

Improved Methods for Solving Monomer Partitioning in Emulsion Copolymer Systems

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SYNOPSIS

A new algorithm for the calculation of monomer partitioning in emulsion copolymer systems is presented. The algorithm can be applied both to monodisperse and polydisperse systems and the outputs of the algorithm include the distribution of the volume fractions of the monomers according to the particle size distribution, the volume fractions of the monomers in the monomer droplets, and the aqueous phase and the total volumes of all the phases in the system. The algorithm can handle both Interval II and Interval III conditions, using the same set of equations. This results in substantial computer time savings during the simulation of emulsion copolymerization systems. Examples of applications are given.

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INTRODUCTION

Prediction of the monomer partitioning is of paramount importance for the modelling of emulsion copolymerization systems, because the polymerization rate and the composition of the copolymer, obtained in both the polymer particles and the aqueous phase, are determined by the concentrations of the monomers in those phases. Under most circumstances, the ratio of the rate of monomer mass transfer to the rate of polymerization is large enough to attain the thermodynamic equilibrium of the monomers between the phases. Since the pioneering article of Morton et al.,¹ much work has been carried out to establish the thermodynamic equations that control that equilibrium. References 2–5 are some representative works. On the other hand, those thermodynamic equilibrium equations have been extensively used to predict the concentration of the monomers in the different phases of the system. References 6–9 are just a few examples of this application. In order to calculate the partition of the monomers, the equilibrium equations are combined with the overall material balances and the resulting system of nonlinear, algebraic equations is solved. This can be

carried out using a standard Newton–Raphson algorithm, but experience shows that this is a time-consuming algorithm and the convergence of the algorithm depends strongly on the initial guess. In addition, the number of equations to be solved varies, depending on whether there are or are not monomer droplets in the system. Therefore, the presence of monomer droplets has to be checked iteratively and this increases the computer time consumption.

For monodisperse systems, in which the equilibrium can be described by means of partition coefficients, Omi¹⁰ developed an efficient algorithm that ensured rapid convergence to the solution. The main limitations of this algorithm are that it cannot handle systems in which the equilibrium is described in terms of thermodynamic equations, and different sets of equations should be used for interval II and interval III conditions, namely, in the presence and in the absence of monomer droplets in the system, respectively.

Most latexes are polydisperse and it is well known that, because of the interfacial free energy, swelling increases with particle diameter. However, to our knowledge no algorithm for solving monomer partitions in polydisperse emulsion copolymer systems has been proposed.

In this article, an algorithm for the calculation of the monomer partitioning in polydisperse emulsion copolymer systems is presented. In this algo-

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gorithm, the polydispersity of the latex is accounted for, the equilibrium is described in terms of the thermodynamic equations, and that there is no need for removing from the system of nonlinear algebraic equations those corresponding to the monomer droplets when there are no monomer droplets in the system. Consequently, the presence of monomer droplets does not need to be checked, but it is one output of the algorithm. This results in substantial computer time savings when emulsion copolymerization systems are simulated.

BASIC EQUATIONS

Let us consider a polydisperse unswollen latex, in which the unswollen size distribution, PSD, is defined by the number distribution function $n(v)$, with which $n(v) dv$ yields the total number of particles of size v to $v + dv$. A monodisperse system is just a special case of the polydisperse one and, hence, it is included in the general formulation described below. The number of polymer particles and volume of polymer in the latex are, respectively, given by:

$$N_p = \int_{v_0}^{v_1} n(v) dv \tag{1}$$

$$V_{pol} = \int_{v_0}^{v_1} vn(v) dv \tag{2}$$

where v_0 and v_1 are chosen in such a way that the whole PSD is included between the values. In addition, the latex contains a volume of water W , as well as some volume of monomers A and B (V_A and V_B , respectively), which are assumed to be distributed between the phases according to the thermodynamic equilibrium. Under these conditions, the partial molar free energy of each monomer is equal in each of the three phases. Therefore, the following equilibrium can be written:

$$\bar{G}_j^d = \bar{G}_j^w = \bar{G}_{j,v}^p \tag{3}$$

where $j = A, B$ and $v_0 < v < v_1$. If the same standard state for component j is used in all phases, one has:

$$\Delta\bar{G}_j^d = \Delta\bar{G}_j^w = \Delta\bar{G}_{j,v}^p \tag{4}$$

where $j = A, B$ and $v_0 < v < v_1$. The partial molar free energy of the monomers in the different phases is given by^{4,5}:

$$\left(\frac{\Delta\bar{G}}{RT}\right)_{j,v}^p = \ln \phi_j^p(v) + (1 - m_{ji})\phi_i^p(v) + \phi_p^p(v) + \chi_{ji}(\phi_{iw}^p(v))^2 + \chi_{jp}(\phi_p^p(v))^2$$

$$+ \phi_i^p(v)\phi_p^p(v)(\chi_{ji} + \chi_{jp} + \chi_{ip}m_{ji}) + \frac{2\sigma v_j(4\pi\phi_p^p(v))^{1/3}}{(3v)^{1/3}RT} \tag{5}$$

$$\left(\frac{\Delta\bar{G}}{RT}\right)_j^d = \ln \phi_j^d + (1 - m_{ji})\phi_i^d + \chi_{ji}(\phi_i^d)^2 \tag{6}$$

$$\left(\frac{\Delta\bar{G}}{RT}\right)_{j,v}^w = \ln \left[\frac{\phi_j^w}{\phi_{js}^w} \right] \tag{7}$$

where ϕ_j^d and ϕ_j^w are the volume fractions of monomer j in monomer droplets and aqueous phases, respectively; ϕ_{js}^w is the volume fraction of monomer j in the aqueous phase at saturation in the absence of other monomers, $\phi_j^p(v)$ and $\phi_p^p(v)$ are the volume fraction of monomer j and polymer in a polymer particle of unswollen volume v , m_{ji} is the ratio of the equivalent number of segments of monomers j and i , v_j is the molar volume of monomer j , σ is the interfacial tension, R is the gas constant, T is the temperature, and χ_{ji} is the interaction parameter. The last term of the right-hand side of eq. (5) accounts for the interfacial free energy. The other terms give the free energy of mixing of monomer and polymer, expressed in terms of the classical Flory–Huggins theory.¹¹

Equation (6) uses the Flory–Huggins lattice theory to calculate the partial free energy of the monomers in the droplets.⁴ In addition, in this equation, the interfacial contribution to the partial free energy of the monomer droplets has been neglected because of the usually large size of the monomer droplets. According to published results,⁵ eq. (7) assumes that Henry’s law holds for the monomer in the water phase. The volume fractions of monomer j in monomer droplets and the aqueous phase are, respectively:

$$\phi_j^d = V_j^d/V_d \quad \text{where } j = A, B \tag{8}$$

$$\phi_j^w = V_j^w/V_w \quad \text{where } j = A, B \tag{9}$$

and where V_j^d and V_j^w are the total volumes of monomer j in monomer droplets and aqueous phase, respectively, V_d is the total volume of the monomer droplets, and V_w is the total volume of the aqueous phase.

A combination of eqs. (4)–(9) yields:

$$V_j^d = \frac{V_j^w V_d}{V_w \phi_{js}^w D_j} \quad \text{where } j = A, B \tag{10}$$

$$\phi_j^p(v) = \frac{V_j^w}{V_w \phi_{js}^w P_j(v)} \quad \text{where } j = A, B \text{ and } v_0 < v < v_1 \tag{11}$$

and where

$$D_j = \exp[(1 - m_{ji})\phi_i^d + \chi_{ji}(\phi_i^d)^2] \quad (12)$$

$$P_j(v) = \exp \left[(1 - m_{ji})\phi_i^p(v) + \phi_p^p(v) + \chi_{ji}(\phi_i^p(v))^2 + \chi_{jp}(\phi_p^p(v))^2 + \phi_i^p(v)\phi_p^p(v)(\chi_{ji} + \chi_{jp} + \chi_{ip}m_{ji}) + \frac{2\sigma v_j(4\pi\phi_p^p(v))^{1/3}}{(3v)^{1/3}RT} \right] \quad (13)$$

The overall material balances are as follows:

$$V_j = V_j^d + V_j^w + V_j^p \quad \text{where } j = A, B \quad (14)$$

$$V_p = V_A^p + V_B^p + V_{pol} \quad (15)$$

$$V_d = V_A^d + V_B^d \quad (16)$$

$$V_w = W + V_A^w + V_B^w \quad (17)$$

where V_j is the total volume of monomer j , V_p is the total volume of the polymer particles, and

$$V_j^p = \int_{v_0}^{v_1} \frac{\phi_j^p(v)vn(v) d(v)}{\phi_p^p(v)} = \frac{V_j^w}{V_w\phi_{js}^w} \int_{v_0}^{v_1} \frac{vn(v)}{\phi_p^p(v)P_j(v)} dv \quad (18)$$

The integral in eq. (18) can be calculated by means of any suitable quadrature formula. Integrals can be accurately calculated by orthogonal collocation.¹² To apply this method, the integral is first written in terms of a normalized variable $x = (v - v_0)/(v_1 - v_0)$, as follows:

$$\int_{v_0}^v \frac{vn(v)}{\phi_p^p(v)P_j(v)} d(v) = (v_1 - v_0) \int_0^1 \frac{[x(v_1 - v_0) + v_0]n(x) dx}{\phi_p^p(x)P_j(x)} \quad (19)$$

In the collocation method, integrals can be calculated with high accuracy via the following summation formula.

$$\int_0^1 \frac{[x(v_1 - v_0) + v_0]n(x) dx}{\phi_p^p(x)P_j(x)} = \sum_{h=1}^{N+2} w_h \frac{[x_h(v_1 - v_0) + v_0]n(x_h)}{\phi_p^p(x_h)P_j(x_h)} \quad (20)$$

which requires the values of the weights w_h and the values of $n(x_h)$, $\phi_p^p(x_h)$, and $P_j(x_h)$ at the $N + 2$ collocation points. The position of the collocation points, that is, the value of x_h , and the values of w_h , depend only on the number of collocation points. Algorithms to calculate both w_h and x_h are presented by Villadsen and Michelsen.¹³

Substitution of eqs. (10), (18), (19), and (20) into eq. (14) yields:

$$V_j = V_j^w \left[\frac{V_d}{V_w\phi_{js}^w D_j} + 1 + \frac{(v_1 - v_0)}{V_w\phi_{js}^w} \sum_{h=1}^{N+2} \frac{w_h[x_h(v_1 - v_0) + v_0]n(x_h)}{\phi_p^p(x_h)P_j(x_h)} \right] \quad (21)$$

ALGORITHM

The algorithm, used to calculate the monomer distribution for a given PSD, and the volumes of the two monomers and water, is as follows:

1. Guess initial values of V_p , V_d , and V_w .
2. Assume

$$\phi_p^p(v) = V_{pol}/V_p \quad (22)$$

$$\phi_A^p(v) = (1 - \phi_p^p(v))V_A/(V_A + V_B) \quad (23)$$

$$\phi_B^p(v) = 1 - \phi_A^p(v) - \phi_p^p(v) \quad (24)$$

$$\phi_A^d = V_A/(V_A + V_B) \quad (25)$$

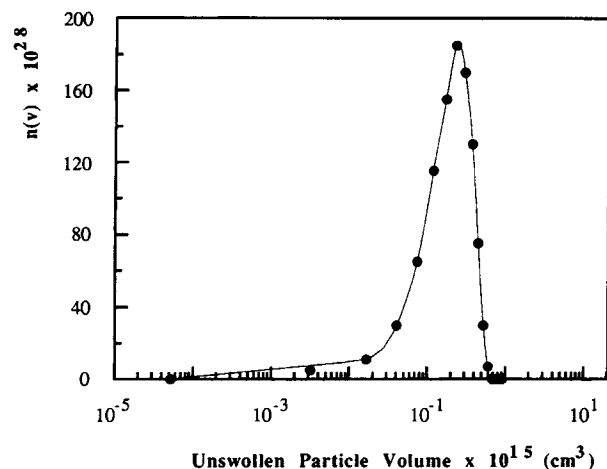
$$\phi_B^d = 1 - \phi_A^d \quad (26)$$

3. Calculate V_A^w and V_B^w using eq. (21).
4. Calculate V_A^d and V_B^d with eq. (10). Then, calculate

$$\phi_A^d = V_A^d/(V_A^d + V_B^d); \quad \phi_B^d = 1 - \phi_A^d \quad (27)$$

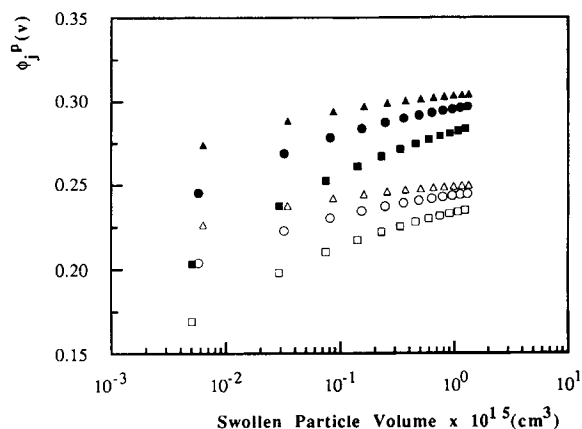
5. Calculate $\phi_j^p(v)$ at the collocation points, using eq. (11), $\phi_p^p(v) = 1 - \phi_A^p(v) - \phi_B^p(v)$, and V_j^p , by means of eq. (18).
6. Calculate V_p , V_d , and V_w (eqs. (15)–(17)).
7. Repeat steps 3–6 until convergence in V_p is reached.

Notice that in step 2, $\phi_p^p(v)$ and $\phi_j^p(v)$ are assumed to be volume independent. This restriction is relaxed in step 5, where they are calculated as a function of the volume. On the other hand, convergence in V_p is the best convergence criterion, be-


Figure 1 Seed latex particle size distribution.

cause convergence in V_d fails when there are no droplets in the system and the amount of monomer in the aqueous phase is too small to significantly change V_w .

In order to validate the algorithm, the swelling of a latex with the PSD, shown in Figure 1, with two monomers was considered. Unswollen latex particle diameters ranged from 20 nm to 100 nm. The number of polymer particles and the total volume of polymer were calculated by means of eqs. (1) and (2): $N_p = 5.89 \times 10^{14}$, and $V_{pol} = 0.158 \text{ cm}^3$. Two different swelling conditions were considered (Table I). In the first, the amount of the two monomers was large enough to have monomer droplets present in the system. In the second, the conditions of the so-called interval III of emulsion polymerization, namely in the absence of monomer droplets, were reproduced, swelling the latex with a small amount of the two monomers. Table I and Figures 2 and 3 present the outputs of the algorithm, calculated using the arbitrary but reasonable values of the parameters presented in Table II. In order to check the algorithm, there is no need that these values correspond to a given monomer system. The necessary condition is that they are similar to those found in different emulsion copolymerization systems.¹⁴⁻¹⁶ The results in Table I and Figures 2 and


Figure 2 Monomer volume fraction distributions for interval II conditions (presence of monomer droplets):

σ (N/m)	Monomer A	Monomer B
6×10^{-3}	▲	△
12×10^{-3}	●	○
24×10^{-3}	■	□

3 were insensitive to the initial guess. Figures 2 and 3 show that, as expected, the volume fraction of the monomers in the polymer particles increased with particle size. The effect is more intense for large interfacial tensions and small particle sizes. This latter effect during polymerization makes small particles grow in volume less than large ones. Also, it can be seen that the algorithm can handle both interval II (presence of monomer droplets) and interval III (absence of monomer droplets) conditions, without any change in the equations of the model. Notice that the volume of the monomer droplets, calculated for the interval III conditions, is 7 orders magnitude lower than the volume of polymer particles and aqueous phase, that is, it is negligible. This is a definitive advantage in the modelling of emulsion copolymerization systems, since otherwise, especially in semicontinuous and continuous emulsion polymerization reactors, the existence of monomer droplets has to be systematically checked.

Table I Simulated Conditions and Outputs of the Algorithm ($\sigma = 12 \times 10^{-3} \text{ N/m}$)

V_{pol} (cm^3)	V_A (cm^3)	V_B (cm^3)	W (cm^3)	V_p (cm^3)	V_d (cm^3)	V_w (cm^3)	ϕ_A^d	ϕ_B^d	ϕ_A^w	ϕ_B^w
0.158	0.316	0.237	0.474	0.340	0.364	0.482	0.576	0.424	1.43×10^{-2}	1.80×10^{-3}
0.158	0.032	0.016	0.474	0.200	3×10^{-8}	0.480	0.649	0.351	0.99×10^{-2}	0.84×10^{-3}

Therefore, this algorithm also offers considerable advantages over existing methods for the calculation of the monomer partitioning in monodisperse systems. Simulations, carried out for different emulsion copolymerization systems considering monodisperse latexes, showed that the computer time was reduced by a factor of 4 when the algorithm used in this article was used. The extension of the algorithm to n -component emulsion polymerization is simple, although the availability of the values of the required parameters is dubious.

CONCLUSIONS

A new algorithm for the calculation of the monomer partitioning in emulsion copolymer systems has been presented, and examples of the application are given. The outputs of the algorithm include the volumes of the monomer swollen polymer particles: monomer droplets and aqueous phase, as well as the volume fractions of the monomer in the aqueous phase and monomer droplets, and the distribution of volume fractions of the monomers in the polymer particles of varying sizes. The outputs of the algorithm are not affected by the initial guess. The algorithm can handle both interval II and interval III conditions without any change in the equations of the model. The algorithm also improves existing methods for

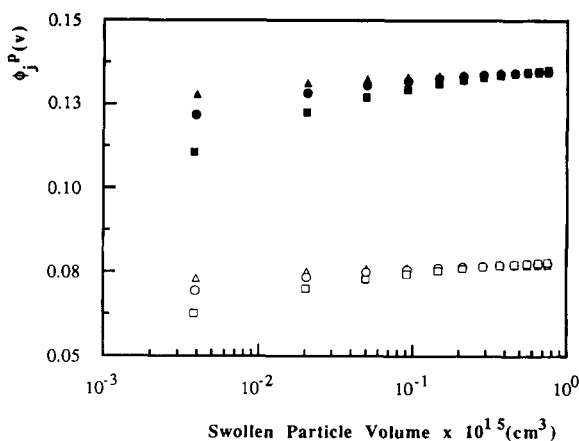


Figure 3 Monomer volume fraction distributions for interval III conditions (absence of monomer droplets):

σ (N/m)	Monomer A	Monomer B
6×10^{-3}	▲	△
12×10^{-3}	●	○
24×10^{-3}	■	□

Table II Values of the Parameters

ϕ_{As}^w, ϕ_{Bs}^w	0.025	3.33×10^{-3}
m_{AB}, m_{BA}	1.19	0.87
χ_{AB}, χ_{AB}	0.4	0.5
χ_{AP}, χ_{AP}	0.35	0.36
v_A, v_B (m ³ /mol)	1×10^{-4}	1.2×10^{-4}
σ (N/m), T (K)	6×10^{-3} – 24×10^{-3}	333

the calculation of the monomer partitioning in monodisperse systems.

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NOMENCLATURE

- A, B Monomers.
 D_j Parameter defined by eq. (12).
 \bar{G}_j^k Partial molar free energy of monomer j in the phase k (J/mol).
 m_{ij} Ratio of the equivalent number of segments of monomers i and j .
 $n(v)$ Number particle size distribution function (cm⁻³).
 N_p Total number of polymer particles.
 $P_j(v)$ Parameter defined by eq. (13).
 R Gas constant (J/mol K).
 T Temperature (K).
 v_j Molar volume of monomer j (m³/mol).
 V_d Total volume of the monomer droplets (cm³).
 V_j^k Volume of monomer j in the phase k (cm³).
 V_j Total volume of monomer j (cm³).
 V_p Total volume of the polymer particles (cm³).
 V_{pol} Total volume of the polymer (cm³).
 V_w Total volume of the aqueous phase (cm³).
 v_0, v_1 Volumes chosen in such a way that the whole PSD is included between them (cm³).
 w_h Weighting factor, produced by the orthogonal collocation method.
 x Normalized volume (–).

SUPERSCRIPTS

- d Monomer droplets phase.
 p Polymer particles phase.
 w Aqueous phase.

GREEK SYMBOLS

ϕ_j^k Volume fraction of monomer j in the phase k
(-).

σ Interfacial tension (N/m).

χ_{ij} Interaction parameter (-).

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