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Prediction of Polymer Composition in Batch Emulsion Copolymerization

LILIAN F. J. NOËL, JAN M. A. M. VAN ZON, IAN A. MAXWELL,* and ANTON L. GERMAN†

Department of Polymer Chemistry and Technology, Eindhoven University of Technology,
5600 MB Eindhoven, The Netherlands

SYNOPSIS

Monomer partitioning in emulsion copolymerization plays a key role in determining composition drift and polymerization rates. The combination of recently developed thermodynamically based monomer partitioning relationships with mass balance equations, makes predictions of monomer partitioning in emulsion copolymerizations possible in terms of monomer mole fractions and monomer concentrations in the particle and aqueous phases. Using this approach, the effects of monomer to water ratios and polymer volumes on the monomer mole fraction within the polymer particle phase in a nonpolymerizing system at thermodynamic equilibrium can be determined. Comparison of these monomer partitioning predictions with experiments for the monomer system methyl acrylate–vinyl acetate shows good agreement. Furthermore, composition drift occurring in a polymerizing system as a function of conversion can be predicted if the assumption is made that equilibrium is maintained during reaction. Comparison of predictions with experimental results for emulsion copolymerizations of the monomer systems methyl acrylate–vinyl acetate and methyl acrylate–indene shows good agreement. © 1994 John Wiley & Sons, Inc.

Keywords: emulsion copolymerization • monomer partitioning • composition drift • modelling

INTRODUCTION

Attempts to model emulsion copolymerization have been made by several investigators.^{1–8} For this purpose, basic theories for emulsion homopolymerization were mathematically extended to emulsion copolymerization. Due to the complexity of the emulsion polymerization process, most data on kinetics have been fitted with empirical models. Based on this, the values of many rate parameters have been fitted. For correct model predictions of emulsion homopolymerization the values for the rate parameters for entry, exit, termination, transfer, and propagation have to be known, in addition to the number of particles. For emulsion copolymerization, finding correct values for rate parameters is even

more complex than in the case of homopolymerizations. The use of emulsion copolymer models also incorporates the knowledge of monomer concentrations in the particle phase, where reaction takes place. For describing monomer partitioning behavior that determines the monomer concentration in the polymer phase, both empirical and a thermodynamic approaches have been proposed in the literature.^{1–8} In the first approach, empirical relationships describing monomer partitioning were developed often based on questionable assumptions, e.g., assuming constant concentrations of monomers in the polymer phase during interval II of emulsion copolymerization⁶ or neglecting the monomer in the aqueous phase.^{1,2} Another empirical approach is the experimental determination of monomer partitioning coefficients^{3,4,5} fitted with empirical relationships. The thermodynamic approach developed by Morton⁹ for emulsion homopolymerizations and later extended to emulsion copolymerizations^{7,8,12} is a very fundamental and promising approach. However, it involves many parameters of which the val-

* Present address: Sydney University Polymer Centre, School of Chemistry F11, University of Sydney, NSW 2006, Australia.

† To whom all correspondence should be addressed.

ues are often not known. Furthermore, the physical significance of the interaction parameters used is rather vague since they often include temperature-dependent enthalpic and temperature-independent entropic effects—parameters that often depend on the polymer concentration. It is of great importance to have (simple) relationships that correctly predict monomer concentrations in the polymer phase since this is the basis of all models for predicting (instead of fitting) copolymer composition and rates of polymerization.

Recently, simplifications of generally accepted thermodynamic relationships,^{9–13} resulting in simple theories, have been developed by Maxwell et al.¹⁴ for saturation swelling and by Noël et al.¹⁵ for partial swelling of particles by two monomers. The use of these new and simple relationships is very convenient since they only require the homo-monomer saturation values of the water solubility and maximum swellability in the polymer phase of the individual monomers to be known. It is very important to realize that the use of these relationships does not involve the use of ambiguous interaction parameters.

Based on these new relationships for monomer partitioning, combined with mass balance equations, monomer mole fractions and absolute concentrations of monomers in the particle and aqueous phases can be calculated. Using this approach the effects of different monomer to water ratio (M/W) and polymer volume (V_{po}) on monomer partitioning in a certain mixture of water, monomer, and polymer can be determined in terms of the mole fraction of monomer i in the polymer particle phase, f_{pi} . In this article results of these experiments are compared with model predictions for the monomer system methyl acrylate–vinyl acetate (MA–VAc). From these nonpolymerizing static experiments, a better understanding of monomer partitioning occurring in emulsion polymerizations can be gained leading to better control of copolymer formed during reactions. The effects of water solubility of the monomers, maximum swellability of the monomers in the polymer, and different monomer feed ratios on monomer partitioning are described herein.

Apart from predicting monomer partitioning under nonpolymerizing conditions, predictions under polymerizing conditions are also possible if the assumption is made that thermodynamic equilibrium in monomer partitioning is maintained during emulsion copolymerization. Although model predictions are compared with experimental results of emulsion copolymerization reactions for only two monomer systems, i.e., methyl acrylate–vinyl acetate

(MA–VAc) and methyl acrylate–indene (MA–Ind), the model in principle encompasses any given monomer pair where polymer swells with the monomer and of which the monomers have a limited water solubility (i.e., monomers that are not miscible with water). For monomer combinations in which the more water soluble monomer is also the more reactive one, the heterogeneity of the emulsion system in theory can be used to minimize composition drift occurring during batch emulsion copolymerization. The unconventional monomer system MA–Ind is chosen because it meets these requirements. Results of these copolymerizations will be briefly discussed herein and will be presented in more detail in a forthcoming study.²⁵

THEORY

In emulsion systems (co)polymerization is assumed to occur mainly within the polymer particle phase. Therefore, predictions of composition drift and/or rates of polymerization can only be performed in a correct manner if the mole fraction of monomer i in the polymer particle phase is known as a function of conversion. Recently, simplifications of existing thermodynamic models describing two monomer partitioning in a polymer latex^{7,11,12} have been described for saturation swelling^{14,16} (intervals I and II) and partial swelling¹⁵ (interval III). Combining these monomer partitioning relationships with mass balance equations enables one to predict the mole fraction of monomer i in the particle phase, f_{pi} , for a certain monomer–water–polymer mixture. The use of these thermodynamically based new relationships in combination with mass balance equations is very convenient since, to determine the mole fraction of monomer i in the polymer phase at a given monomer–water–polymer mixture, it only requires that the homo-monomer saturation values of the individual monomers in both the aqueous and polymer particle phases be known. This makes the above-described approach very useful for predicting monomer mole ratios as well as monomer concentrations in emulsion polymerization systems.

The assumptions made to arrive at the new and simple theory will be presented in this section, resulting in the basic monomer partitioning equations [eqs. (1)–(2b)]. The monomer partitioning relationships resulting from the basic eqs. (1)–(2b) are combined with mass balance equations for saturation and partial swelling in the following sections. The models developed in this way are capable of predicting monomer mole fractions in the polymer

phase for any monomer–water–polymer mixture. Using this approach, extensions to emulsion copolymer compositional predictions as a function of conversion are made assuming that thermodynamic equilibrium in monomer partitioning is maintained during reaction.

Monomer Partitioning in Latex Systems with Two Monomers

The derivation of the simplified models for two monomer partitioning is based on the following three assumptions:^{14–16}

1. For many pairs of monomers, the differences between the molar volumes of the monomers are slight; therefore the ratio of the molar volumes of monomer i and j is approximated by unity.
2. The contribution to the partial molar free energy arising from the mixing of the two monomers is small relative to all other terms in the expression describing the partial molar free energy of monomers in both the droplet and particle phases.
3. The interaction parameters for each monomer with the same polymer are equal.

The use of the three assumptions leads to the following equation:^{14,15}

$$\ln\left(\frac{v_{pi,sat}(r)}{v_{pj,sat}(r)}\right) = \ln\left(\frac{v_{di,sat}(r)}{v_{dj,sat}(r)}\right) \\ = \ln\left(\frac{\frac{[M_i]_a(r)}{[M_i]_{a,sat}(h)}}{\frac{[M_j]_a(r)}{[M_j]_{a,sat}(h)}}\right) \quad (1)$$

where v stands for volume fraction, $[M]$ for concentration (mol/L), the subscripts i, j, p, d , and a , respectively stand for monomer i , monomer j , the polymer phase, the monomer droplet phase, and the aqueous phase; the subscripts $_{sat}(r)$ and $_{sat}(h)$ represent the saturation concentrations at a certain monomer ratio (r) or at homo-monomer saturation swelling (h) (i.e., v_{pi} means the volume fraction of monomer i in the polymer phase).

Using the left-hand side of this equation leads to the following relationships between monomer concentrations in the droplet phase and the particle phase:¹⁴

$$f_{pi,sat} = f_{di,sat} \quad (2a)$$

$$f_{pj,sat} = f_{dj,sat} \quad (2b)$$

where $f_{pi,sat}$, $f_{di,sat}$, $f_{pj,sat}$, and $f_{dj,sat}$ represent, the monomer mole fraction of monomers i and j in the polymer particle and monomer droplet phases, respectively, at saturation swelling. Note that in the particle phase the monomer mole fraction does not include the mole fraction of polymer. Equations (2a)–(b) were shown to hold satisfactorily over a wide range of conditions typical of emulsion polymer systems. In a sensitivity analysis¹⁶ it was shown that, given reasonable values of all interaction parameters and molar volumes of the monomers, the results represented by eqs. (2a)–(b) are almost always correct. Equations (2a)–(b) appear to be insensitive to the validity of assumptions 1–3, i.e., the three assumptions are of algebraic necessity only.

With eq. 1, relationships for saturation and partial swelling can be derived describing monomer partitioning in latex systems with two monomers. However, to predict monomer concentrations in all phases for a given monomer–water–polymer mixture, the monomer mole fraction in the polymer phase must be known. These monomer mole fractions in the polymer phase can be calculated when combining monomer partitioning relationships with mass balance equations. When using this combination, predictions of monomer mole fractions in the polymer phase can be made in nonpolymerizing monomer partitioning experiments. Moreover, this procedure can be extended to model predictions of emulsion copolymer composition and polymerization rate. Since different relationships are valid for saturation and partial swelling, separate model developments are described in the next two sections.

Saturation Swelling of Latex Particles by Two Monomers: Determination of the Mole Fraction of Monomer i in the Polymer Phase

With the result given in eqs. (2a)–(b) and the assumptions that, (1) the total monomer concentration in the latex particles is just equal to the sum of the concentrations of the individual monomers, and (2) the total monomer concentration is a linear function of the fraction of the monomers in the droplet phase, Maxwell et al.¹⁴ developed an empirical description for the concentration of two monomers at saturation swelling within polymer latices. For a particular seed latex the concentration of monomer i within the particles at a certain monomer

ratio, r , $[M_i]_{p,sat}(r)$ as a function of the fraction of monomer i in the droplets is given by:¹⁴

$$[M_i]_{p,sat}(r) = f_{di,sat}([M_i]_{p,sat}(h) - [M_j]_{p,sat}(h))f_{di,sat} + [M_j]_{p,sat}(h) \quad (3a)$$

Similarly, for monomer j :

$$[M_j]_{p,sat}(r) = f_{dj,sat}([M_j]_{p,sat}(h) - [M_i]_{p,sat}(h))f_{dj,sat} + [M_i]_{p,sat}(h) \quad (3b)$$

where $[M_i]_{p,sat}(h)$ and $[M_j]_{p,sat}(h)$ are the maximum swellabilities of monomers i and j in the latex particles at homo-monomer saturation swelling. Note that the monomer mole fraction in the droplets just equals the monomer mole fraction in the polymer particles; thus, in eqs. (3a)–(b) the monomer mole fractions can be replaced by $f_{pi,sat}$ and $f_{pj,sat}$ if required.

For concentrations of monomers i and j in the aqueous phase the following relationships were found:¹⁴

$$[M_i]_{a,sat}(r) = [M_i]_{a,sat}(h)f_{pi,sat} \quad (4a)$$

$$[M_j]_{a,sat}(r) = [M_j]_{a,sat}(h)f_{pj,sat} = [M_j]_{a,sat}(h)(1 - f_{pi,sat}) \quad (4b)$$

Based on eqs. (4a)–(b), the following simple relationships between the mole fraction of monomer i in the polymer phase ($f_{pi,sat}$) and in the aqueous phase ($f_{ai,sat}$) were developed:¹⁵

$$\begin{aligned} f_{ai,sat} &= \frac{[M_i]_{a,sat}(r)}{[M_i]_{a,sat}(r) + [M_j]_{a,sat}(r)} \\ &= \frac{f_{pi,sat}}{f_{pi,sat}(1 - \alpha) + \alpha} \end{aligned} \quad (5a)$$

where α is the ratio of the water solubilities of monomer j over monomer i ($\alpha = [M_j]_{a,sat}(h)/[M_i]_{a,sat}(h)$). The self evident relationship between the monomer mole fractions and the monomer mole ratios ($q_i = [M_i]/[M_j]$) is given by:

$$f_{pi,sat} = \frac{q_{pi,sat}}{q_{pi,sat} + 1} \quad (5b)$$

where $q_{pi,sat}$ is the mole ratio of monomer i over monomer j in the polymer phase at saturation swelling. Using eq. (5b) to rewrite eq. (5a) gives:

$$q_{pi,sat} = q_{ai,sat}\alpha \quad (5c)$$

where $q_{ai,sat}$ is the mole ratio of monomer i over monomer j in the aqueous phase at saturation swelling. The result shown in eq. (5c) is consistent with the right-hand side of eq. (1). Eqs. (5a)–(c) have been shown¹⁵ to be valid for both partial and saturation swelling. In case of partial swelling the subscript sat and the extension (r) should be removed from relationships (5a)–(c).

Using eqs. (4)–(5) enables one to predict monomer partitioning for known mole fractions of monomer i in the polymer phase. However, for model development this mole fraction of monomer i in the polymer phase needs to be predicted for known monomer–water–polymer mixtures. This can be done by taking mass balance equations for monomers i and j at saturation swelling into account. For this reason, the following mass balance equations were formulated and used for the first time in this context:

$$M_{i,t} = [M_i]_{a,sat}(r)V_a + [M_i]_{p,sat}(r)V_p + [M_i]_{d,sat}(r)V_d \quad (6a)$$

$$M_{j,t} = [M_j]_{a,sat}(r)V_a + [M_j]_{p,sat}(r)V_p + [M_j]_{d,sat}(r)V_d \quad (6b)$$

where $M_{i,t}$ and $M_{j,t}$ are the total moles of monomers i and j in the system; V_a , V_p , and V_d are the volumes of the saturated aqueous phase (the volume of water + monomer dissolved in it), the monomer swollen polymer phase (the volume of the polymer + monomer in the saturated polymer), and the monomer droplet phase. Using eq. (2a) and rewriting $f_{di,sat}$ in terms of monomer ratios we find for $[M_j]_d$:

$$[M_j]_{d,sat}(r) = \frac{(1 - f_{pi,sat})}{f_{pi,sat}} [M_i]_{d,sat}(r) \quad (7)$$

Combining eqs. (6a)–(b) and (7) leads to a more simple equation in which the monomer droplet phase does not appear any more. Using this simplified expression together with eqs. (3a)–(b) and (4a)–(b) yields:

$$\begin{aligned} \frac{M_{i,t}}{f_{pi,sat}} - \frac{M_{j,t}}{(1 - f_{pi,sat})} \\ = V_a([M_i]_{a,sat}(h) - [M_j]_{a,sat}(h)) \end{aligned} \quad (8)$$

in which $f_{pi,sat}$ and V_a are the two unknowns.

A second expression of V_a as a function of $f_{pi,sat}$

can be determined from the mass balance equation of the aqueous phase when volume additivity of water and monomer dissolved in the aqueous phase is assumed. This will result in a relationship between V_a (volume of the aqueous phase including monomer) and V_w (volume of the aqueous phase without monomer):

$$V_a = \frac{V_w}{1 - [M_i]_{a,\text{sat}}(r) MW_i / \rho_i - [M_j]_{a,\text{sat}}(r) MW_j / \rho_j} \quad (9)$$

in which MW_i and MW_j are the molecular masses of monomers i and j and ρ_i and ρ_j are the densities of monomers i and j . Using eqs. (4a)–(b) to replace the unknowns $[M_i]_{a,\text{sat}}$ and $[M_j]_{a,\text{sat}}$ by a relationship in $f_{pi,\text{sat}}$ in eq. (9), and thereafter combining eqs. (8) and (9), will lead to a second-order equation in $f_{pi,\text{sat}}$. This can be solved to yield $f_{pi,\text{sat}}$.

Solving the resulting relationship for saturation swelling gives the mole fraction of monomer i in the polymer phase for a certain monomer–water–polymer mixture at saturation swelling. This prediction of monomer partitioning can be used to describe monomer partitioning in interval I and II situations in emulsion copolymerization reactions.

Partial Swelling of Latex Particles by Two Monomers: Determination of the Mole Fraction of Monomer i in the Polymer Phase

At partial swelling there is no droplet phase present so the middle expression in eq. (1) is redundant, resulting in the following equality:

$$\frac{v_{pi}}{v_{pj}} = \frac{[M_i]_a [M_j]_{a,\text{sat}}(h)}{[M_j]_a [M_i]_{a,\text{sat}}(h)} \quad (10)$$

Note that below saturation the subscript $\text{sat}(r)$ is removed. Rewriting eq. (10) in terms of monomer mole ratios will give similar relationships to eqs. (5a) and (5c). As stated before it can be concluded from this that eqs. (5a)–(c) hold for both saturation and partial swelling of latex particles by two monomers with limited water solubility. Furthermore it has been shown¹⁵ that at equilibrium and at a certain monomer ratio, r , the monomer concentrations of both monomers in the aqueous phase and also in the polymer phase are equally far away from saturation values at that ratio. For the aqueous phase this leads to:

$$\frac{[M_i]_a}{[M_i]_{a,\text{sat}}(r)} = \frac{[M_j]_a}{[M_j]_{a,\text{sat}}(r)} = \% \text{ sat } a \quad (11)$$

and for the polymer phase:

$$\frac{[M_i]_p}{[M_i]_{p,\text{sat}}(r)} = \frac{[M_j]_p}{[M_j]_{p,\text{sat}}(r)} = \% \text{ sat } p \quad (12)$$

where the degree of saturation of the aqueous and polymer phases is expressed by $\% \text{ sat } a$ and $\% \text{ sat } p$, respectively.

The relationship between monomer i in the polymer and aqueous phase is given by:¹⁵

$$\ln v_{pi} + v_p + \text{corr}_i(r) = \ln \frac{[M_i]_a}{[M_i]_{a,\text{sat}}(r)} \quad (13a)$$

where the correction term, $\text{corr}_i(r)$, for monomer i at a certain monomer mole ratio, r , accounts for both nonconfigurational entropy and enthalpy terms. It has been shown that this is well approximated by:

$$\text{corr}_i(r) = -[\ln v_{pi,\text{sat}}(r) + v_{p,\text{sat}}(r)] \quad (13b)$$

Using eqs. (10)–(13b) allows one to predict monomer partitioning for known mole fractions of monomer i in the polymer phase. However, for model development this mole fraction of monomer i in the polymer phase needs to be predicted for known monomer–water–polymer mixtures. This again can be done by taking mass balance equations for monomers i and j at partial swelling into account. For this reason the mass balance eqs. (6a)–(b) were reduced to (14a)–(b):

$$M_{i,t} = [M_i]_a V_a + [M_i]_p V_p \quad (14a)$$

$$M_{j,t} = [M_j]_a V_a + [M_j]_p V_p \quad (14b)$$

Note that in the following model development for partial swelling the monomer ratio (q_{pi}) replaces the monomer mole fraction (f_{pi}) of monomer i in the polymer phase. With eq. (5b), a direct relationship between the monomer ratio and fraction is given. From eqs. (14a)–(b) and (5b), we find for $[M_i]_a$ and $[M_j]_a$:

$$[M_i]_a = \frac{M_{i,t} - M_{j,t} q_{pi}}{V_a (1 - \alpha)} \quad (15a)$$

$$[M_j]_a = [M_i]_a \alpha / q_{pi} \quad (15b)$$

and for $[M_i]_p$ and $[M_j]_p$:

$$[M_i]_p = \frac{\alpha M_{i,t} - M_{j,t} q_{pi}}{V_p(\alpha - 1)} \quad (16a)$$

$$[M_j]_p = [M_i]_p / q_{pi} \quad (16b)$$

Assuming volume additivity of water and monomers dissolved in the aqueous phase the volume of the aqueous phase V_a (water + monomers), can be calculated with a mass balance equation similar to eq. (9):

$$V_a = \frac{V_w}{1 - [M_i]_a MW_i / \rho_i - [M_j]_a MW_j / \rho_j} \quad (17)$$

The volume of the swollen polymer phase can be calculated by a mass balance equation of the polymer phase assuming volume additivity of polymer and monomer located in the polymer phase:

$$V_p = \frac{V_{po}}{1 - [M_i]_p MW_i / \rho_i - [M_j]_p MW_j / \rho_j} \quad (18)$$

where V_{po} is the volume of the polymer in the polymer phase (i.e., without monomer). Combining eqs. (15a)–(b) and (17) results in a relationship for V_a (the volume of the aqueous phase + monomer dissolved in it) with q_{pi} as the only unknown parameter. A similar relationship in q_{pj} can be found for V_p when combining eqs. (16a)–(b) with eq. (18). With known monomer mole ratio in the polymer phase, the volume of the aqueous phase including dissolved monomer (V_a) and the swollen volume of the polymer phase (V_p) can be calculated. Using eqs. (3a)–(b) and (4a)–(b) gives the aqueous and polymer phase monomer concentrations at saturation at that monomer mole ratio, r (i.e., $[M_i]_{a,sat}(r)$, $[M_j]_{a,sat}(r)$, $[M_i]_{p,sat}(r)$, and $[M_j]_{p,sat}(r)$). Using the values for V_a and V_p , $[M_i]_a$ and $[M_i]_p$ the degree of saturation in the aqueous (% sat a) and polymer (% sat p) phases can be calculated using eqs. (15a), (16a), and (11)–(12).

Combining eqs. (11), (12), (13a)–(b), and knowing that $v_{pi}/v_{pi,sat}(r)$ equals $[M_i]_p/[M_i]_{p,sat}(r)$ we find:

$$\ln\left(\frac{\% \text{ sat } p}{\% \text{ sat } a}\right) = v_{p,sat}(r) - v_p \quad (19)$$

Knowing that $v_p = 1 - v_{pi} - v_{pj}$, $v_{pi} = [M_i]_p MW_i /$

ρ_i , $v_{pj} = [M_j]_p MW_j / \rho_j$ and combining eqs. (16b) and (19) yields:

$$q_{pi,calc} = \frac{\rho_i \rho_j q_{pi} \ln\left(\frac{\% \text{ sat } p}{\% \text{ sat } a}\right)}{MW_i \rho_j ([M_i]_p - [M_i]_{p,sat}(r))} - \frac{MW_j \rho_i}{MW_i \rho_j} \quad (20)$$

where $q_{pi,calc}$ stands for the calculated mole ratio of monomer i in the polymer phase at partial swelling. With known q_{pi} (or f_{pi}) the right-hand term of eq. (20) can be calculated resulting in $q_{pi,calc}$. Continued iteration until $\text{abs}(q_{pi} - q_{pi,calc})$ reaches a small tolerance value gives the correct mole ratio of monomer i in the polymer phase.

Based on the model for partial swelling presented in this section the mole fraction of monomer i in the polymer phase can be calculated for a certain monomer–water–polymer mixture. This prediction of monomer partitioning can be used to describe monomer partitioning at partial swelling, i.e., in interval III situations in emulsion copolymerization reactions.

Model Calculations in Emulsion Copolymerization

Since polymerization in emulsions is assumed to occur in the polymer particle phase, the monomer mole fraction in the polymer phase, f_{pi} , has to be used instead of the overall monomer mole fraction ($f_{oi} = M_{it}/(M_{it} + M_{jt})$) to calculate the instantaneous copolymer composition. In the previous two sections, models have been developed to predict the monomer mole fraction in the polymer phase for a given monomer–water–polymer mixture at both saturation and partial swelling. Using the models for saturation and partial swelling a program has been written to predict the course of emulsion copolymerization (available upon request; the program is in Fortran 77). A flow diagram of this program is presented in Figure 1 where the conversion is represented by x . Based on the homo-monomer saturation values of monomers i and j in the polymer ($[M_i]_{p,sat}(h)$, $[M_j]_{p,sat}(h)$) and aqueous ($[M_i]_{a,sat}(h)$, $[M_j]_{a,sat}(h)$) phases it can be determined in a quite straightforward way whether the model for saturation or partial swelling should be applied to a given monomer–water–polymer mixture (V_a , V_p , M_{it} , and M_{jt}). From these water solubility and maximum polymer swellability values combined with recipe conditions, the monomer mole fractions

Figure 1. Flow diagram of the program used for predictions of emulsion copolymerization. Tol stands for a small tolerance value, C1 and C2 are constants, x is conversion, and $q_{pi,i-1}$, $q_{pi,in}$ and $q_{pi,calc}$ are the mole ratios of monomer i at the end of saturation swelling, and the start value and resulting value of consecutive conversions steps at partial swelling, respectively.

can be calculated using eqs. (3)–(9) in the case of saturation swelling, and eqs. (10)–(20) and repeated iteration in the case of partial swelling. Using the

instantaneous copolymerization equation^{17,18} [eq. (21)] will give the copolymer composition in mole fraction of monomer i (F_i) as a function of the reac-

tivity ratios and the mole fraction of monomer i in the polymer particle phase (f_{pi}):

$$F_i = \frac{r_i f_{pi}^2 + f_{pi} f_{pj}}{r_i f_{pi}^2 + 2 f_{pi} f_{pj} + r_j f_{pj}^2} \quad (21)$$

Assuming that monomer partitioning equilibrium is maintained despite polymerization, complete emulsion polymerization can be predicted in the following manner, provided that small successive conversion steps are taken until complete conversion. The conversion steps taken need to be small enough to ensure a nearly constant mole fraction of monomer i in the polymer, and as a consequence an also almost constant copolymer composition during this conversion step. As a result of polymerization the total monomer (M_{it} , M_{jt}) and polymer (V_{po}) quantities will change slightly during each conversion step. The monomer mole fraction in the polymer phase at the next small conversion step can then be calculated with slightly different monomer and polymer concentrations, again using eqs. (3)–(9) for saturation swelling and eqs. (10)–(20) for partial swelling. Based on this approach, prediction is possible of inter alia, f_{pi} , F_i , $[M_i]_a$ and $[M_i]_p$ as a function of conversion.

The use of the models presented herein for saturation swelling and partial swelling only require that the homo-monomer saturation values in the polymer phase and aqueous phase are known for a given monomer–water–polymer mixture. Predictions of monomer partitioning experiments for a given monomer–water–polymer mixture in terms of mole fraction of monomer i in the polymer phase and based on this predictions of complete emulsion copolymerizations as a function of conversion now can be made quite easily.

EXPERIMENTAL

Materials

The following materials were used in the emulsion copolymerization reactions: reagent-grade methyl acrylate (MA, Janssen Chimica, Tilburg, The Netherlands), vinyl acetate (VAc, Janssen Chimica, Tilburg, The Netherlands) and indene, tech., 90+ % (Ind, Janssen Chimica, Tilburg, The Netherlands), doubly distilled water, sodium persulfate (p.a., Fluka AG, Buchs, Switzerland) as initiator, sodium dodecyl sulfate (SDS, Fluka AG, Buchs, Switzerland) and antrox CO-990 (ANT CO-990, GAF, Delft, The Netherlands) as surfactant, and

sodium carbonate (p.a., Merck, Darmstadt, Germany) as buffer. Before use, the MA and VAc were distilled under reduced pressure to remove inhibitor. The middle fraction was cut and stored at 4°C. The indene was purified by shaking 0.5 L indene with 0.4 L, 6M HCL for 24 h to remove basic nitrogenous material, then refluxed with 40% NaOH for 2 h to remove benzonitrile. Extraction by *n*-hexane was followed by washing with water (three times), drying with MgSO₄ and evaporation of the *n*-hexane. Fractionized distillation under reduced pressure is repeated until gas chromatography showed that indene fractions with purities higher than 98% were obtained. Gas chromatography in combination with mass spectroscopy (GC-MS) showed that the amount of polymerizable impurities were negligible (undecene concentration < 0.03 %). From this, it was concluded that the indene could be used without further purification. The indene is stored under argon at 4°C. To prevent polymerization during monomer partitioning experiments MA and VAc were applied as received without any further purification and some inhibitor (hydroquinone) was added to the indene after purification.

Emulsion Polymerization Reactions

Emulsion polymerizations were performed in a 1.3 L stainless-steel reactor fitted with four baffles at 90° intervals and a six-bladed turbine impeller. The emulsion polymerization recipes of both seed latex preparation on behalf of monomer partitioning experiments, and of reactions performed to compare the developed model with experiments are given in Table I for the MA–VAc monomer system and in Table II for the MA–Ind monomer system.

All MA–VAc reactions including the seed preparation took place under nitrogen at 50°C for 8 h. After the seed preparation the temperature was

Table I. MA–VAc Recipes (in grams) for Seed Latex Preparation for Monomer Partitioning Experiments and a Kinetic Polymerization with a Monomer to Water Ratio (M/W) of 0.1

Ingredient	Seed	Kinetic Run
MA	80	45
VAc	80	45
Water	800	917.4
NaPS	0.256	0.219
SDS	1.317	1.313
Na ₂ CO ₃	0.141	0.098

Table II. MA–Ind Recipes (in grams) for Seed Latex Preparation for Monomer Partitioning Experiments and Kinetic Runs with Different Monomer to Water Ratios (M/W)

Ingredient	Seed	Kinetic Runs		
		M/W = 0.4	M/W = 0.3	M/W = 0.1
MA	25.68	165.47	144.87	62.09
Ind	34.53	74.41	64.46	27.83
Water	599.1	600.1	700.3	898.8
NaPS	3.534	3.759	4.177	5.329
ANT CO-990	20.806	20.651	24.258	31.306
Na ₂ CO ₃	0.660	0.643	0.736	0.956

raised to 80°C for 15 h to reach high conversion and to dissociate the remainder of the initiator.

The MA–Ind polymerizations were performed under nitrogen pressure at 70°C for 12 h. In the MA–Ind polymerization, high initiator concentrations were needed to give reasonable polymerization rates, resulting in colloiddally unstable latices due to high electrolyte concentrations. The use of the non-ionic ANT CO-990 instead of SDS resulted in more colloiddally stable latices. All reactions performed to compare the developed model with experiments were followed by gravimetry to obtain conversion time curves and by gas chromatography to determine the overall monomer ratios as a function of time. Combining these data yields the overall conversion of both monomers.

Before using the poly(methyl acrylate–vinyl acetate) and poly(methyl acrylate–indene) seed latices in monomer partitioning experiments, the latices were dialyzed in membrane tubes to remove excess surfactant, initiator, oligomers, buffer, and monomer. The dialysis water was changed every 2 h until the conductivity of the water surrounding the membrane tube remained constant in time at a value close to the value for distilled water. After this, the solids content was determined by gravimetry (solids content MA–VAc = 16.5 wt %, MA–Ind = 10.4 wt %), the mole fraction of monomer MA in the polymer (F_{MA}) was determined by ¹H-NMR (F_{MA} = 0.50 for both latices) and the weight average particle diameter was determined using dynamic light scattering (weight-average particle diameter, MA–VAc = d_w = 90 nm, MA–Ind = d_w = 30 nm).

Monomer Partitioning

Static monomer partitioning experiments were performed for the monomer system MA–VAc and for Ind using the ultracentrifuge method.^{14,15,19} A latex

with known solids content was mixed with known amounts of MA and/or VAc or Ind at room temperature in the absence of initiator. Equilibrium was reached within 24 h of shaking. The different phases, two in partial swelling and three in saturation swelling, were separated using an ultracentrifuge (45000 rpm Centrikon T-2060, 1–2 h) at room temperature. The concentrations of MA, VAc, and Ind in the aqueous phase were determined by gas chromatography (GC) using 2-propanol as internal standard for MA and VAc and acetone as internal standard for Ind. Assuming that (1) the volumes of monomer and polymer are additive^{20–22} and (2) that the copolymer density is the average of the homopolymer densities,²² the monomer content in the polymer particles was determined by mass balance for partial swelling.^{14,15,19} At saturation swelling a separate droplet phase prevents determination of the monomer content in the polymer particles by mass balance. Monomer concentrations in the particles were then determined by GC after dissolving the monomer swollen polymer phase in toluene with 2-propanol as internal standard. Determination of the dry solids content of the sample gave the polymer content which was needed to make corrections for the amount of aqueous phase within the polymer phase. The monomer droplet phase was analyzed by GC in terms of monomer ratios. Due to temperature limitations of the ultra centrifuge, the ultra-centrifugation method could not be used above 45°C. The maximum water solubilities at temperatures higher than 45°C were determined using a densitometer for MA and VAc,²⁵ and using gas chromatography for Ind. The Ind concentration at 70°C in the aqueous phase was determined by taking a sample from the saturated aqueous phase of a thermostated water–indene mixture at equilibrium with complete phase separation, using an acetone solution as internal standard. The maximum swellabilities

Table III. Homo-Monomer Saturation Concentrations for MA, VAc, and Ind Determined at Several Temperatures

Conditions	$[M_{ij}]_{x,\text{sat}}(h)$ (mol/L)		
	MA	VAc	Ind
20°C, aqueous phase	0.60 ^a	0.30 ^a	0.0028 ^a
50°C, aqueous phase	0.55 ^b	0.28 ^b	—
70°C, aqueous phase	0.53 ^b	—	0.0028 ^c
20°C, polymer phase	7.1 ^a	6.1 ^a	2.9 ^a

^a Determined by the ultra-centrifugation method.^b Determined by densimetry.^c Determined by gas chromatography from the saturated aqueous phase of a water-indene mixture at 70°C using acetone as internal standard.

in the polymer phase ($[M_{ij}]_{p,\text{sat}}(h)$) and the maximum concentration of monomers in the aqueous phase at homo-saturation swelling ($[M_{ij}]_{a,\text{sat}}(h)$) at 20°C are listed in Table III.

RESULTS AND DISCUSSION

Monomer partitioning in latex systems at partial swelling with one or two monomers can be described by eq. (19) as can be concluded from Figure 2 where monomer partitioning predictions are successfully compared with experimental results for homo-MA and MA-VAc combinations if the experimental er-

ror resulting from gas chromatography is taken into account. Furthermore, from Figure 2, it can be concluded that at partial swelling the aqueous phase is closer to saturation than the polymer phase, i.e., % sat $a >$ % sat p . Thus, for monomers with a relatively high but limited water solubility, a considerable amount of the monomer can be located in the aqueous phase. Note that the curvature of lines predicted with eq. (19) depends upon the volume fraction of polymer at saturation swelling and therefore also on the maximum swellabilities of monomer in polymer. However, the difference in volume fraction of polymer at saturation swelling for homo-monomer swelling of MA compared with VAc is relatively small (0.37 for MA and 0.44 for VAc), and therefore all monomer partitioning results for homo-monomer as well as for co-monomer experiments can be compared with one theoretical line.

General Monomer Partitioning Considerations

In this article monomer i has been chosen to be the monomer with the higher water solubility. Adding more water to a certain monomer-water-polymer mixture will especially withdraw monomer i from the polymer phase into the aqueous phase leading to lower values of the mole fraction of monomer i in the polymer phase. In general, this means that by choosing a monomer to water ratio or polymer volume one is able to control the monomer composition in the polymer particle phase. This is the main issue in the following section.

Figure 2. Comparison of the predictions of eq. 19 (---) with experiments for homo-saturation of ($\square$) MA, and two monomer (MA-VAc) experiments at several overall monomer fractions for (Δ) MA and ($\circ$) VAc.

Two extreme monomer partitioning situations may occur in emulsion polymerization resulting in a maximum and a minimum value for the mole fraction of monomer i in the polymer particle phase.

The maximum value of the mole fraction of monomer i in the polymer phase is reached if all monomer is located in the monomer droplet and polymer particle phase. In this case, the mole fraction of monomer i in the polymer phase equals the overall mole fraction of monomer i , i.e., $f_{pi,max} = f_{oi}$. This will occur at saturation swelling when the amount of monomer dissolved in the aqueous phase is negligible as compared with the total amount of monomer (large monomer droplet and polymer particle phases as compared with aqueous phase) or if the water phase concentration is too low to significantly affect the monomer amounts within the monomer droplet and polymer particle phases.

The minimum value for the mole fraction of monomer i in the polymer particle phase is reached when all monomer is dissolved in the aqueous phase. In this case the mole fraction of monomer i in the aqueous phase equals the overall mole fraction of this monomer, $f_{ai} = f_{oi}$. From this mole fraction of monomer i in the aqueous phase, the minimum mole fraction of monomer i within a hypothetical polymer phase, $f_{pi,min}$, can be determined with eqs. (5a)–(c) if the ratio of the water solubilities of monomer j over monomer i , i.e., if $\alpha = [M_j]_{a,sat}(h)/[M_i]_{a,sat}(h)$ is known. In the absence of polymer the minimum

mole fraction of monomer i in the polymer phase is only a hypothetical quantity. However, if there would be a small amount of polymer in the monomer–water–polymer mixture, with a negligible effect on monomer partitioning, the mole fraction in the polymer phase would be very close to the hypothetical minimum mole fraction. The value of $f_{pi,min}$ strongly depends upon the α -value as can be seen in Figure 3 where it is clearly shown that the difference between $f_{pi,max}$ and $f_{pi,min}$ is larger for smaller α -values. This $f_{pi,min}$ can be reached only if the monomers have high water solubilities, if the monomer to water ratio is low and if the amount of polymer phase is too small to affect monomer partitioning.

For a nonpolymerizing monomer partitioning experiment with an arbitrary monomer–water–polymer mixture, the value of the mole fraction of monomer i in the polymer phase can be calculated using the relationships presented in the "Theory" section for saturation or partial swelling. Depending on mixture conditions, e.g., monomer to water ratio (M/W) and the polymer volumes (V_{po}), the value for the mole fraction of monomer i in the polymer phase will vary between $f_{pi,max}$ and $f_{pi,min}$. From Figure 3, we can conclude that the effect of different monomer–water–polymer mixture conditions on monomer partitioning is the largest for small values of α . Furthermore, in Figure 3 the effect of overall monomer mole feed fractions (f_{oi}), on $f_{pi,max}$, and $f_{pi,min}$

Figure 3. The extreme values of the mole fraction of monomer i in the polymer phase (f_{pi}) is given by the maximum (—) $f_{pi,max}$ (all monomers in the polymer particle and monomer droplet phases), and the minimum, $f_{pi,min}$ (all monomers in the aqueous phase) monomer mole fraction in the polymer phase for several values of $\alpha = [M_j]_{a,sat}(h)/[M_i]_{a,sat}(h)$. $\alpha =$ (---) 0.5, (— · —) 0.267 (---) 0.005.

and the maximum difference between this maximum and minimum value for the mole fraction of monomer i in the polymer phase, i.e., $f_{pi,max} - f_{pi,min}$, can be seen. Note that if $\alpha = 1$ there will be no effect of different monomer to water ratios and polymer volumes on the mole fraction of monomer i in the polymer phase, i.e., $f_{pi,max} = f_{pi,min}$. However, if $\alpha \neq 1$, and if the monomer amount is kept constant, the volume of the droplet phase will decrease with increasing water amount (i.e., decreasing monomer to water ratio) or increasing polymer volume at saturation swelling. At partial swelling the absolute concentrations of monomers in both the polymer particle and aqueous phase will decrease with increasing water amount (decreasing monomer to water ratio) and increasing polymer volume due to dilution effects.

Monomer Partitioning of Methyl Acrylate-Vinyl Acetate Monomer Systems

The effect of different monomer-water-polymer mixture conditions, e.g., the monomer to water ratio and the polymer volume, upon the monomer mole fractions in the polymer phase can be predicted by the models developed herein. In the MA-VAc monomer system, MA will be the monomer with (only slightly) higher water solubility resulting in a ratio of water solubilities of VAc over MA of $\alpha = 0.5$. The extreme values of the monomer mole fractions in the polymer phase for MA-VAc with

an overall monomer mole fraction of MA equal to 0.5, are $f_{pi,max} = 0.5$ and $f_{pi,min} = 0.333$ as can be seen in Figure 3. For the MA-VAc monomer system the effect of increasing monomer to water ratio in the absence and presence of polymer at an overall monomer feed fraction of 0.5 was investigated.

If there is no polymer phase present at an overall monomer mole fraction of 0.5 and if the aqueous phase is kept constant at a volume of $V_w = 1$ L, the effect of different monomer to water ratios on the mole fraction of MA in the hypothetical polymer phase is the largest, i.e., going from the hypothetical minimum monomer mole fraction at low monomer to water ratios ($f_{pMA,min} = 0.33$) to the maximum monomer mole fraction at high monomer to water ratios ($f_{pMA,max} = 0.5$), as shown in Figure 4.

At similar overall monomer mole fractions of 0.5, in the presence of polymer with a volume of V_{po} that can swell with MA and VAc, the minimum value for the mole fraction of MA in the polymer phase, $f_{pMA} = 0.33$, will not be reached at similar values for the aqueous phase volume (V_w) and the monomer to water ratio, due to monomer partitioning between the polymer and aqueous phase. In Figure 5 ($V_w = 1$ L, $V_{po} = 0.05$ L, changing M/W) one can see that in the presence of a polymer with volume $V_{po} = 0.05$ L, the lowest value for the monomer mole fraction of MA in the polymer phase is indeed higher than $f_{pMA,min} = 0.33$. The presence of polymer makes the maximum difference in mole fraction of MA in the

Figure 4. Predictions for saturation and partial swelling of the mole fraction of MA in the polymer phase (f_{pMA}) as a function of the monomer to water ratio (M/W) for the monomer combination MA-VAc at an overall monomer mole fraction of $f_{oMA} = 0.5$ in the absence of polymer.

Figure 5. Comparison of (---) predictions with (Δ) experimental values of the mole fraction of MA in the polymer phase (f_{pMA}) for partial and saturation swelling as a function of the monomer to water ratio (M/W) for the MA-VAc monomer combination at overall fractions of MA of $f_{oMA} = 0.5$, in the presence of polymer with a volume of 50 mL polymer/L water.

polymer phase ($f_{pi,max} - f_{pi,min}$) smaller. Furthermore, the saturation swelling region will start at higher monomer to water ratios (Fig. 4 as compared with Fig. 5) in the presence of polymer.

The effects of different monomer–water–polymer mixtures, i.e., different monomer to water ratios and polymer volumes, on the monomer mole fraction in the polymer phase, are based on withdrawing monomer from the monomer droplet and polymer particle phase into the aqueous phase. Therefore, changing these monomer–water–polymer mixture conditions will have the largest effect on the monomer mole fraction in the polymer if only one of the monomers has a relatively high but limited homo-monomer saturation concentration in the aqueous phase. For monomer systems in which monomer i is the more

water-soluble monomer, the effects of increasing monomer (at constant volumes of polymer and water), polymer (at constant volumes of water and monomer) and water (at constant volumes of monomer and polymer) volumes on the mole fraction of monomer i in the polymer phase at constant overall monomer mole fractions are combined in Table IV. The increasing, decreasing, or constant mole fraction of monomer i in the polymer phase as a result of different water (V_w), polymer (V_{po}), and monomer (M_{it} and M_{jt}) are represented in Table IV by +, –, and 0 respectively. It is trivial that increasing the volume of the aqueous phase at partial swelling in the absence of polymer in the monomer–water–polymer mixture will have no effect on the, in this case hypothetical mole fraction of monomer i

Table IV. The Effects of Increasing Water, Polymer, or Monomer Volumes at Constant Overall Monomer Mole Fraction on the Monomer Mole Fraction of the More Water-Soluble Monomer i in the Polymer Phase^a

Constant f_{oi} at Increasing Volume of:	Saturation Swelling, $f_{pi,sat}$	Partial Swelling, f_{pi}
Water: V_w	–	–/0
Monomer: M_{it} , M_{jt}	+	+
Polymer: V_{po}	0	+

^a (–) decreases, (+) increases, (0) no effect.

in the polymer phase (see also Fig. 4), while in the presence of polymer a decrease in the mole fraction of monomer i in the polymer phase will appear for an increased volume of the aqueous phase (see also Fig. 5). Furthermore, in Table IV it is shown that increasing the polymer volume at saturation swelling will lead to more saturated polymer phase and a smaller volume of monomer droplet phase leaving the mole fraction of monomer i in the polymer phase unaffected. However, one should realize that, starting at saturation swelling, a large increase in polymer volume will lead to a shift from saturation towards partial swelling resulting in a constant mole fraction of monomer i in the polymer phase at saturation swelling followed by an increase in mole fraction of monomer i in the polymer phase at partial swelling. Using the results represented in Table IV one can predict all effects on mole fraction of monomer i in the polymer phase of different monomer, polymer, and water volumes and combinations of these quantities such as monomer to water ratios at constant overall monomer mole fractions. Knowing whether the mole fraction of monomer i in the polymer phase will increase or decrease, predictions of monomer concentrations in the polymer phase and aqueous phase can be made using eqs. (3a)–(b) and (4a)–(b) at saturation swelling and (15a)–(b) and (16a)–(b) at partial swelling.

The models developed in this article for saturation and partial swelling are compared with experimental monomer partitioning results for MA–VAc in Figure 5. From good agreement between predictions and experiments, it can be concluded that the models are capable of correctly predicting monomer mole fractions in the polymer phase for static monomer partitioning experiments including a certain polymer volume.

Previous work^{14,15} showed that the monomer mole fraction is equal in the polymer and monomer droplet phase, $f_{pi,sat} = f_{di,sat}$. The maximum swellability of monomer in the polymer is determined by an equilibrium between the interfacial tension and the mixing of monomer with polymer. Nomura et al.²³ found that the maximum swellabilities were independent of copolymer composition for MMA–Sty. However, Maxwell et al.¹⁴ and van Doremaele et al.⁴ showed that copolymer composition does have an effect on the homo-monomer swellabilities of monomer in the polymer phase for MA–Sty. Van Doremaele⁴ concludes, however, that this small effect of copolymer composition on homo-monomer saturation values is negligible in practical simulations. Furthermore, Maxwell et al.¹⁹ pointed out that temperature effects upon monomer partitioning are

within experimental error for MA–Sty in the temperature range from 20 to 45°C. However, it is known that water phase concentrations of monomers are temperature dependent. From model predictions and theory it can be concluded that at partial swelling the water solubilities (i.e., homo-monomer saturation concentrations in the aqueous phase), the ratio of the water solubilities of both monomers (α -value), the maximum swellabilities in the polymer phase (homo-monomer saturation concentrations in the polymer phase) of monomers i and j , and the presence and volume of polymer, will effect the monomer mole fraction in the particle phase. The point where saturation swelling should be used instead of partial swelling depends on the same parameters—namely the water solubilities, the maximum swellabilities, and the polymer volume. At saturation swelling, the water solubility of the monomers and the ratio of these water solubilities (α -value) affect the monomer mole fraction in the polymer phase while the maximum swellabilities of monomer in the polymer phase will only affect the absolute concentrations of monomers i and j in the polymer phase and the volume of the monomer droplet phase, leaving the monomer mole fraction in the polymer phase unchanged. Since equal monomer mole fractions are found in the monomer droplet and polymer particle phase at saturation swelling, i.e., $f_{pi} = f_{di}$, the use of polymer volume in the case of saturation swelling only affects the volume of the polymer and the monomer droplet phases and certainly not the monomer mole fraction in the polymer phase. This result, already represented in Table IV is also illustrated by the similarity between Figures 4 and 5 at saturation swelling. In other words, at saturation swelling one can control monomer composition by changing the monomer to water ratio but not by changing the polymer volume.

Prediction of Emulsion Copolymerizations Composition

To predict the course of emulsion polymerizations using the models for saturation and partial swelling presented herein, the homo-monomer saturation values in the polymer and aqueous phase and the reactivity ratios for the chosen monomer system must be known. For the MA–VAc monomer combination, the reactivity ratios can be found in the literature²⁴ ($r_{MA} = 6.3 \pm 0.4$, $r_{VAc} = 0.031 \pm 0.006$). For less known monomer systems as MA–Ind, the reactivity ratios were determined by low conversion bulk polymerizations ($r_{MA} = 0.92 \pm 0.16$ and $r_{ind} = 0.086 \pm 0.025$). More detailed results of the de-

termination of these reactivity values can be found elsewhere.²⁵ The homo-monomer saturation values in the polymer and aqueous phase are listed in Table III. In predictions of complete emulsion copolymerization reactions, it is important to have accurate data on homo-monomer saturation data and reactivity ratios since the calculations are sensitive to the values of the homo-monomer saturation values and reactivity ratios. Typical confidence intervals for homo-monomer saturation swelling are in the range of 5% accuracy, while the accuracy in reactivity values strongly depends on the calculation method used²⁶ in combination with the number of experiments, and also on the accuracy of the experimental method used.

For reactions with high monomer to water ratios starting in interval II, the homo-monomer saturation concentrations in the polymer phase only affect the absolute monomer concentrations in the polymer phase leaving the monomer mole fraction in the polymer phase ($f_{pi,sat}$) unaffected. The large effect of the α -value can be taken into account when using homo-monomer saturation values in the aqueous phase determined at reaction temperature (values are listed in Table III). Predictions of the course of emulsion polymerization in terms of monomer mole fractions in the polymer phase as a function of conversion, or numbers of mole of monomers i and j as a function of conversion result in important composition drift data. Since gas chromatography of reaction samples will give overall values of the mono-

mer mole fraction of monomer i , experimental values for this overall monomer mole fraction as a function of conversion will be compared with model predictions.

Emulsion Copolymerization of Methyl Acrylate-Vinyl Acetate

For the MA-VAc monomer system, experimental and predicted results of the overall monomer mole fraction as a function of conversion are compared in Figure 6 (initial reaction recipe is shown in Table I). As can be seen by the strong decrease in the overall monomer mole fraction with increasing conversion, there is strong composition drift. This could be expected since the reactivity values in MA-VAc copolymerizations are very far apart (by a factor of 200). Gas chromatography yields, as well as the overall monomer mole fractions, the total moles in the reaction mixture, i.e., $M_{MA,t}$ and $M_{VAc,t}$, as a function of conversion. The number of moles as a function of conversion are presented in Figure 7. Again a strong composition drift occurs leading to faster reaction of MA (stronger decrease) due to the higher reactivity ratio of MA ($r_{MA} = 0.63$) as compared with VAc ($r_{VAc} = 0.03$). At 70% conversion, the MA has completely disappeared resulting in homopolymerization of VAc.

From the good agreement shown in Figures 6 and 7 between model predictions and experimental results for the overall monomer mole fraction (f_{oMA})

Figure 6. Comparison of (---) predictions with (O) experimentally determined values of the overall mole fraction of MA (f_{oMA}) as a function of conversion for the MA-VAc monomer system (initial recipe: $M/W = 0.1$, $V_{po} = 0$, $f_{oMA} = 0.5$).

Figure 7. Comparison of predictions for the number of moles of MA ($M_{MA,t}$ = ---) and VAc ($M_{VAc,t}$ = - · - · -) with experimentally determined results for (○) MA and (□) VAc as a function of conversion (initial recipe: $M/W = 0.1$, $V_{p0} = 0$, $f_{oMA} = 0.5$).

and the numbers of moles ($M_{MA,t}$ and $M_{VAc,t}$) as a function of conversion, it can be concluded that the relationships used to predict the monomer mole fractions in the polymer phase are indeed capable of correctly predicting the course of emulsion polymerization for saturation swelling and partial swelling. Note that the reactivity ratios and the homo-monomer saturation values used for model predictions are accurate enough to obtain good agreement between experimental results and model predictions.

Emulsion Copolymerization of Methyl Acrylate-Indene

Comparison of model predictions of emulsion copolymerization composition as a function of conversion with experimental results for the MA-Ind monomer system show good agreement as can be seen in Figure 8 (initial reaction recipes are shown in Table II). From this, it can be concluded that the above described approach can be used not only for MA-VAc, but also for other monomer systems. The reactivity ratios of the monomer system MA-Ind ($r_{MA} = 0.92$ and $r_{Ind} = 0.086$) are less far apart than those of MA-VAc (a factor of 10 for MA-Ind as compared with a factor of 200 for MA-VAc) leading to less composition drift. The large effect of different monomer to water ratios on a system like MA-Ind, where one of the monomers (MA) is very water soluble, can be seen in Figure 8. If one of the monomers has a relatively high but limited water solubility and the second monomer has a low water solubility (low

α -values) a considerable amount of the more water-soluble monomer can be located in the aqueous phase. Decreasing the monomer to water ratio then will lead to a larger amount of the more water-soluble monomer in the aqueous phase. Since polymerization is assumed to occur mainly in the polymer particle phase, the more water-soluble monomer is temporarily unavailable to the reaction. In the case of MA-Ind, more MA will be buffered in the aqueous phase at lower monomer to water ratios. As can be seen in Figure 8, changing the monomer to water ratio can lead to minimization of the composition drift and may even lead to composition drift in the opposite direction! Note that it is important to realize that minimizing composition drift in MA-Ind reactions is possible due to the relatively small difference in reactivity values of the monomers (a factor of 10) combined with a large difference in homo-monomer saturation concentrations in the aqueous phase ($\alpha^{-1} = 200$). In this and similar cases the water phase can buffer an amount of the more reactive monomer such that composition drift can be minimized. For the MA-VAc monomer system this is not possible since the relatively small difference in homo-monomer saturation concentrations in the aqueous phase ($\alpha^{-1} = 2$) cannot make up for the large difference in reactivity of the monomers (a factor of 200). Lowering the monomer to water ratio in MA-VAc batch copolymerizations will only lead to decreasing composition drift but not to the absence of composition drift.

From the good agreement shown in Figures 6–8

Figure 8. Predicted and experimentally determined overall monomer mole fractions for MA-Ind batch emulsion copolymerizations with initial overall monomer mole fraction of $f_{oMA} = 0.75$ and different monomer to water ratios (M/W) values of 0.1 (prediction ---, experiment ○), 0.3 (prediction - · - · -, experiment □) and 0.4 (prediction · · · · ·, experiment △).

between experimental results and model predictions it can be concluded that the models for saturation and partial swelling developed herein provide a good description of the course of emulsion copolymerization. Furthermore, it can be concluded that the reactivity ratios and homo-monomer saturation values used in the model predictions of MA-VAc and MA-Ind emulsion copolymerizations were determined accurately enough to obtain good agreement between predicted and experimental results. The approach presented here is valid for all monomer systems that obey eqs. (2a)–(b) at saturation swelling. This condition is met for several monomer systems.^{14,15} Furthermore, a sensitivity analysis¹⁶ has shown that eqs. (2a)–(b) still hold even when one or more of the assumptions made to arrive to these results are not fully met. Possible exceptions are monomers that do not swell their polymer and monomers that are fully miscible with water. It must be realized that the approach presented here is very convenient since it only requires the homo-monomer saturation values in the polymer and aqueous phase, which can easily be obtained from experiments. Model calculations can be used not only to describe the course of emulsion copolymerizations, but also to predict it. For instance, model predictions show that it is possible to make a homogeneous MA-Ind copolymer in batch emulsion copolymerization (Fig. 8). The monomer–water–polymer mixture needed to achieve this minimum composition drift can be found from model predictions. Furthermore, model predictions of maximum achievable composition drift can be calculated for any monomer system.

CONCLUSIONS

Combining thermodynamically-based monomer partitioning relationships for saturation¹⁴ and partial swelling¹⁵ with mass balance equations results in a model for saturation and a model for partial swelling that predict the mole fraction of a certain monomer i in the polymer phase. Comparison of experimental results with model predictions shows excellent agreement with monomer partitioning experiments.

The effect of monomer to water ratio and polymer volume on the monomer mole fraction in the polymer phase can be well predicted with the relationships described in this article. Predictions of monomer partitioning experiments results in better understanding of the features determining monomer partitioning in heterogeneous emulsion systems. For instance, it has been shown in this paper that the

ratio of homo-monomer saturation concentrations in the aqueous phase of monomer j over monomer i (monomer i being the more water-soluble monomer) plays a key role in determining the resulting mole fraction of monomer i in the polymer phase. This ratio of water solubilities also determines the range between which the monomer mole fraction in the polymer phase can vary with both different monomer to water ratios and varying polymer volumes, going from a maximum (all monomers in the polymer and monomer droplet phase) to a minimum (all monomers in the aqueous phase) monomer mole fraction in the polymer phase ($f_{pi,max} - f_{pi,min}$).

With the models presented in this article, it is possible to predict emulsion copolymerization in terms of monomer mole fractions within the particle phase (composition drift) and absolute monomer concentrations as a function of conversion. Predicted emulsion polymerization behavior compares quite acceptably with experimental results for MA-VAc and MA-Ind, especially considering that these predictions were without any adjustable parameters. The approach presented herein is valid for all monomer systems that have equal monomer mole fractions in the polymer and droplet phase at saturation swelling. It has been shown experimentally^{14,15} and theoretically¹⁶ that this condition is met for several monomer systems. Possible exceptions are monomers that do not swell their polymer and monomers that are fully miscible with water. It must be realized that the approach presented here is very convenient since it only requires the homo-monomer saturation values in the polymer and aqueous phase, which can easily be obtained from experiments. That is, the copolymer composition in a batch emulsion copolymerization can be predicted, *a priori*, without any adjustable parameters!

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