Modeling Poly(Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization. I. Theory

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SYNOPSIS

A mathematical model for particle nucleation and growth in the isothermal semibatch emulsion polymerization of vinyl acetate stabilized with poly(vinyl alcohol) is presented. In addition to the particle nucleation and growth mechanisms governing ionically stabilized polymerizations of relatively water-soluble monomers, the model accommodates grafting onto the poly(vinyl alcohol) backbone during nucleation, and polymeric stabilization. The user supplies the emulsion recipe, process conditions and kinetic parameters, and the model predicts the various species concentrations, along with the conversion and particle size and number profiles. In part II, model predictions are compared with semibatch and batch experimental results, and particle nucleation implications are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Increased environmental awareness challenges the chemical industry to attain zero-defect standards through the use of model-based process control strategies. Commercial application of such strategies is especially limited in emulsion polymer manufacture, where the process mechanism is very complex and few usable models exist. For example, poly(vinyl acetate) latexes stabilized by poly(vinyl alcohol) have been widely used in the adhesives and coatings industries since the mid-1930s, but product quality and consistency often remain subject to subtle, uncontrolled raw material and process variations.

Poly(vinyl alcohol) has long been identified as a major culprit in causing highly variable final product quality. While several factors have been found to vary in the nominal 88% hydrolyzed poly(vinyl alcohol),[1] few have been correlated with final latex properties. Thus, the use of poly(vinyl alcohol) introduces complications that yet elude thorough understanding and quantitative treatment.

This paper presents a mathematical model for particle nucleation and growth in the isothermal semibatch emulsion polymerization of vinyl acetate stabilized with poly(vinyl alcohol). In addition to the particle nucleation and growth mechanisms governing ionically-stabilized polymerizations of relatively water-soluble monomers, the model accommodates grafting onto the poly(vinyl alcohol) backbone during nucleation, and polymeric stabilization. The user supplies the emulsion recipe, process conditions and kinetic parameters, and the model predicts the various species concentrations, along with the conversion and particle size and number profiles.

The remainder of this paper details the equations and underlying assumptions comprising the mathematical model. First, polymeric stabilization as applied in poly(vinyl alcohol)-stabilized vinyl acetate emulsion polymerization is briefly reviewed to provide a theoretical foundation for the model. Next, the subject system is detailed with respect to the reactor configuration and the assumed reaction mechanism. Then, the governing equations are presented as aqueous-phase and overall material balances, population balances, and particle-related parameter equations. Lastly, the model solution requirements are summarized. In part II, model predictions are compared with semibatch and batch experimental results, and particle nucleation implications are discussed.

THEORY

Poly(Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization

Emulsion polymerization is predicated upon the successful stabilization of colloidal-sized particles in a continuous phase. The emulsifying agent forms an adsorbed film around the dispersed particles that helps to prevent coagulation and coalescence. In a conventional electrostatic system, the ionic emulsifier imparts stability by the mutual repulsion of electrical double layers surrounding the particles. In polymerically stabilized systems, polymer molecules are attached (by grafting or physical adsorption) to the surface of the particles and stability is imparted by several different possible mechanisms.[2]

Polymeric stabilization is typically exploited in the use of poly(vinyl alcohol) as a protective colloid in vinyl acetate emulsion polymerization. In this system, the most effective polymeric stabilizers are amphipathic block or graft copolymers. The nominally insoluble polymer anchors the soluble stabilizing moieties to the colloidal particles (Fig. 1). When two particles collide, the mutually repulsive stabilizing moieties try to escape from the stress zone by either desorption from or lateral movement over the particle surface. Effective anchoring precludes both escape routes, and stability is imparted by osmotic and volume restriction repulsion. Medium molecular weight (77,000–79,000), partially hydrolyzed (up to 90% molar), blocky poly(vinyl alcohol) stabilizes poly(vinyl acetate) latexes most effectively.[3-7] The hydrophobic poly(vinyl acetate) blocks provide the primary anchoring segments and the hydrophilic poly(vinyl alcohol) blocks project
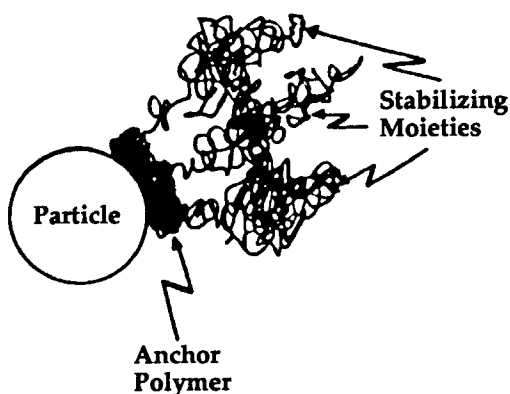

Figure 1   Schematic representation of the steric stabilization of a colloidal particle by an amphipathic block copolymer.[3]

into the aqueous phase as stabilizing moieties (Fig. 1).

Extensive evidence supports grafting as a primary method of attachment of poly(vinyl alcohol) molecules to poly(vinyl acetate) particles,[8-12] but adsorption as depicted in Figure 2 may also be significant. The poly(vinyl acetate) blocks would comprise the trains while the poly(vinyl alcohol) blocks would form the tails and loops (chains terminally attached at one or both ends, respectively). These types of poly(vinyl alcohol) are uniquely suited to vinyl acetate emulsion polymerization because both the stabilizing anchors and latex particles contain poly(vinyl acetate).

Presumably due to the aforementioned variances in poly(vinyl alcohol) characteristics and experimental conditions, there is virtually no agreement between investigators concerning the empirical orders for the polymerization rate and the number of particles with respect to poly(vinyl alcohol) and initiator concentrations. Authors do agree, however, on certain qualitative features of the reaction and the role of poly(vinyl alcohol).[4,5,9-15] Specifically,

1. Hydrophobic acetate blocks aggregate and hydrophilic hydroxy blocks extend into the aqueous phase to form poly(vinyl alcohol) pseudomicelles.
2. Particles are generated continuously, primarily via a homogeneous nucleation mechanism.
3. Poly(vinyl acetate) grafts onto partially hydrolyzed poly(vinyl alcohol) chains, enhancing latex stability.
4. Conversion profiles are qualitatively similar to those obtained with ionic surfactants, but polymerization rates are typically lower.

Polymerization in the presence of polymeric emulsifiers such as poly(vinyl alcohol) alters reaction kinetics and polymer structure (cf. surfactants) caused by both transfer reactions to poly(vinyl alcohol) and the specific character of the aqueous macromolecular aggregates. For ionically stabilized systems, empirical data and theoretical considerations support a homogeneous coagulative particle nucleation mechanism with significant free radical mobility (e.g., absorption into/desorption from latex particles) during most of the polymerization. A similar nucleation mechanism is assumed to prevail in a poly(vinyl alcohol)-stabilized system since vinyl acetate remains relatively water-soluble. However, poly(vinyl alcohol) pseudomicelles and grafting onto poly(vinyl alcohol) chains suggest, at the least, al-
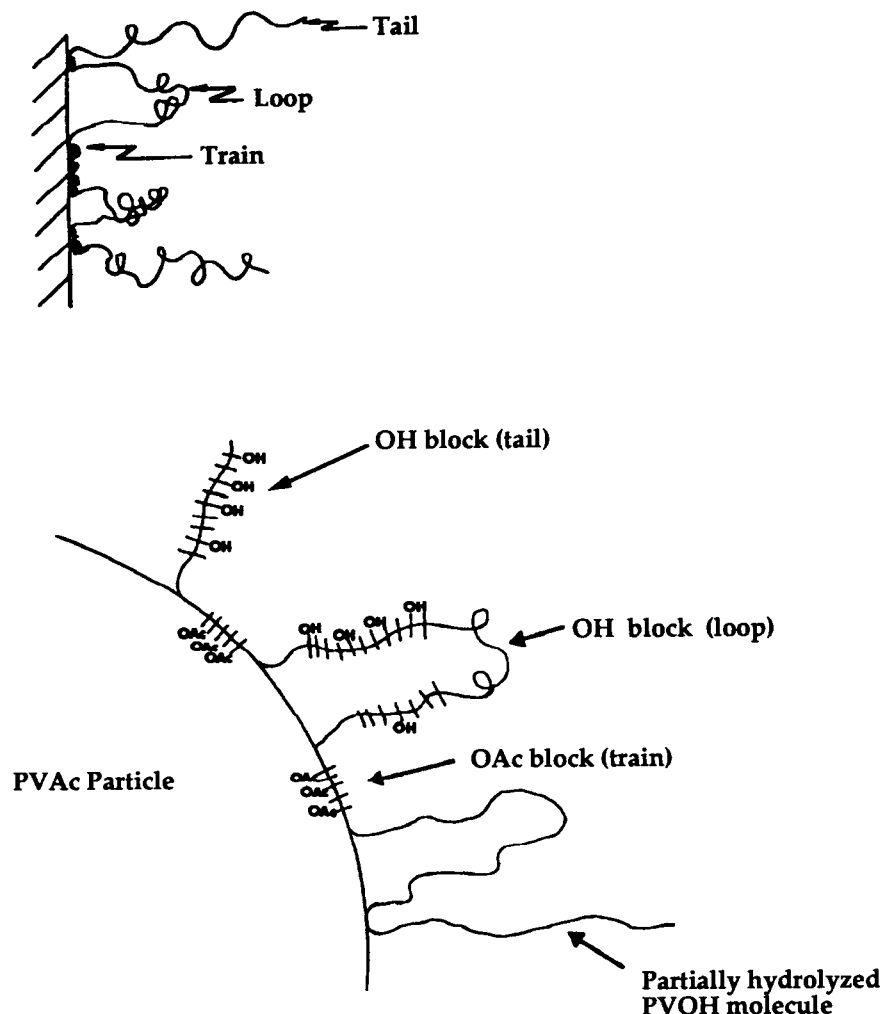
Figure 2   Adsorption of a macromolecule at the surface of a colloidal particle showing schematic trains, loops, and tails.

tered kinetics. Free radical mobility may also be reduced, potentially altering every polymerization parameter.

Polymeric Stabilization Model

Due to the complexity of the emulsion polymerization system, detailed modeling requires a reasonable amount of mathematical sophistication. There are basically two levels of complexity in modeling emulsion polymerization reactors. The first involves reactor material and energy balances, and is used to predict the reactor temperature, pressure, and monomer conversion. In addition to these quantities, second level models predict polymer properties such as particle size and distribution (PSD). Monodispersed approximation models are limited to the prediction of the number of particles and the total par-

ticle volume, while second level models employ a population balance approach (or an age distribution analysis) to obtain the full PSD.

The subject model employs a modified monodispersed approximation in that it assumes that, although the particle size distribution is polydisperse, the measurable average particle diameter may be predicted by lumping particles at or above a given size. This requires rigorous accounting of particles below this size, but avoids the complexity of a full-blown population balance. Another consideration is the detection limit of the particle size analyzer used. Smaller particle concentrations are calculated, but the measurable particle concentration P refers only to those particles at or above the experimentally detectable size, excluding the potentially large population of small primary particles. However, the primary particles formed by homogeneous nucleation

of grafted poly (vinyl alcohol) molecules are included in P. Unlike the ungrafted primary particles, these particles are potentially stabilized by the grafted poly (vinyl alcohol) and tend to grow by polymerization rather than flocculation.

Another key assumption is the applicability of the quasi-steady-state approximation (QSSA) for aqueous-phase free radical concentrations. This assumption is widely accepted and introduces little error. Aqueous-phase and particle-phase concentrations are subscripted w and p, respectively.

System Description

The mathematical model is specific in the underlying reactor configuration and mechanism assumptions. Namely, a semibatch reactor accommodates the poly (vinyl alcohol)-stabilized vinyl acetate emulsion polymerization, and the reaction mechanism is expanded to include grafting onto the poly (vinyl alcohol) backbone. These features are further discussed prior to presenting the model equations.

Reactor Configuration. The semibatch reactor is modelled because of its widespread use in specialty emulsion polymer production and its potential utility in particle size and distribution control. In fact, the general policy for particle size and PSD control in semibatch emulsion polymerization reactors has been identified,[16-19] and investigators have suggested the use of optimal control techniques,[18] but to date none have demonstrated such a scheme for PSD control in emulsion polymerization reactors.

Reaction Mechanism. The model accounts for the possibility that both growing ungrafted poly (vinyl acetate) and grafted poly (vinyl alcohol)/poly (vinyl acetate) chains participate in the homogeneous nucleation process. Chemical grafting is not assumed to be the primary method of poly (vinyl alcohol) attachment to the poly (vinyl acetate) particles, but the possibility that grafting supplements physical adsorption of poly (vinyl alcohol) onto the particle surface is not precluded.

Prior to initiation, poly (vinyl alcohol) exists a pseudomicelles (acetate blocks forming hydrophobic interior; hydroxyl blocks, hydrophilic extensions) and as unaggregated molecules in solution. Vinyl acetate occupies the interior of these pseudomicelles and is also present in the aqueous phase, possibly associated with the dissolved poly (vinyl alcohol) or in droplets. The poly (vinyl alcohol) concentration and intramolecular structure determines how many pseudomicelles are present, and the vinyl acetate

solubility in water and vinyl acetate : water ratio determine the vinyl acetate distribution between pseudomicelles, the aqueous phase, and droplets.

When initiator (H_2O_2/Fe^{2+}) is added to the system, hydroxy radicals ($HO \cdot$) produced from the redox reaction attack vinyl acetate in the aqueous phase, and grow to form oligomeric free radicals. Depending primarily upon the aqueous-phase vinyl acetate concentration, an oligomeric radical (in relative proportions) either (a) absorbs into a pseudomicelle, converting it into a particle (micellar nucleation); (b) absorbs into an existing particle; (c) coagulates with another dissolved radical; or (d) continues to add vinyl acetate units until it reaches a critical chain length and precipitates to form a primary particle (homogeneous nucleation). Initiation of monomer droplets is considered negligible because of the smaller total droplet surface area relative to micelles. Depending upon the aqueous-phase poly (vinyl alcohol) concentration and the dynamics of its adsorption, the primary particles either coagulate (adsorb) onto existing stable particles or become stable growing particles by adsorbing poly (vinyl alcohol) and vinyl acetate from solution. H_2O_2 as an initiator, does not enhance the stability of the primary particles because OH endgroups provide minimal electrostatic stabilization.

Hydroxy radicals entering the system may also abstract H atoms from poly (vinyl alcohol) at the OH site) in addition to initiating vinyl acetate molecules. The polymeric macroradicals then initiate polymerization of vinyl acetate in the aqueous phase. The polymeric radicals may be generated by H abstraction from both aggregated (i.e., pseudomicellar) and free poly (vinyl alcohol) molecules. The relative concentrations of monomeric (vinyl acetate) and polymeric [poly (vinyl alcohol)] radicals depend on the relative vinyl acetate and poly (vinyl alcohol) concentrations and the respective rate constants.

Theoretically, the poly (vinyl alcohol) macroradicals have many of the same options available to the monomeric and hydroxy radicals. Early in the reaction, however, most continue to add vinyl acetate units until they reach a critical chain length and precipitate. Considering the size of a poly (vinyl alcohol) molecule and the multiple potential grafting sites per molecule, it is not difficult to envision the growing graft copolymer turning on itself at some critical point, with the growing vinyl acetate chains forming a particle interior. These precipitated particles are somewhat stable [steric stabilization provided by grafted poly (vinyl alcohol)] and would probably adsorb poly (vinyl alcohol) to maintain stability rather than coagulating with existing par-

ticles. Also, the growing graft copolymer may co-agulate with another dissolved radical, both forming one polymer particle, or growing poly(vinyl acetate) chains on two different poly(vinyl alcohol) chains may terminate and subsequently flocculate, again forming one particle. However, to maintain final particle sizes in the observed range (i.e., $\approx$ 0.1–0.6 micron), the macroradicals would have to terminate and/or coagulate when the grafted poly(vinyl acetate) chains were short compared to the critical chain length. Both occurrences are of low probability considering conformational constraints.

As polymerization continues with steady addition of initiator to the aqueous phase, uninitiated pseudomicelles serves as monomer [and poly(vinyl alcohol)] reservoirs to the growing particles. Homogeneous nucleation continues in the aqueous phase with most of the primary particles (or oligomeric radicals) flocculating onto existing stable particles. It is unlikely, but possible, that some primary particles are stabilized by adsorbing poly(vinyl alcohol) freed from uninitiated pseudomicelles.

Also during the polymerization, growing poly-(vinyl acetate) chains transfer to vinyl acetate molecules or poly(vinyl alcohol) chains, producing mobile monomeric free radicals or less mobile macroradicals, respectively. The concentrations of the two radical types depend on the relative concentrations of poly(vinyl alcohol) and vinyl acetate. The mobile monomeric radicals can desorb from particles into the aqueous phase and reabsorb into other particles until they either reinitiate or terminate, most probably with a polymeric macroradical in a particle. The monomeric radical concentration is assumed to be less than that observed in a ionically stabilized vinyl acetate system because (a) competing macroradicals are formed and (b) the diffusive activity is probably reduced because of adsorbed poly(vinyl alcohol) layer resistance. Thus, as the viscosity in the particles increases with conversion, the average number of free radicals per particle increases. As a result, the gel effect may be more pronounced than that observed in an ionically stabilized vinyl acetate system. Polymerization eventually ceases when the vinyl acetate is nearly depleted.

Aqueous-Phase Balances

Aqueous-phase balances are written for the monomer (M_w), poly(vinyl alcohol) (G_w), reductant (F_w), oxidant or initiator (I_w), primary radicals $([R\cdot]$ and $[G\cdot])$, and oligomeric radicals $([RM_i\cdot]$, $[M_i\cdot]$ and $[GM_i\cdot])$.

M_w—Vinyl acetate transfers through the aqueous phase from the monomer droplets to the polymer particles, and is consumed by initiation, propagation, and chain transfer reactions. Assuming that thermodynamic equilibrium is reached quickly and maintained, M_w is adequately expressed by the Morton equation.[20] Also, the interfacial tension term (and thus the particle size dependence) in the Morton equation may be neglected and $[1 - (1/DP)]$ $\approx$ 1 for the subject high polymer system.[21] The aqueous-phase monomer concentration is then expressed by

$$M_w = M_{ws}\exp[1 - \phi + \ln \phi + \chi(1 - \phi)^2] \quad (1)$$

when the aqueous phase is subsaturated. When monomer droplets are present, the aqueous-phase monomer concentration is equal to the saturated level, i.e., $M_w = M_{ws}$, and ϕ can be determined from a knowledge of χ.

G_w—In lieu of a rigorous balance, an overall balance expresses the free aqueous-phase poly(vinyl alcohol) concentration (G_w) as the initial charge (G_{wi}) less that on the particle (assumed spherical) surfaces. The aqueous-phase poly(vinyl alcohol) concentration is expressed as

$$G_w = G_{wi}\left(\frac{V_{wi}}{V_w}\right) - \frac{6000v_{ps}P}{(AG)D_{ps}} \quad (2)$$

where V_{wi} and V_w are the initial and current aqueous-phase volumes, respectively, v_{ps} is the average volume of a single swollen particle, D_{ps} is the diameter, AG is the area covered by a poly(vinyl alcohol) molecule, and P is the particle concentration.

F_w—A redox reaction between ferrous sulfate (F) and hydrogen peroxide (I) produces the hydrogen peroxide radical $(R\cdot)$. Neglecting any side reactions, ferrous sulfate is consumed according to

$$\frac{dF_w}{dt} = -\frac{F_w}{V_w}\frac{dV_w}{dt} - k_dF_wI_w. \quad (3)$$

I_w—While ferrous sulfate is added in a batch mode, hydrogen peroxide (assumed inhibitor-free) is fed throughout the polymerization at a rate I_f. It is consumed in the redox reaction. Assuming that hydrogen peroxide is present only in the aqueous phase, and neglecting inhibitor kinetics, a mass balance yields

$$\frac{dI_w}{dt} = \frac{I_f}{V_w} - k_dF_wI_w - \frac{I_w}{V_w}\frac{dV_w}{dt}. \quad (4)$$

$[R \cdot]$—Primary radicals are generated by the redox reaction and consumed by initiating vinyl acetate molecules and poly(vinyl alcohol) chains. The reaction with poly(vinyl alcohol) is actually a chain transfer reaction, but it is referred to as an initiation reaction since it initiates a poly(vinyl alcohol) molecule. Assuming primary radicals do not absorb into particles or droplets or participate in aqueous-phase chain transfer or termination reactions, the mass balance yields

$$[R \cdot] = \frac{f k_d I_w F_w}{k_{iwm} M_w + k_{iwe} G_w + \frac{1}{V_w} \frac{dV_w}{dt}} \quad (5)$$

where f is the initiation efficiency, expressing the fraction of $R \cdot$ radicals actually involved in the initiation reactions.

$[G \cdot]$—Poly(vinyl alcohol) radicals are generated when poly(vinyl alcohol) molecules undergo chain transfer reactions with hydroxy radicals $(R \cdot)$, primary monomeric radicals $(M_1 \cdot)$, or oligomeric radicals $(RM_i \cdot, GM_i \cdot, \text{or } M_i \cdot)$. The poly(vinyl alcohol) radicals then propagate, forming graft copolymer. The rate constants for the $R \cdot$ and $M_1 \cdot$ chain transfer reactions are distinguished from the $RM_i \cdot$ and $M_i \cdot$ constants because of expected differences in reactivities. Assuming primary poly(vinyl alcohol) radicals do not absorb into particles or participate in termination reactions, the mass balance yields

$$[G \cdot] = \frac{G_w}{k_{pw} M_w + \frac{1}{V_w} \frac{dV_w}{dt}} (k_{iwe}[R \cdot]$$

$$+ (k'_{iwe} - k_{tre})[M_1 \cdot] + k_{tre}[R_w \cdot]) \quad (6)$$

where

$$[R_w \cdot] = \sum_{i=1}^{n^*-1} ([RM_i \cdot] + [M_i \cdot])$$

$$+ \sum_{i=1}^{n^*_g - 1} [GM_i \cdot]. \quad (7)$$

$[RM_1 \cdot]$—Oligomeric radicals with one monomer unit are generated by aqueous-phase initiation, and consumed by propagation, chain transfer, and termination reactions. They may also be captured by particles. Assuming termination is by combination only[22,23] and radical capture is adequately characterized by an average rate constant, k_c, the mass balance yields

$$[RM_1 \cdot] = \alpha_{Mp} \left(\frac{k_{iwm}}{k_{pw}} \right) [R \cdot] \quad (8)$$

where α_{Mp}, the probability that a monomeric oligomeric radical will propagate in the aqueous phase, is given by

$$\alpha_{Mp} = \frac{k_{pw} M_w}{k_{pw} M_w + k_{trm} M_w + k_{tre} G_w} {+ k_{tw}[R_w \cdot] + k_c P + \frac{1}{V_w} \frac{dV_w}{dt}} \quad (9)$$

and $k_c = (\sum_{j=1}^{\infty} k_{cj} P_j)/P$ (the subscript j denotes particles of class j). Note that the assumption of termination by combination only may be argued, but is not essential since most radicals are terminated in the particle phase.

$[RM_i \cdot]$—Oligomeric radicals propagate, chain transfer, terminate, and are captured by particles. With assumptions similar to those governing $[RM_1 \cdot]$, the mass balance yields

$$[RM_i \cdot] = \alpha_{Mp}^{i-1} [RM_1 \cdot]. \quad (10)$$

The total concentration of radicals propagating from $R \cdot$, $\sum_{i=1}^{n^*-1} [RM_i \cdot]$ or $[RM \cdot]$, is expressed in the following closed form

$$[RM \cdot] = [RM_1 \cdot] \frac{\alpha_{Mp}^{n^*-1} - 1}{\alpha_{Mp} - 1}. \quad (11)$$

$[M_1 \cdot]$—Primary monomeric radicals either escape from particles or are generated by aqueous-phase chain transfer reactions. They are consumed by initiation and termination reactions, and are captured by particles. Again, with similar assumptions concerning termination and radical capture/escape, the mass balance yields

$$[M_1 \cdot] = [k_{trm} M_w[R_w \cdot] + k_e \bar{m}_1 P] \Big/$$

$$\left[(k'_{iwm} + k_{trm}) M_w + k'_{iwe} G_w + k_{tw}[R_w \cdot] + k_c P \right.$$

$$\left. + \frac{1}{V_w} \frac{dV_w}{dt} \right] \quad (12)$$

where $\bar{m}_1$ is the average number of radicals with chain length 1 per particle, and is expressed by

$$\bar{m}_1 = \frac{(k_{trm} M_p \bar{n} + k_c[M_1 \cdot]) V_{ps}}{\frac{dV_{ps}}{dt} + k_{pp} M_p V_{ps} + k_e V_{ps} + k_{tp} \bar{n} P V_w}. \quad (13)$$

$[M_2 \cdot]$—Monomeric radicals of chain length 2 are formed by an initiation reaction and are consumed by propagation, chain transfer, termination, and capture. The initiation reaction is actually a propagation reaction, but the rate constant is distinguished from k_{pw} because of expected reactivity differences. With the aforementioned assumptions, the mass balance yields

$$[M_2 \cdot] = \alpha_{Mp}\left(\frac{k'_{iwm}}{k_{pw}}\right)[M_1 \cdot]. \tag{14}$$

$[M_i \cdot]$—Monomeric radicals of chain length i are formed by propagation and consumed by propagation, chain transfer, termination, and capture. With the aforementioned assumptions, the mass balance yields

$$[M_i \cdot] = \alpha_{Mp}^{i-2}[M_2 \cdot]. \tag{15}$$

The total concentration of radicals propagating from $M_1 \cdot$, $\sum_{i=1}^{n^*-1} [M_i \cdot]$ or $[M \cdot]$, is expressed in the following closed form

$$[M \cdot] = [M_1 \cdot] + [M_2 \cdot] \frac{\alpha_{Mp}^{n^*-2} - 1}{\alpha_{Mp} - 1}. \tag{16}$$

$[GM_1 \cdot]$—Primary grafted radicals are generated by initiation, and consumed by propagation, chain transfer, and termination. Here, assume that, due to mobility restrictions, reaction between two grafted radicals is negligible and, also due to restricted mobility, these bulky polymeric radicals do not traverse the particle surface. The mass balance yields

$$[GM_1 \cdot] = \alpha_{GMp}[G \cdot] \tag{17}$$

where α_{GMp}, the probability that a grafted radical will propagate in the aqueous phase, is given by

$$\alpha_{GMp} = \frac{k_{pw}M_w}{k_{pw}M_w + k_{trm}M_w + k_{tre}G_w + k_{tw}([RM \cdot] + [M \cdot]) + \frac{1}{V_w}\frac{dV_w}{dt}}. \tag{18}$$

$[GM_i \cdot]$—Grafted radicals propagate, chain transfer, and terminate. With assumptions similar to those governing $[GM_1 \cdot]$, the mass balance yields

$$[GM_i \cdot] = \alpha_{GMp}^{i-1}[GM_1 \cdot]. \tag{19}$$

The total concentration of radicals propagating

from $G \cdot$, $\sum_{i=1}^{n^*-1} [GM_i \cdot]$ or $[GM \cdot]$, is expressed in the following closed form

$$[GM \cdot] = [GM_1 \cdot] \frac{\alpha_{GMp}^{n_g^*-1} - 1}{\alpha_{GMp} - 1} \tag{20}$$

Overall Balances

Overall balances are written for particle and monomer concentrations (P and M), and reactor, droplet, particle, and aqueous-phase volumes (V_r, V_d, V_{ps}, and V_w). Recall that the experimental particle concentration is assumed to be represented by a semi-rigorous population balance. Specifically, populations below a given size are rigorously accounted for while the remaining particles are lumped, and unsubscripted P refers to the sum of all populations at and above the experimentally detectable size. For clarity, explicit equations are presented for a 3-population system, but the method may be applied to any number of populations.

P_1—The ungrafted primary particle concentration is increased via homogeneous nucleation and decreased via flocculation. Aqueous-phase oligomers originating from initiator radicals ($RM_i \cdot$) and primary monomeric radicals ($M_i \cdot$) propagate to a critical chain length, n^*, and then precipitate to form primary particles. The critical chain length may also be reached by aqueous-phase termination. Neglecting micellar nucleation and any contribution to nucleation from aggregates formed from dead aqueous-phase chains shorter than n^*, the ungrafted primary particle formation rate is

$$\frac{dP_1}{dt} = k_{pw}M_w([RM_{n^*-1} \cdot] + [M_{n^*-1} \cdot])$$

$$+ k_{tw} \sum_{i=n^*-1}^{n^*/2} \sum_{k=n^*-i}^{i} \{[RM_i \cdot][RM_k \cdot]$$

$$+ [RM_i \cdot][M_k \cdot] + [M_i \cdot][M_k \cdot]\} - k_{f11}P_1^2$$

$$- k_{f12}P_1P_2 - k_{f13}P_1P_{3,3+} - \frac{P_1}{V_w}\frac{dV_w}{dt} \tag{21}$$

if n^* is even. The summation is $\sum_{i=n^*-1}^{[(n^*+1)/2]} \sum_{k=n^*-i}^{i}$ if n^* is odd. Here, $P_{3,3+}$ refers to the combined population of particles consisting of 3 or more primary particles.

P_2—The second or doublet population is increased and decreased by flocculation reactions. The mass balance yields

$$\frac{dP_2}{dt} = \frac{1}{2} k_{f11} P_1^2 - k_{f12} P_1 P_2 - k_{f22} P_2^2$$

$$- k_{f23} P_2 P_{3,3+} - \frac{P_2}{V_w} \frac{dV_w}{dt}. \quad (22)$$

$P_{3,3+}$—The remaining or lumped particle concentration is affected by homogeneous nucleation of primary grafted particles and flocculation. Aqueous-phase oligomers originating from grafted poly(vinyl alcohol) $(GM_i \cdot)$ propagate to a critical chain length, n_g^*, and then precipitate to form primary particles. The critical chain length may also be reached by aqueous-phase termination. With the aforementioned assumptions, the lumped particle formation rate is

$$\frac{dP_{3,3+}}{dt} = k_{pw} M_w [GM_{n_g^*-1} \cdot]$$

$$+ k_{tw} \sum_{i=n^*-1}^{1} \sum_{k=n_g^*-i}^{n_g^*-1} \{ [RM_i \cdot][GM_k \cdot]$$

$$+ [M_i \cdot][GM_k \cdot] \} + \frac{1}{2} k_{f12} P_1 P_2 + \frac{1}{2} k_{f22} P_2^2$$

$$- \frac{1}{2} k_{f33} P_{3,3+}^2 - \frac{P_{3,3+}}{V_w} \frac{dV_w}{dt} \quad (23)$$

P—The measured particle concentration, P, is simply the sum of all populations at or above the experimentally detectable size. If, for example, particles in the P_2 population can be detected, $P = P_2 + P_{3,3+}$.

M—Vinyl acetate is consumed by (a) propagation in the particle and (b) initiation, propagation, and chain transfer reactions in the aqueous phase. Initiator radicals $(R \cdot)$ and poly(vinyl alcohol) radicals $(G \cdot)$ are initiated and then propagate along with primary monomeric radicals $(M_1 \cdot)$, or chain transfer to vinyl acetate. Assuming both $G \cdot$ and $RM_i \cdot$ propagate at the same rate,[24] and the reactivity of the vinyl acetate free radical $(M_1 \cdot)$ is greater than that of the poly(vinyl acetate) free radical $(RM_1 \cdot)$,[24] the monomer consumption rate is

$$\frac{dM}{dt} = -k_{pp} M_p \bar{n} P \frac{V_w}{V_r}$$

$$- \{ k_{iwm}[R \cdot] + k_{pw}([G \cdot] + [R_w \cdot] - [M_1 \cdot])$$

$$+ k'_{iwm}[M_1 \cdot] + k_{trm}([R_w \cdot] - [M_1 \cdot]) \} M_w$$

$$\times \frac{V_w}{V_r} - \frac{M}{V_r} \frac{dV_r}{dt}. \quad (24)$$

Actually, stable particles are distinguished from unstable particles in the first term on the right-hand-side of the above equation. The stable particles, protected by a layer of poly(vinyl alcohol), are probably characterized by a higher monomer concentration and a larger average number of free radicals per particle. This is accounted for in the simulation studies.

V_r—During semibatch operation, the reactor volume is increased by initiator and poly(vinyl alcohol) feeds and decreased by the shrinkage that occurs when monomer is converted to polymer. Thus,

$$V_r = \frac{V_{ri} + v_f t}{1 + (M_i - M) MW_m \left(\frac{1}{\rho_m} - \frac{1}{\rho_p} \right)} \quad (25)$$

where V_{ri} is the initial reaction volume, v_f is the combined initiator and poly(vinyl alcohol) feedrate, M_i is the initial monomer concentration, MW_m is the monomer molecular weight, and ρ_m and ρ_p are the monomer and polymer densities, respectively.

V_d—Assuming the droplet volume decreases linearly with conversion until the droplets disappear,

$$V_d = V_{di} \left(1 - \frac{x}{xdd} \right) \quad (26)$$

where V_{di} is the initial droplet volume, x [$= (M_i - M)/M_i$] is the fractional conversion, and xdd is the fractional conversion at which the droplets disappear.

V_{ps}—Given v_{ps}, the average volume of a single swollen particle, the total swollen particle volume is given by

$$V_{ps} = v_{ps} N V_w \quad (27)$$

where N $(=N_A P)$ is the total measured particle number concentration and V_w is the total aqueous phase volume.

V_w—The total reactor volume is the sum of the aqueous, particle, and droplet volumes. Expressed algebraically after substituting the expression for V_{ps},

$$V_w = \frac{V_r - V_d}{1 + v_{ps} N}. \quad (28)$$

Particle-Related Parameter Equations

Equations are presented for the unswollen and swollen particle diameters and the swollen volume (D_p, D_{ps}, v_{ps}), the monomer volume fraction and concentration in the particles (ϕ, M_p), the average

rate constants of radical capture by and escape from particles (k_c, k_e), and the termination and flocculation rate constants (k_{tp}, k_{fij}).

D_p—All of the polymer is assumed to be in the measured particles, which are spherical and characterized by an average diameter, D_p. Thus, the aqueous-phase polymer and the polymer in the smaller particles is assumed negligible. This assumption, examined in the simulation studies, yields

$$D_p = \left(\frac{6000 M_i x M W_m V_{ri}}{\pi \rho_p N V_w}\right)^{1/3}. \quad (29)$$

D_{ps}—Given the average unswollen diameter, the average swollen diameter is simply expressed as

$$D_{ps} = \frac{D_p}{(1 - \phi)^{1/3}}. \quad (30)$$

v_{ps}—Given the average swollen particle diameter, and continuing with the spherical particle assumption,

$$v_{ps} = \frac{\pi}{6000} D_{ps}^3. \quad (31)$$

ϕ—Nomura et al.[25] suggest that the volume fraction of monomer in the particles is constant while monomer droplets exist, and then decreases linearly to zero as the polymerization proceeds. Thus,

$$\phi = \text{const} \quad \text{when} \quad 0 \leq x \leq xdd$$

$$\phi_{(x)} = \phi_{(xdd)} \frac{1 - x}{1 - xdd} \quad \text{when} \quad x > xdd. \quad (32)$$

M_p—Given ϕ, the monomer concentration in the particles is given by

$$M_p = \frac{\phi \rho_m}{M W_m}. \quad (33)$$

k_c—Assuming a diffusion model with irreversible absorption, Fick's first law gives

$$k_c = (0.002 \pi D_{ps} D_w N_A) \, eff \quad (34)$$

where D_w is the diffusion coefficient of monomeric radicals in the aqueous phase and eff accounts for the less than 100% capture efficiency. It is unlikely that radicals will be irreversibly absorbed until they have added enough monomer units to become practically water insoluble. Nonetheless, Ugelstad and Hansen[26] and Song[27] found the diffusion model to be adequate for vinyl acetate data.

k_e—For vinyl acetate emulsion polymerization (assuming the majority of escaping radicals are monomeric), Nomura et al.[25] successfully used

$$k_e = \left(\frac{12 D_w \delta}{m D_{ps}^2}\right)\left(\frac{k_{trm}}{k_{pp}}\right)$$

where m [$= (M_p/M_w)$] is the partition coefficient of monomeric radicals between the aqueous and particle phases and $\delta = [1 + (D_w/D_{pa}m)]^{-1}$. The diffusion coefficient of monomeric radicals in the polymer particles, D_{pa}, may be empirically estimated by $D_{pa} = D_{pa_0}\phi^2$ (Litt and Chang[28]). With these substitutions,

$$k_e = \left(\frac{12 D_w \delta}{D_{ps}^2} \frac{M_w}{M_p}\right)\left(\frac{k_{trm}}{k_{pp}}\right) \quad (35)$$

where

$$\delta = \left(1 + \frac{D_w}{D_{pa_0}\phi^2} \frac{M_w}{M_p}\right)^{-1}.$$

k_{tp}—Again, Nomura et al.[25] observed the following relation for the isothermal emulsion polymerization of vinyl acetate using sodium lauryl sulfate and potassium persulfate at 50°C,

$$k_{tp} = k_{tpo}\exp(-8.3w) \quad (36)$$

where $k_{tpo} = 4.7 \times 10^8$ at 50°C and $w \{ = (1 - \phi)\rho_p/[\phi\rho_m + (1 - \phi)\rho_p]\}$ is the weight fraction of polymer in the particles. Note that this expression explicitly accounts for the gel effect, but the temperature dependence (Arrhenius' law) is implicit in k_{tpo}. Nomura noted a relative insensitivity to other experimental conditions.

k_{fij}—The flocculation rate constants k_{fij} may be represented by Fuchs formulation[29] without the DLVO expression for W_{ij}. Thus, in the required units,

$$k_{ij} = \frac{\left(\frac{4}{3000}\right)\left(\frac{k_B T N_A}{\eta W_{ij}}\right)\left(1 + \frac{r_i}{r_j}\right)^2}{2 r_i / r_j} \quad (37)$$

where
k_{ij} = flocculation rate coefficient
k_B = Boltzmann constant
T = absolute temperature
η = viscosity of the medium
W_{ij} = Fuchs stability ratio
r_j = particle radius

When $i \neq j$, $r_i/r_j = (i/j)^{1/3}$.

Model Solution Requirements

In summary, when six ordinary differential equations are required to predict the measurable average particle diameter (i.e., nodes = 6), and the critical lengths for precipitation of ungrafted and grafted chains are 60 and 70, respectively, the mathematical model is comprised of 244 equations, only nine of which are differential. The bulk of the algebraic equations express aqueous-phase balances, including ungrafted and grafted radical concentrations. The cummulative number of unknown variables is 297, and thus 53 variables, in addition to the nine initial conditions for the ordinary differential equations, must be specified to solve the model. Of the 53 unspecified variables, 22 are provided by the polymerization recipe or literature estimates, while the remaining 31 must be inferred or hypothesized based on probable mechanisms. Variable specification (and model solution) is addressed further in Part II, after a polymerization recipe and experimental data are presented.

NOMENCLATURE

AG	Area covered by an emulsifier molecule, cm^2/molecule
D_p	Average unswollen number-averaged particle diameter, cm
D_{pa_o}	Initial diffusion coefficient of monomeric radicals in particle phase, cm^2/s
D_{ps}	Average swollen number-averaged particle diameter, cm
D_w	Diffusion coefficient of monomeric radicals in aqueous phase, cm^2/s
eff	Capture efficiency, dimensionless
f	Initiation efficiency, dimensionless
F_w	Aqueous-phase ferrous sulfate concentration, mol/L-aq
$[G \cdot]$	Total concentration of primary initiator radicals from grafting species, mol/L-aq
$[GM \cdot]$	Total concentration of radicals originating from propagation of $[G \cdot]$, mol/L-aq
$[GM \cdot_i]$	Total concentration of radicals of chain length i originating from propagation of $[G \cdot]$, mol/L-aq
G_w	Aqueous-phase grafting species concentration, mol/L-aq
G_{wi}	Initial aqueous-phase grafting species concentration, mol/L-aq
I_f	Initiator feed rate to reactor, mol/s

I_w	Aqueous-phase initiator concentration, mol/L-aq
k_c	Average rate constant or radical capture by particle, l-aq/mol-s
k_{cj}	Rate constant for radical capture by particles of class j, L-aq/mol-s
k_d	Rate constant of initiator decomposition, L-aq/mol-s
k_e	average rate constant of radical escape from particles, s^{-1}
k_f	Average rate constant of particle coagulation, L $-$ aq/mol-s
k_{fij}	Rate constant for coagulation between P_i and P_j particles, L-aq/mol-s
k_{iwe}	Rate constant for formation of $G \cdot$ radicals from initiator primary radicals $(R \cdot)$ and grafting species (G), L-aq/mol-s
k'_{iwe}	Rate constant for formation of $G \cdot$ radicals from desorbed primary monomeric radicals $(M \cdot_1)$ and grafting species (G), L-aq/mol-s
k_{iwm}	Rate constant for propagation of initiator primary radicals $(R \cdot)$, L-aq/mol-s
k'_{iwm}	Rate constant for propagation of desorbed primary monomeric radicals $(M \cdot_1)$, L-aq/mol-s
k_{pw}	Rate constant for propagation in the aqueous phase, L-aq/mol-s
k_{pp}	Rate constant for propagation in the particle phase, L-particle/mol-s
k_{tp}	Rate constant for termination in the particle phase, L/mol-s
k_{tre}	Rate constant for chain transfer to emulsifier (G), L-aq/mol-s
k_{trm}	Rate constant for chain transfer to monomer (M), L-aq/mol-s
k_{tw}	Rate constant for termination in the aqueous phase, L-aq/mol-s
m	Variable used in $\bar{n}$ calculation, dimensionless
$\bar{m}_1$	Average number of radicals with chain length 1 per particle, dimensionless
M	Total monomer concentration in the latex, mol/L-latex
$[M \cdot]$	Total concentration of radicals originating from propagation of desorbed primary monomeric radicals, mol/L-aq
M_i	Initial total monomer concentration, mol/L-latex
$[M \cdot_i]$	Total concentration of radicals of chain length i originating from propagation of desorbed primary monomeric radicals mol/L-aq
M_p	Particle-phase monomer concentration, mol/L-particle

M_w	Aqueous-phase monomer concentration, mol/L-aq
M_{ws}	Aqueous-phase monomer concentration at saturation, mol/L-aq
MW_m	Monomer molecular weight, g/gmol
n^*	Critical chain length for homogeneous nucleation of ungrafted species, dimensionless
n_g^*	Critical chain length for homogeneous nucleation of grafted species, dimensionless
$\bar{n}$	Average number of radicals per particle, dimensionless
N	Total stable particle number concentration, particles/L-aq
N_A	Avogadro's constant, mol^{-1}
P	Total stable particle concentration, mol/L-aq
P_i	Concentration of particles of class i, mol/L-aq
$[Pm_1]$	Concentration of radicals with chain length 1 in the particle phase, mol/L-aq
R_i	Initiation rate of primary initiator radicals, radicals/L-aq-s
$[R \cdot]$	Total concentration of primary radicals from initiator, mol/L-aq
$[R \cdot_w]$	Total aqueous-phase concentration of oligomeric radicals, mol/L-aq
$[RM \cdot]$	Total concentration of radicals originating from propagation of $[R \cdot]$, mol/L-aq
$[RM \cdot_i]$	Total concentration of radicals of chain length i originating from propagation of $[R \cdot]$, mol/L-aq
t	Time, s
v_f	Total feed rate to reactor, L/s
v_{ps}	Average swollen particle volume, L/particle
V_d	Total droplet volume, L-droplet
V_{di}	Initial total droplet volume, L-droplet
V_{ps}	Total swollen particle volume, L-particle
V_r	Total reactor (latex) volume, L-latex
V_{ri}	Initial total reactor (latex) volume, L-latex
V_w	Total aqueous-phase volume, L-aq
V_{wi}	Initial total aqueous-phase volume, L-aq
W_{ij}	Fuchs stability ratio for i, j particle combination, dimensionless
x	Fractional conversion, dimensionless
xdd	Fractional conversion at which droplets disappear, dimensionless
Y	Variable used in $\bar{n}$ calculation, dimensionless

Greek Symbols

α'	Variable used in $\bar{n}$ calculation, dimensionless
α_{GMp}	Probability of propagation for a grafted oligomeric radical radical in the aqueous phase, dimensionless
α_{Mp}	Probability of propagation for an ungrafted oligomeric radical in the aqueous phase, dimensionless
χ	Monomer–polymer interaction parameter, dimensionless
δ	Variable used in k_e calculation, dimensionless
ϕ	Monomer volume fraction in particles, dimensionless
ρ_m	Monomer density, g/L
ρ_p	Polymer density, g/L

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