equations of moments of dead polymer concentrations in each element (discretized grid for particle size) are developed and the pseudo steady state kinetic rate constants method (Hamielec *et al.*, 1987) is applied.

In the first tier, state variables in the model (moments of dead polymer concentrations) are fixed and variables for rate equations are calculated; for example, monomer concentrations in the particle are calculated using partition coefficient, and moments of living polymer concentrations are determined under pseudo steady state assumption. Then, in an algebraic manipulation, the change of moments of living polymer concentration in the element by coagulation is taken into account based on the probability of coagulation obtained from the intrinsic coagulation rate. In the second tier, the rate equations for moments of dead polymer concentration, which is a function of living polymer moments, are calculated and updated using a numerical integration technique. In such a way, the model for average molecular weight in the element becomes a differential algebraic equation of zeroth order.

On the basis of moments in each element, number and weight averaged molecular weights are calculated as follows:

$$\bar{M}_n(r_p) = \frac{\int_0^t \frac{d\{\mu_1(r_p)V(r_p)\}}{dt} M_{av}(r_p) dt}{\int_0^t \frac{d\{\mu_0(r_p)V(r_p)\}}{dt} dt} \quad (1)$$

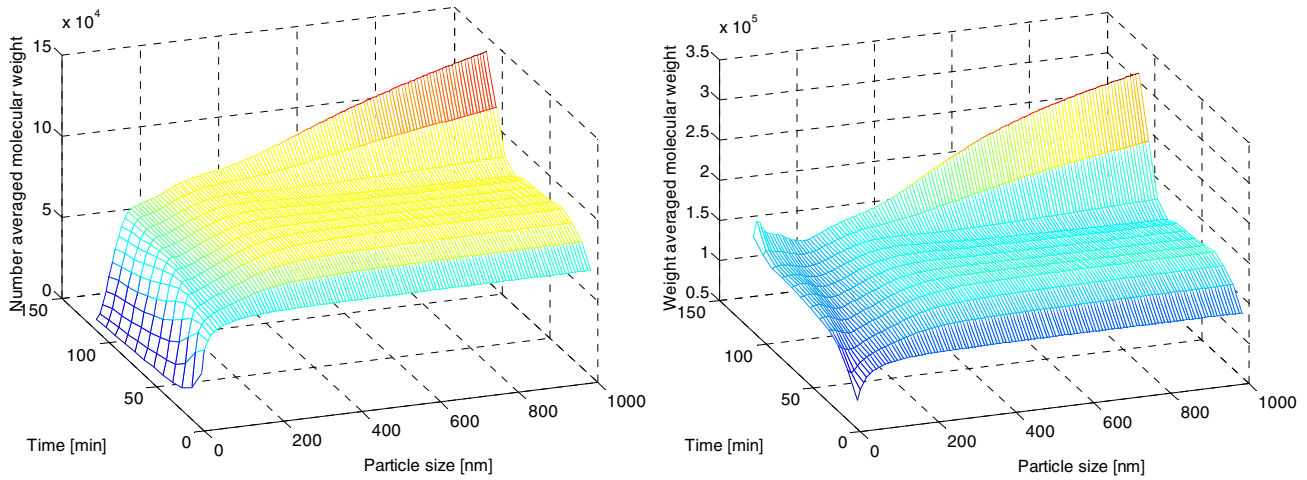
$$\bar{M}_w(r_p) = \frac{\int_0^t \frac{d\{\mu_2(r_p)V(r_p)\}}{dt} M_{av}^2(r_p) dt}{\int_0^t \frac{d\{\mu_1(r_p)V(r_p)\}}{dt} M_{av}(r_p) dt} \quad (2)$$

Here, average molecular weight of monomer ( $M_{av}(r_p)$ ) is calculated as  $W_{m1}F_1(r_p) + W_{m2}F_2(r_p)$  where  $W_{mi}$  denotes molecular weight of monomer  $i$  and  $F_i(r_p)$  represents instantaneous copolymer composition which is determined as a function of monomer ratio in the element by Mayo and Lewis's rule. In Equations (1) and (2),  $r_p$  denotes the particle size,  $\bar{M}_n$  and  $\bar{M}_w$  are the number averaged and weight averaged molecular weights, and  $\mu_i$  is the  $i^{\text{th}}$  moment of the dead polymer concentration.

Average molecular weights of polymer chains from Equations (1) and (2) are combined with the particle density function calculated by population balance equation (Immanuel and Doyle, 2003) to calculate overall molecular weights of the product:

$$\bar{M}_{n,overall} = \frac{\sum_{j=1}^{250} \bar{M}_{n,j} \mu_{0,j} \left( \frac{4}{3} \pi r_j^3 \times 10^3 \right) F_j N_A}{\sum_{j=1}^{250} \mu_{0,j} \left( \frac{4}{3} \pi r_j^3 \times 10^3 \right) F_j N_A} \quad (3)$$

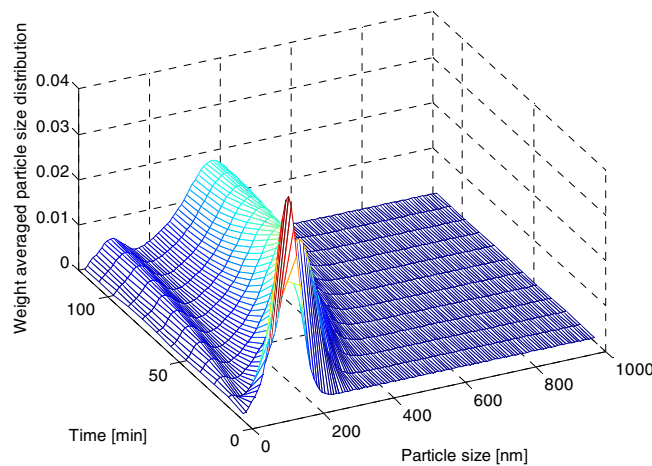
$$\bar{M}_{w,overall} = \frac{\sum_{j=1}^{250} \bar{M}_{w,j} \mu_{0,j} \left( \frac{4}{3} \pi r_j^3 \times 10^3 \right) F_j N_A}{\sum_{j=1}^{250} \mu_{0,j} \left( \frac{4}{3} \pi r_j^3 \times 10^3 \right) F_j N_A} \quad (4)$$



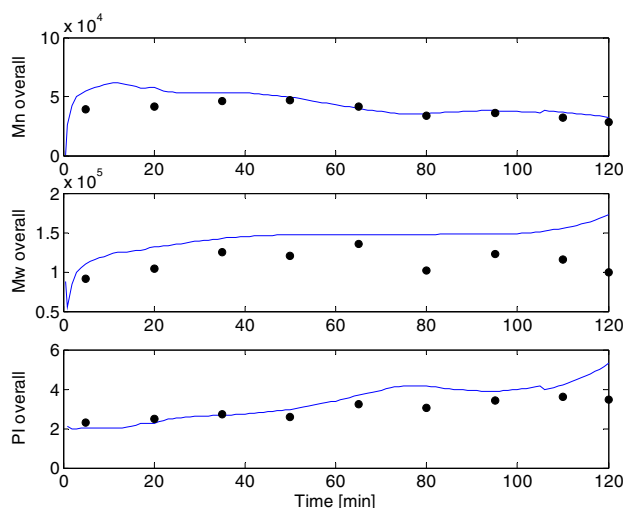
**Figure 1.** Time evolution of (a) number averaged molecular weight in the element and (b) weight averaged molecular weight in the element.

where  $\mu_{0,j}$ ,  $r_j$ ,  $F_j$ , and  $N_A$  denote zeroth moment of dead polymer concentration in the  $j$ -th element, particle size, particle density function, and Avogadro's number, respectively.

In simulation studies, the particle size is discretized into 250 elements with a width of 2 nm, and each element has equations for the zeroth, first, and second moments of dead polymer concentrations. Numerical integration is conducted using the 'ode45' function in MATLAB which utilizes an explicit fourth order Runge-Kutta method. Simulation results in Fig. 1 show that number of radicals in the element for small particle is greater than that for large particle, and thus, number averaged molecular weights in the region smaller than 200 nm are lower than those in other region. In the elements larger than 200 nm, average molecular weights are same because the number of radicals are same and monomer concentration in the particles is assumed to be constant (not a function of particle size). Considering the particle



**Figure 2.** Time evolution of weight averaged particle size distribution.



**Figure 3.** Time evolution of overall molecular weights under base condition.

size distribution presented in Figure 2, polymer particles generated by micellar nucleation (smaller than 200 nm) have lower number averaged molecular weight than particles by homogeneous nucleation while weight averaged molecular weights are nearly same. As a result, different polydispersity indices show that small particles have a broader distribution, which means that particles with different sizes are involved with different molecular properties.

The model is validated by the comparison between the simulated data and the experimental results for overall molecular weights by gel permeation chromatography (GPC). As shown in Figure 3, the model satisfactorily predicts the evolution of overall molecular weight. Using this model, the relationship between particle size distribution (morphological property) and molecular weight distribution (molecular property) will be evaluated and sensitivity analysis of those properties to a variety of operating conditions such as feed flow rates of monomers, surfactant, oxidizer and reducer, and the amount of chain transfer agent will be detailed to illustrate the design of an effective strategy for molecular property control.

### Literature Cited

- Elizalde, O., M. Vicente, J. R. Leiza, and J. M. Asua, "Control of the Adhesive Properties of n-Butyl Acrylate/Styrene Latexes," *Polym. React. Eng.*, **10**, 265-283 (2002).
- Hamielec, A. E., J. F. MacGregor, and A. Penlidis, "Multicomponent Free-radical Polymerization in Batch, Semibatch and Continuous Reactors," *Makromolekulare Chemie-Macromolecular Symposia*, **10**, 521-570 (1987).
- Immanuel, C. D. and F. J. Doyle III, "Computationally Efficient Solution of Population Balance Models Incorporating Nucleation, Growth and Coagulation: Application to Emulsion Polymerization," *Chem. Eng. Sci.*, **58**, 3681-3698 (2003).