Kinetics of Multimonomer Emulsion Polymerization. The Pseudo-Homopolymerization Approach

G. STORTI and S. CARRÀ, *Dipartimento di Chimica Fisica Applicata, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy,* M. MORBIDELLI,* *Dipartimento di Ingegneria Chimica e Materiali Università di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy,* and G. VITA, *Montefluos C.R.S., Via S. Pietro, 50, 20021 Bollate (Milano), Italy*

Synopsis

By generalizing the Smith–Ewart theory, a system of polymer particle population balances is developed for describing the kinetics of emulsion polymerization processes involving any number of monomer species. Each population is characterized by the number of active radicals of each type present inside each particle, and described through a size distribution function. An approximation procedure is proposed for reducing the original system to that typical of homopolymerization processes, thus characterizing each population only through the overall number of radicals, without any significant loss of accuracy. The reliability of such "pseudo-homopolymerization approach" is tested by comparison with polymer composition vs. monomer conversion experimental data for the ternary system acrylonitrile–styrene–methyl methacrylate.

INTRODUCTION

The continuous research activity of polymeric materials suitable for new applications has increased the number of instances where more than one monomer is used in the polymer synthesis. Particularly in emulsion polymerization, a large number of multimonomer polymers have recently received much industrial interest.

Since the classical work by Min and Ray[1] in the context of emulsion homopolymerization, it has been recognized that the accurate simulation of the process kinetics requires the description of the distribution function of each population of particles in terms of both size and number of active radicals. The knowledge of these particle populations is a necessary condition for determining the microstructure of the final product. This includes the molecular weight distribution, the monomer sequence distribution, the ending groups distribution, and other characteristics[2–4]—all of paramount importance in assessing the application properties of the final material.

*To whom correspondence should be addressed.

In the case of homopolymerization the relevant kinetic equations are those based on the classical theory originally proposed by Smith and Ewart.[5] These constitute a system of population balance equations in two dimensions: the volume and the number of radicals per particle. These equations can be easily generalized to the case of multimonomer polymerization, by introducing a multidimensional particle distribution whose independent variables are the volume and the number of radicals of each type. However, the difficulties in the mathematical treatment of these equations increase quite rapidly, and the computer time for numerical solution increases exponentially with the number of monomer species in the system. Thus, probably even for binary systems, the approach of solving the generalized Smith–Ewart equations is not feasible in practice.

The aim of this work is to present a new approach, which we refer to as the "pseudo-homopolymerization approach," which allows us to reduce the Smith–Ewart equations relative to a multimonomer system to those of a suitable homopolymerization system. The kinetic parameters appearing in the latter, i.e., the "pseudo-homopolymerization parameters," are evaluated *a priori* as suitable averages of the true kinetic parameters of the original system. This greatly reduces the numerical effort for solving kinetic models of multimonomer polymerization systems, and makes it identical to that typical of homopolymerization systems independently of the number of monomer species involved.

In the following, we first analyse in detail the case of the ternary system, since this is the case where the mathematical formalism can still be kept quite simple without any significant loss of generality. As a particular case of this, the solution for the most common binary copolymerization system is then derived. The obtained relationships are also discussed in comparison with the results of previous analysis reported in the literature. Next, the solution for the most general case, involving any number of monomer species, is presented. Finally, the reliability of the pseudo-homopolymerization approach has been tested by comparison with experimental data relative to the polymer composition vs. overall monomer behavior, for the ternary system: acrylonitrile–styrene–methyl methacrylate.

KINETICS OF EMULSION TERPOLYMERIZATION

Let us consider a quite general form of the population balance equations which account for some more phenomena than those included in the original Smith–Ewart theory. The development of these equations is a straightforward generalization of the extension from homopolymerization to binary copolymerization described in detail by Ballard et al.[2] Therefore, it will not be discussed here in any detail. However, it is worth pointing out that in the following we will account also for particle growth and generation, so that the resulting equations can be adopted very conveniently for developing a comprehensive model (cf. Min and Ray[1] for emulsion homopolymerization) of the entire kinetic process. On the other hand, for the sake of simplicity, polymer particle breakup and coalescence will be neglected.

Thus, considering three reacting monomer species, the following population balance equation can be written:

$$\frac{\partial f_{i,j,k}}{\partial t} + \frac{\partial}{\partial v}\left(g_{ijk} f_{i,j,k}\right)$$

$$= \rho_1\left[f_{i-1,j,k} - f_{i,j,k}\right]$$

$$+ \rho_2\left[f_{i,j-1,k} - f_{i,j,k}\right] + \rho_3\left[f_{i,j,k-1} - f_{i,j,k}\right]$$

$$+ k_1\left[(i+1)f_{i+1,j,k} - if_{i,j,k}\right]$$

$$+ k_2\left[(j+1)f_{i,j+1,k} - jf_{i,j,k}\right]$$

$$+ k_3\left[(k+1)f_{i,j,k+1} - kf_{i,j,k}\right]$$

$$+ c_{11}\left[(i+2)(i+1)f_{i+2,j,k} - i(i-1)f_{i,j,k}\right]$$

$$+ c_{22}\left[(j+2)(j+1)f_{i,j+2,k} - j(j-1)f_{i,j,k}\right]$$

$$+ c_{33}\left[(k+2)(k+1)f_{i,j,k+2} - k(k-1)f_{i,j,k}\right]$$

$$+ 2c_{12}\left[(i+1)(j+1)f_{i+1,j+1,k} - ijf_{i,j,k}\right]$$

$$+ 2c_{13}\left[(i+1)(k+1)f_{i+1,j,k+1} - ikf_{i,j,k}\right]$$

$$+ 2c_{23}\left[(j+1)(k+1)f_{i,j+1,k+1} - jkf_{i,j,k}\right]$$

$$+ \alpha_{12}\left[(i+1)f_{i+1,j-1,k} - if_{i,j,k}\right]$$

$$+ \alpha_{13}\left[(i+1)f_{i+1,j,k-1} - if_{i,j,k}\right]$$

$$+ \alpha_{21}\left[(j+1)f_{i-1,j+1,k} - jf_{i,j,k}\right]$$

$$+ \alpha_{23}\left[(j+1)f_{i,j+1,k-1} - jf_{i,j,k}\right]$$

$$+ \alpha_{31}\left[(k+1)f_{i-1,j,k+1} - kf_{i,j,k}\right]$$

$$+ \alpha_{32}\left[(k+1)f_{i,j-1,k+1} - kf_{i,j,k}\right]$$

$$+ \left(r_{h1}\delta_{i,1} + r_{h2}\delta_{j,1} + r_{h3}\delta_{k,1}\right)\delta(v - v_h)$$

$$+ \left(r_{m1}\delta_{i,1} + r_{m2}\delta_{j,1} + r_{m3}\delta_{k,1}\right)\delta(v - v_m) \tag{1}$$

where $f_{i,j,k}(v)\,dv$ represents the number of polymer particles having i radicals of type 1, j of type 2, and k of type 3, whose volume lies between v and

$v + dv$; g_{ijk} is the volume growth rate of such particles:

$$g_{ijk} = \left[i(\beta_{11} + \beta_{12} + \beta_{13}) + j(\beta_{21} + \beta_{22} + \beta_{23}) \right.$$

$$\left. + k(\beta_{31} + \beta_{32} + \beta_{33}) \right] \qquad (2)$$

where $\beta_{ij} = k_{pij} M_j \, \mathrm{MW}_j / \rho_p N_A$ indicates the rate of polymer volume production due to the propagation reaction of an active chain of type i with the monomer j (M_j is the monomer concentration inside the particle and MW_j its molecular weight). ρ_p and N_A indicate polymer density and Avogadro's number, respectively. Furthermore, ρ_i is the first-order rate coefficient for entry of radicals i into polymer particles; k_i is the first-order rate coefficient for exit (or desorption) of radical i; α_{ij} is the pseudo-first order rate constant (since it includes the relevant monomer concentration, i.e., j in this case) for propagation of radical i with monomer j; $2c_{ij}$ is the rate constant for the termination reaction between the radical species i and j. Finally, $r_{h,i}$ and $r_{m,i}$ represent the rate of homogeneous and micellar nucleation, respectively. In describing the nucleation processes, it is assumed that the generated nuclei are of fixed volume (v_h and v_m for those generated through the homogeneous or the micellar mechanism, respectively), and contain at most one active radical of some type. This is conveniently represented in mathematical form through the Dirac delta function $\delta(v - \bar{v})$ and the Kroeneker function $\delta_{i,1}$.[1,6]

It is worth noting that the kinetic processes described by eq. (1) occur on widely different time scales. In particular, the chain propagation processes are about 2–3 orders of magnitude faster than any of the termination processes—which is unavoidable when large molecular weight values have to be obtained. This provides a highly stiff character to eq. (1), whose solution becomes quite complex and tedious, even using advanced numerical techniques. However, this same observation suggests to simplify eq. (1) by neglecting all terms but those relative to propagation, as follows:

$$f_{i,j,k} \left[(i(\alpha_{12} + \alpha_{13}) + j(\alpha_{21} + \alpha_{23}) + k(\alpha_{31} + \alpha_{32}) \right]$$

$$= (i + 1)\left(\alpha_{12} f_{i+1,j-i,k} + \alpha_{13} f_{i+1,j,k-1} \right)$$

$$+ (j + 1)\left(\alpha_{21} f_{i-1,j+1,k} + \alpha_{23} f_{i,j+1,k-1} \right)$$

$$+ (k + 1)\left(\alpha_{31} f_{i-1,j,k+1} + \alpha_{32} f_{i,j-1,k+1} \right) \qquad (3)$$

This is a rather accurate approximation, which actually means that the faster reactions (i.e., propagation) are at quasi-steady-state conditions with respect to all the slower reactions (i.e., initiation and termination).

It is worth noting that only particles containing the same overall number of active radicals ($n = i + j + k$) appear in eq. (1), as it is expected since only propagation processes are accounted for. Thus, eq. (3) can be regarded as an approximation of the complete population balance (1) where only transitions among states characterized by the same overall number of active radicals are considered. These are certainly much faster than transitions involving states

with a different overall number of radicals, which are all due to kinetic processes other than propagation, thus justifying the approximation.

Equation (3) constitutes a system of homogeneous finite-difference equations, whose solution can be obtained by various techniques. The one adopted in the sequel has been chosen because of its simplicity, particularly in view of the generalization to multimonomer systems.

The solution of eq. (3) can be represented as follows:

$$f_{i,j,k} = P_{ijk} f_n \tag{4}$$

where f_n refers to particles containing n radicals of any type, and P_{ijk} is the probability that one such particle contains i radicals of type 1, j of type 2, and k of type 3, being $i + j + k = n$. Such a probability can be computed by multiplying the multinomial coefficient,[7] indicating the number of possible combinations among the different radicals, by the probability of the simultaneous presence inside the particle of a given number of radicals of each type. Since all the involved kinetic events are independent of each other, the following relationship holds:

$$P_{ijk} = (n; i, j, k)P_1^i P_2^j P_3^k \tag{5}$$

where $(n; i, j, k)$ is the trinomial coefficient $(= n!/i!\,j!\,k!)$, and P_1, P_2, and P_3 are the probabilities associated with the single radicals of types 1, 2, and 3, respectively. These can be easily computed through the steady state balance of the transitions among various states, each representing one radical type, according to the scheme shown in Figure 1. For the first two states the following equations are obtained:

$$P_1(\alpha_{12} + \alpha_{13}) - P_2\alpha_{21} - P_3\alpha_{31} = 0 \tag{6}$$

$$- P_1\alpha_{12} + P_2(\alpha_{21} + \alpha_{23}) - P_3\alpha_{32} = 0 \tag{7}$$

Since the analogous equation for the third and last state would be redundant, it is replaced by the consistency equation

$$P_1 + P_2 + P_3 = 1 \tag{8}$$

The resulting linear algebraic system (6)–(8) can be easily solved, leading to the following expressions for the probability coefficients:

$$P_1 = (\alpha_{21}\alpha_{32} + \alpha_{21}\alpha_{31} + \alpha_{23}\alpha_{31})/\Phi \tag{9}$$

$$P_2 = (\alpha_{12}\alpha_{32} + \alpha_{12}\alpha_{31} + \alpha_{32}\alpha_{13})/\Phi \tag{10}$$

$$P_3 = (\alpha_{12}\alpha_{23} + \alpha_{21}\alpha_{13} + \alpha_{23}\alpha_{13})/\Phi \tag{11}$$

where

$$\Phi = \alpha_{12}\alpha_{23} + \alpha_{23}\alpha_{13} + \alpha_{21}\alpha_{13} + \alpha_{21}\alpha_{32} + \alpha_{21}\alpha_{31} + \alpha_{23}\alpha_{31}$$

$$+ \alpha_{12}\alpha_{32} + \alpha_{12}\alpha_{31} + \alpha_{32}\alpha_{13} \tag{12}$$
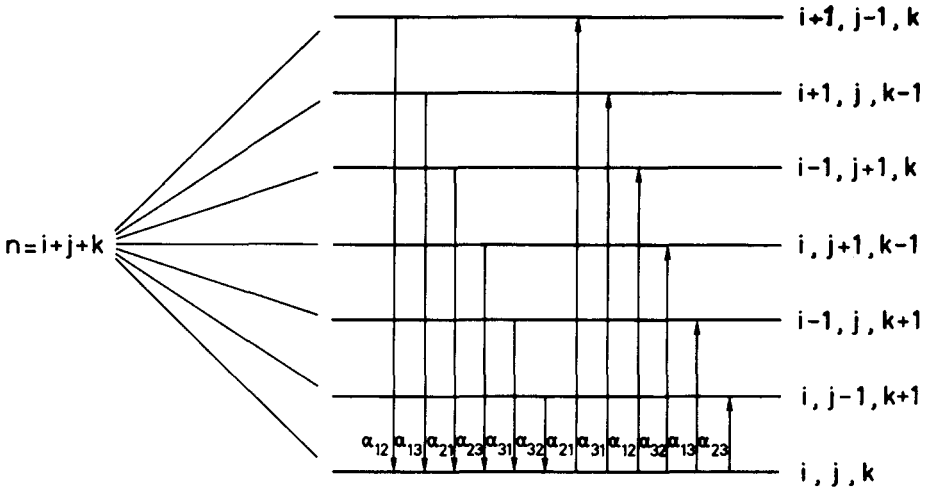
STORTI ET AL.

Fig. 1. Schematic representation of the transitions between states due to cross propagation for particles with n active chains [eq. (3)].

These expressions, substituted in eq. (5), yield the solution of the approximated population balance (3), thus relating the detailed size distribution function $f_{i,j,k}$ to that lumped with respect to the radical type, f_n. Substituting such a solution in the complete population balance (1), and adding all terms for $j = 0, n - i$ and $i = 0, n$ with $k = n - i - j$, after some algebraic manipulations the following equation is obtained:

$$\frac{\partial f_n}{\partial t} + \frac{\partial}{\partial v}(g_n^* f_n) = \rho^*(f_{n-1} - f_n) + k^*[(n + 1)f_{n+1} - nf_n]$$

$$+ c^*[(n + 2)(n + 1)f_{n+2} - n(n - 1)f_{n-1}]$$

$$+ r_h^* \delta(v - v_h)\delta_{n,1} + r_m^* \delta(v - v_m)\delta_{n,1} \tag{13}$$

where the following new parameters have been introduced:

$$\rho^* = \rho_1 + \rho_2 + \rho_3 \tag{14}$$

$$k^* = k_1 P_1 + k_2 P_2 + k_3 P_3 \tag{15}$$

$$c^* = c_{11}P_1^2 + c_{22}P_2^2 + c_{33}P_3^2 + 2c_{12}P_1 P_2$$

$$+ 2c_{13}P_1 P_3 + 2c_{23}P_2 P_3 \tag{16}$$

$$g_n^* = [P_1(\beta_{11} + \beta_{12} + \beta_{13}) + P_2(\beta_{21} + \beta_{22} + \beta_{23})$$

$$+ P_3(\beta_{31} + \beta_{32} + \beta_{33})]n \tag{17}$$

$$r_h^* = r_{h,1} + r_{h,2} + r_{h,3} \tag{18}$$

$$r_m^* = r_{m,1} + r_{m,2} + r_{m,3} \tag{19}$$

It should be noted that eq. (13) is actually coincident with the classical Smith–Ewart population balance for homopolymerization, whose kinetic parameters ρ^*, k^*, c^*, g_n^*, r_h^*, and r_m^* are suitable averages of the true multimonomer polymerization parameters. These will be referred to as pseudo-homopolymerization parameters.

By inspection of the above averaging equations it can be seen that their mathematical form depends solely upon the reaction order of the kinetic process under examination with respect to the radical species inside the particle. Namely, the nucleation (18) and (19) and radical entry (14) processes are zeroth order, the radical desorption (15) and particle growth (17) processes are first order and the bimolecular termination (16) process is second order. This provides a simple rule for readily extending the pseudo-homopolymerization approach to other kinetic processes, not accounted for in this work, which can be of relevance in some specific emulsion polymerization process.

It is worth stressing that the procedure for obtaining the pseudo-homopolymerization parameters does not involve any additional assumption, besides the validity of eq. (3). The most important point, which makes this approach feasible, is that the obtained parameters do not depend on the overall radical number n, thus really reducing the original population balance to that typical of homopolymerization systems.

Thus summarizing, the application of the pseudo-homopolymerization approach consists in the following steps. First, the pseudo-homopolymerization parameters are evaluated from the true ones based on eqs. (14)–(19); next, the population balance (13) is solved using any of the methods proposed in the literature for emulsion homopolymerization. Once f_n has been computed, the detailed distribution function $f_{i,\,j,\,k}$ can be readily obtained through eq. (4).

THE CASE OF EMULSION COPOLYMERIZATION

The pseudo-homopolymerization approach can easily be applied to the case of a binary polymerization system, which is worth reporting here in some detail since it is probably the most common in applications. In this case only two types of radical species are present (i and j), thus generating a bidimensional size distribution function, $f_{i,\,j}(v)$. Following the same procedure described above, the distribution function $f_{i,\,j}(v)$ can be represented, similarly to eqs. (4) and (5), in the following form:

$$f_{i,\,j} = (n;\,i,\,j)P_1^i P_2^j f_n \qquad (20)$$

where $(n;\,i,\,j)$ is the usual binomial coefficient, and the probability coefficients are obtained directly from eqs. (10)–(12), by simply neglecting all terms referring to the third radical species, as follows:

$$P_1 = \alpha_{21}/(\alpha_{21} + \alpha_{12}) \qquad (21)$$

$$P_2 = \alpha_{12}/(\alpha_{21} + \alpha_{12}) \qquad (22)$$

Finally, the lumped distribution function f_n is obtained from the solution of

the homopolymerization population balance (13), whose parameters are defined, similarly to the previous case, by the following expressions:

$$\rho^* = \rho_1 + \rho_2 \tag{23}$$

$$k^* = k_1 P_1 + k_2 P_2 \tag{24}$$

$$c^* = c_{11} P_1^2 + c_{22} P_2^2 + 2 c_{12} P_1 P_2 \tag{25}$$

$$g_n^* = \left[P_1(\beta_{11} + \beta_{12}) + P_2(\beta_{21} + \beta_{22}) \right] n \tag{26}$$

$$r_h^* = r_{h,1} + r_{h,2} \tag{27}$$

$$r_m^* = r_{m,1} + r_{m,2} \tag{28}$$

The kinetics of emulsion copolymerization has been previously analyzed in the literature[2,3]; note that the solution reported by Ballard et al.[2] does not agree with that reported in the present work. In particular, it is important to reiterate that the pseudo-homogeneous parameters do not depend on the overall number of radicals in the particle.

THE GENERALIZED PSEUDO-HOMOPOLYMERIZATION APPROACH

The above-reported procedure can be applied to the most general case where m monomeric species are polymerized simultaneously. This leads to the solution of the generalized form of the Smith–Ewart population balance equation, which involves the size distribution function $f_{n_1, n_2, \ldots, n_m}(v)$, where $n_1, n_2, \ldots, n_m$ indicate the number of active radicals, present inside the growing polymer particle, of type $1, 2, \ldots, m$, respectively. Since in this case the mathematical formalism becomes quite cumbersome, only the final results are reported in what follows.

The detailed size distribution function is expressed as follows:

$$f_{n_1, n_2, \ldots, n_m} = f_n P_1^{n_1} P_2^{n_2} \cdots P_m^{n_m}(n; n_1, n_2, \ldots, n_m) \tag{29}$$

where $n = n_1 + n_2 + \cdots + n_m$ is the overall number of active radicals inside the particle. The probability coefficients can be computed through a pseudo-steady state balance among various states each containing radicals of different type, on the basis of the same arguments discussed above for the ternary system.

The resulting balance equations can be represented in the matrix form:

$$AP = b \tag{30}$$

where $\mathbf{P}$ is the $(m, 1)$ vector containing all the probability coefficients P_i, $\mathbf{b}$ is a similar vector whose terms are all zero, but the last one which is equal to

unity, and A is the following (m, m) matrix:

$$
\begin{array}{cccccc}
\sum_j \alpha_{1j} & -\alpha_{21} & -\alpha_{31} & \cdots & -\alpha_{m-1,1} & -\alpha_{m1} \\[2mm]
-\alpha_{12} & \sum_j \alpha_{2j} & -\alpha_{32} & \cdots & -\alpha_{m-1,2} & -\alpha_{m2} \\[2mm]
-\alpha_{13} & -\alpha_{23} & \sum_j \alpha_{3j} & \cdots & -\alpha_{m-1,3} & -\alpha_{m3} \\[2mm]
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\[2mm]
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\[2mm]
-\alpha_{1,m-1} & -\alpha_{2,m-1} & -\alpha_{3,m-1} & \cdots & \sum_j \alpha_{m-1,j} & -\alpha_{m,m-1} \\[2mm]
1 & 1 & 1 & 1 & 1 & 1
\end{array}
\tag{31}
$$

The system of linear algebraic eqs. (30), can be easily solved by any of the various available numerical techniques.

The last point concerns the evaluation of the lumped size distribution function f_n. Following the same procedure outlined above, it can be shown that the detailed Smith–Ewart equation generalized to multimonomer polymerization reduces to the classical form for homopolymerization (13), where the pseudo-homopolymerization parameters are defined as follows:

$$
\rho^* = \sum_j \rho_j
\tag{32}
$$

$$
k^* = \sum_j k_j P_j
\tag{33}
$$

$$
c^* = \sum_j \sum_i c_{ij} P_i P_j
\tag{34}
$$

$$
g_n^* = \left[\sum_j P_j \sum_i \beta_{ij} \right] n
\tag{35}
$$

$$
r_h^* = \sum_j r_{h,j}
\tag{36}
$$

$$
r_m^* = \sum_j r_{m,j}
\tag{37}
$$

Thus, the procedure for applying the pseudo-homopolymerization approach to a system involving any number of monomeric species remains basically the same as the one described above for ternary systems.

NUMERICAL EXAMPLE

In order to better describe the pseudo-homopolymerization approach, let us consider a numerical example. With illustrative purposes, the parameter values reported in Table I are considered. These values are of practical significance, since they closely reproduce a typical batch emulsion polymerization process of the ternary system acrylonitrile (A)–styrene (S)–methyl

$$a = 9.87 \times 10^{-16}\,\text{cm}^3$$
$$b = 58.46$$
$$c = 1.19 \times 10^{14}\,1/\text{cm}^3$$
$$\alpha_{AA} = 2.409 \times 10^4, \quad \alpha_{AS} = 5.318 \times 10^5, \quad \alpha_{AM} = 9.560 \times 10^4\,1/\text{s}$$
$$\alpha_{SA} = 6.862 \times 10^2, \quad \alpha_{SS} = 2.666 \times 10^2, \quad \alpha_{SM} = 3.456 \times 10^2\,1/\text{s}$$
$$\alpha_{MA} = 4.352 \times 10^2, \quad \alpha_{MS} = 1.002 \times 10^3, \quad \alpha_{MM} = 3.107 \times 10^3\,1/\text{s}$$
$$MW_A = 53.06\,\text{g/mol}$$
$$MW_S = 104.20\,\text{g/mol}$$
$$MW_M = 100.11\,\text{g/mol}$$
$$\rho_p = 1.108\,\text{g/cm}^3$$
$$\rho^* = 1.354 \times 10^8\,v^{2/3} \quad 1/\text{s}$$
$$c^* = 2.126 \times 10^{-14}/v \quad 1/\text{s}$$
$$k^* = r_h^* = r_m^* = 0$$

methacrylate (M).[8] The particle size distribution is described as a perturbation of the Gamma distribution, according to Hulburt and Katz,[9] as follows:

$$f(v) = \sum_{n=0}^{\infty} f_n(v) = \frac{b}{a} \frac{c}{(b-1)!} \left(\frac{bv}{a} \right)^{b-1} \exp\left(-\frac{bv}{a} \right) \tag{38}$$

The three parameters a, b, and c are evaluated from the first three moments of the distribution function $f(v)$[9]; in this example, typical numerical values are assumed, corresponding to the usual values of number of particles, total volume of the particles, and variance of the particle size distribution of polymer produced by emulsion polymerization in a batch reactor (see Table I).

The $f_n(v)$ values can be obtained by solving eqs. (13); in particular, for $r_h^* = r_m^* = 0$, the pseudo-steady-state, constant volume, analytical solution reported by O'Toole[10] has been considered for each volume value:

$$f_n(v) = x^n 2^{(m-1-3n)/2} \frac{I_{m+n-1}(x/\sqrt{2})}{n! I_{m-1}(x)} \tag{39}$$

where $x = \sqrt{8\alpha}$, $\alpha = \rho^*/c^*$, and $m = k^*/c^*$. $I_\nu(x)$ indicates the modified Bessel function of first kind and order ν. The following volume dependence of ρ^*, k^*, and c^* have been introduced in the model equations:

$$\rho^* = \rho' v^{2/3}$$

$$k^* = k' v^{-1/3}$$

$$c^* = c'/v \tag{40}$$

In Figure 2, the 3-dimensional distribution function $f_n(v)$ is shown. The average value of the active chains in the particles is 1.33; the dotted line indicates the locus of the particle volumes corresponding to the maximum
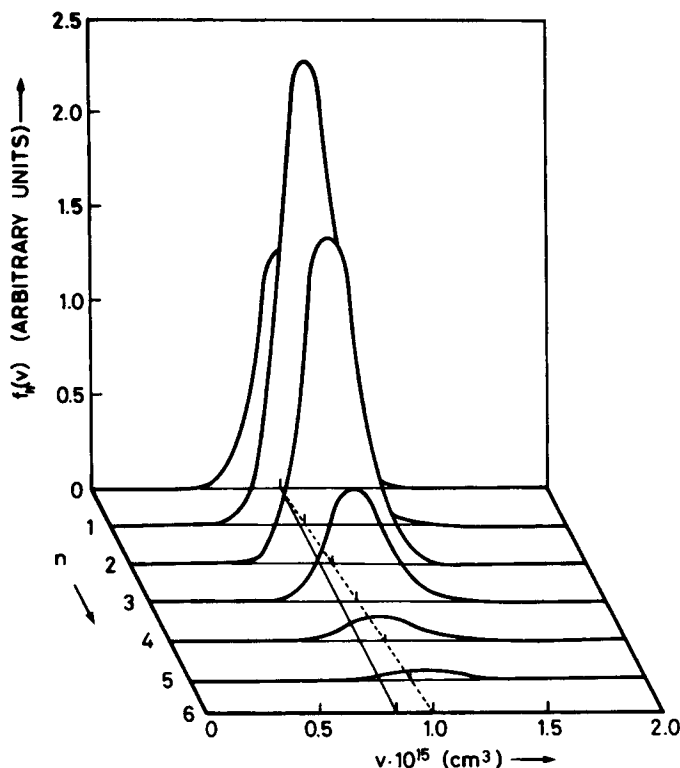
Fig. 2. Three-dimensional distribution function of size and number of active chains within the particle.

values of the distribution functions $f_n(v)$. Note that the radical distribution is affected by the size distribution, i.e., large particles accumulate more active chains than the small ones. This feature is evidenced in Figure 3, where the radical distributions $f_n(v)$ for three different particle volume values are shown.

In Figure 4, the 3-dimensional distribution function $N_{i,j,k} = \int_0^\infty f_{i,j,k}(v)\, dv$ is shown. Three cases are examined: $i + j + k = 3$, 5, and 7. It appears that particles with large values of j, small values of k, and very small values of i are largely dominant. This follows from the values of the intrinsic propagation rate constants, i.e., α_{ij}, adopted in this example and reported in Table I.

EXPERIMENTAL VERIFICATION OF THE
PSEUDO-HOMOPOLYMERIZATION APPROACH

In order to establish the reliability of the pseudo-homopolymerization approach, the calculated results have been compared with the experimental values measured during the batch polymerization of a ternary system. At this stage, such a comparison has been limited to the polymer composition vs. conversion curves, which, although they do not describe the detailed time evolution of the reacting system, are indeed of paramount importance in industrial applications. Moreover, this choice allows a drastic reduction in
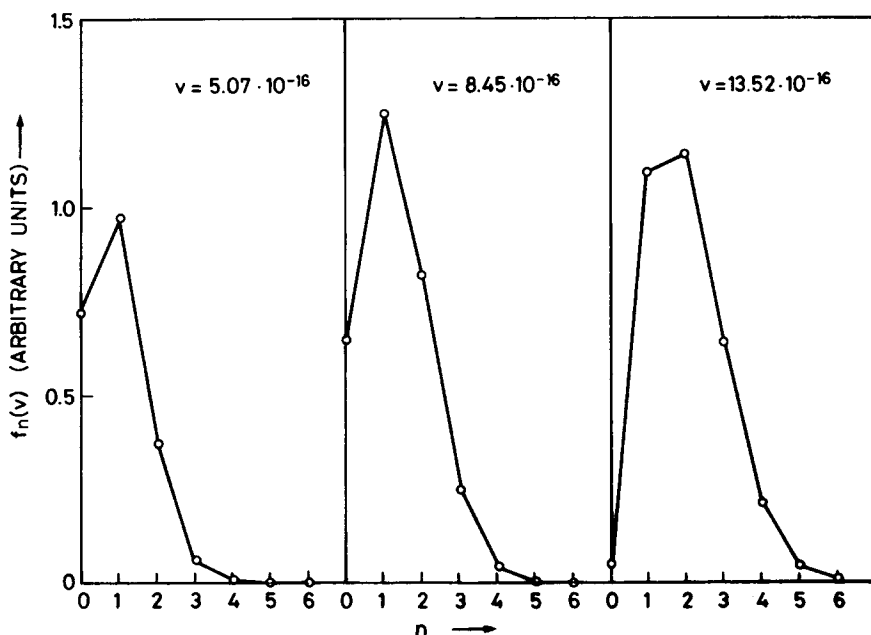
Fig. 3.   Active chain distribution function $f_n(v)$ for three particle volume values (v in cm³).

both the modeling and the experimental efforts required for accomplishing such a comparison.

Let us first derive the model equations needed for calculating the polymer composition versus total conversion curves. The mass balances for each monomer species in a batch, isothermal, and well-stirred reactor are given by

$$\frac{dM_i}{dt} = -R_{pi}V_w \tag{41}$$

where M_i indicates the total unreacted moles of monomer i in the reactor and V_w the total volume of the aqueous phase. R_{pi} is the rate of monomer consumption due to the polymerization reaction, both in the aqueous solution and in the polymer particles. When assuming that the reaction occurs mainly within the polymer particles, the rate of monomer consumption can be evaluated as follows:

$$R_{pi} = \sum_{j=1}^{m} \alpha_{ji} \int_0^\infty \sum_{n=0}^\infty \left\{ \sum_{\substack{n_1 \geq 0 \\ n_1 + \cdots + n_j + \cdots + n_m = n}} \cdots \sum_{n_j \geq 0} \cdots \sum_{n_m \geq 0} f_{n_1, \ldots, n_j, \ldots, n_m}(v) \frac{n_j}{N_A} \right\} dv \tag{42}$$

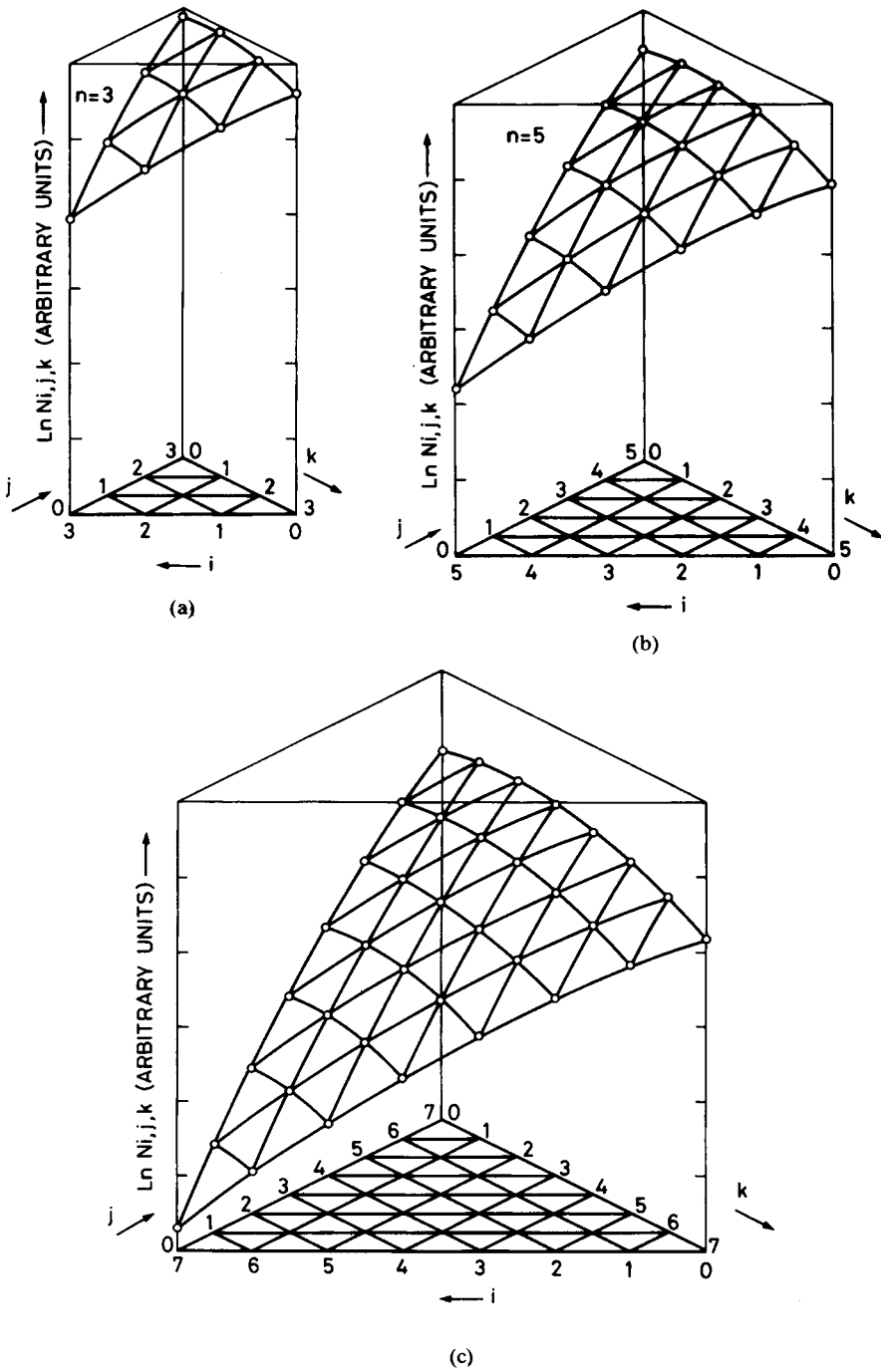which, by substituting the pseudo-homopolymerization approximation (29),

Fig. 4. Three-dimensional distribution function $N_{i,j,k}$ of number and type of active chain within particles (i = type 1; j = type 2; k = type 3) for three values of total active chain number $n = i + j + k$. (a) $n = 3$; (b) $n = 5$; (c) $n = 7$.

reduces as follows:

$$R_{pi} = \sum_{j=1}^{m} \alpha_{ji} \int_0^\infty \sum_{n=0}^\infty f_n(v) \left\{ \sum_{n_1 \geq 0} \cdots \sum_{n_j \geq 0} \cdots \sum_{n_m \geq 0} P_1^{n_1} \cdots P_j^{n_j} \cdots P_m^{n_m} \right. $$

$$\left. \underset{n_1 + \cdots + n_j + \cdots + n_m = n}{} \times (n; n_1, \ldots, n_j, \ldots, n_m) \frac{n_j}{N_A} \right\} dv \quad (43)$$

Using standard mathematical relationships for power series and the normalization condition of **P** [last equation in the system (30)], eq. (43) reduces to:

$$R_{pi} = \sum_{j=1}^{m} \alpha_{ji} \frac{P_j}{N_A} \int_0^\infty \sum_{n=0}^\infty f_n(v) n \, dv \quad (44)$$

where the integral term represents the overall number of active chains inside all polymer particles. By introducing the average number of active chains per polymer particle $\bar{n}$, the integral above can be expressed as $\bar{n}N_p$, and eq. (44) reduces to

$$R_{pi} = \left(\sum_{j=1}^{m} \alpha_{ji} P_j \right) \frac{\bar{n}N_p}{N_A} = K_{pi}\overline{M}_i \frac{\bar{n}N_p}{N_A} \quad (45)$$

where $K_{pi} = \sum_{j=1}^{m} k_{pji} P_j$. The latter equation states that the total rate of monomer consumption is simply given as the product of the total number of active chains times the ith monomer concentration within the particles ($\overline{M}_i$) and the effective rate constant of propagation, K_{pi}, which accounts for the instantaneous distribution of the type of active chains in the particles. Such a parameter K_{pi} can be regarded as the pseudo-homopolymerization propagation rate parameter, which, in the general pseudo-homopolymerization solution reported above, appeared in eq. (35). Finally, it is worthwhile pointing out that, throughout the entire analysis reported in this work, the effect of polymer particle size on monomer solubility has been neglected, i.e., monomer concentration in polymer particle independent of size has been assumed.

Using eq. (45), expressions for the residual moles of the ith monomer (according to eq. 38) as well as for the total moles of polymer produced can be readily obtained as follows:

$$\frac{dM_i}{dt} = -K_{pi}\overline{M}_i \frac{\bar{n}N_p}{N_A} V_w \equiv -\frac{dM_{pi}}{dt} \quad (46a)$$

$$\frac{dM_p}{dt} = \left(\sum_{j=1}^{m} K_{pj}\overline{M}_j \right) \frac{\bar{n}N_p}{N_A} V_w \quad (46b)$$

where M_p and M_{pi} indicate the total moles and the moles of monomer i

reacted to polymer, respectively. By inspection of eq. (46) it appears that the instantaneous polymer composition y_i (i.e., the ratio between the rate of consumption of each monomer and the total rate of polymer production) is simply given by

$$y_i = \frac{dM_{pi}}{dM_p} = \frac{K_{pi}\overline{M}_i}{\sum_{j=1}^m K_{pj}\overline{M}_j} \qquad (47)$$

while the corresponding integral or cumulative composition of the polymer is given by $Y_i = M_{pi}/M_p$. Thus, by integrating eq. (47) for each component $(i = 1{-}m)$ from $M_p = 0$ to $M_p = \sum_{j=1}^m M_j^0$ (where M_j^0 indicates the initial number of moles of monomer j in the reactor), the value of M_{pi} as a function of M_p, and then the corresponding integral polymer composition vs. total conversion curve are obtained. Note that since the model is constituted by the system of ordinary differential equations (47) with initial condition ($M_{pi} = 0$ at $t = 0$ for $i = 1{-}m$), its numerical integration can be easily performed through standard marching techniques. The predictor–corrector Adams method with variable step size and order has been used in this work.

It is worthwhile stressing that eq. (44) is time-independent. Therefore, typical "kinetic" information such as the total number of active chains within the particle are not involved. This result follows from the application of the pseudo-homopolymerization approach, together with the assumption of monomer concentration within the particles independent of size.

When assuming no mass transport limitations for the main reactants (monomers), the concentration of each monomer in each phase (oil droplets, aqueous phase and polymer particles) is solely determined by thermodynamic equilibria. Thus the distribution of the total residual monomer, given by $(M_j^0 - M_{pi})$ for $j = 1{-}m$, among the various phases in the system can be calculated by coupling to eqs. (47) the following equations:

$$M_i = \alpha_i V_d / \tilde{V}_i + M_{wi} V_w + V_p \phi_i / \tilde{V}_i \qquad (48)$$

$$V_P = \left(\sum_{i=1}^m M_{pi} \text{MW}_i \right) \bigg/ (\rho_p \phi_p) \qquad (49)$$

$$\sum_{i=1}^m \alpha_i = 1 \qquad (50)$$

$$\alpha_i = f_i(\mathbf{M}_w) \qquad (51)$$

$$\phi_i = g_i(\mathbf{M}_w) \qquad (52)$$

where α_i and ϕ_i indicate the volume fraction of component i in oil droplets and polymer particles, respectively (note that $\overline{M}_i = \phi_i / \tilde{V}_i$); $\phi_p = (1 - \sum_{i=1}^m \phi_i)$ is the volumetric fraction of polymer in the particles; V_d and V_p are the total volumes of monomer droplets and polymer particles; f_i and g_i indicate the monomer solubility relationships in the oil droplets–aqueous phase and poly-

mer particles–aqueous phase systems, respectively. The system of nonlinear algebraic equations (48)–(52) is constituted by $3m + 2$ relationships and its solution provides the values of the following $3m + 2$ unknowns: α_i, ϕ_i, M_{wi} ($i = 1–m$), V_d, and V_p. The numerical solution of this system is performed at each integration step of eq. (47) using a suitable numerical procedure.[11]

Let us now consider in detail the monomer solubility relationships defined in eqs. (51) and (52). With respect to bulk thermodynamics, the evaluation of the chemical potentials of the various components in each phase is complicated by the colloidal nature of the two involved phases: oil droplets and polymer particles. In general, the mathematical description of multicomponent equilibria in emulsion systems is quite complex and involves a significant number of adjustable parameters.[12,13] In this work, simplified equilibrium relationships are considered.

Monomer Solubility in the Oil Droplets–Aqueous Phase System. In the case where only one monomer species is present, the monomer concentration in the aqueous phase, M_{wi} is equal to its saturation value in water, as long as oil droplets are present in the system. Such saturation values are usually available in the literature.[14] In the case of multicomponent mixtures, the aqueous phase concentrations of each monomer species depends upon the oil droplet composition. When detailed experimental data are available, empirical equilibrium relationships can be developed. Since this is the case for the system under examination, an empirical expression for the equilibrium relationships, f_i will be used in the following.

Monomer Solubility in the Oil Droplets–Particle Phase System. In the case of a binary system the chemical potential of each monomer species in the two phases can be expressed as follows[12,13]:

$$\mu_i^d = \mu_i^0 + RT\left[\ln \alpha_i + (1 - m_{ij})\alpha_j + \xi_{ij}\alpha_j^2\right] + 2\tilde{V}_i\gamma_d/r_d,$$

$$i, j = 1, 2, \ i \neq j \quad (53)$$

$$\mu_i^P = \mu_i^0 + RT\left[\ln \phi_i + (1 - \phi_i) - \phi_j m_{ij} - \phi_p m_{ip}\right.$$

$$\left. + (\phi_j + \phi_p)(\xi_{ij}\phi_j + \xi_{ip}\phi_p) - \xi_{jp}m_{ij}\phi_j\phi_p\right] + 2\tilde{V}_i\gamma_p/r_p,$$

$$i, j = 1, 2, \ i \neq j \quad (54)$$

where μ_i^d, μ_i^P, and μ_i^0 indicate the chemical potential of component i in oil droplets, polymer particles, and reference state, respectively; m_{ij} is the ratio of the numbers of segments per molecule in species i and j, and it can be estimated as the ratio of the molar volumes of the two monomer species[15]; ξ_{ij} is the parameter accounting for the interactions between component i and component j, and its value can be estimated from suitable solubility data[15]; γ_d and γ_p are the interfacial tensions for the systems oil–water and particle–water, respectively; r_d and r_p indicate the radius of a droplet and a particle. Note that the chemical potentials (53) and (54) reduce to the usual bulk form when the surface terms $(2\tilde{V}\gamma/r)$ are neglected.

In the case under examination, the following assumptions can be introduced: (i) $m_{ij} \approx 1$ and $m_{ip} \approx 0$; (ii) $\xi_{ij} \approx 0$ and $\xi_{ip} \approx \xi_{jp} \approx \xi_p$; (iii) negligible surface term in eq. (53), due to the high values of r_d in usual emulsions; (iv) surface term in eq. (54) constant, according to the previous assumption of monomer concentration within the particles independent of size; namely, $2\tilde{V}_i\gamma_p/r_pRT \approx 2\tilde{V}_j\gamma_p/r_pRT \approx A$ is assumed. Equating the chemical potentials as given by eqs. (53) and (54), and accounting for the above assumptions, the following $\phi_i - \alpha_i$ equilibrium relationship arises:

$$\alpha_i = \phi_i \exp\left[\phi_p(1 + \xi_p\phi_p) + A\right] \tag{55}$$

where the bracketted term is independent on the component index. When combined with the monomer droplets–aqueous phase equilibrium relationships, f_i, discussed above, eq. (55) leads to the desired polymer particle–aqueous phase equilibrium relationships, g_i defined by eq. (52).

However, eq. (55) involves two adjustable parameters whose evaluation requires detailed equilibrium data. From the point of view of applications, it is more convenient to directly exploit the implication of eq. (55) that the ratio α_i/ϕ_i is the same for each monomer species, thus leading to the equivalent set of equilibrium relationships:

$$\phi_1/\alpha_1 = \phi_2/\alpha_2, \qquad \phi_1 + \phi_2 = \exp\left[-\phi_p(1 + \xi_p\phi_p) - A\right] = 1 - \phi_p \tag{56}$$

If we have experimental values for ϕ_p, eq. (56) can be used for evaluating the values of ϕ for each oil droplet composition, α. Now, it is worth mentioning that during the first two intervals of an emulsion polymerization ϕ_p remains constant and equal to the so-called maximum swelling. Experimental data for ϕ_p at saturation both for homopolymerization and for copolymerization are usually reported in the literature; therefore, it is convenient to use ϕ_p as a parameter instead of the two parameters ξ_p and A.

When oil droplets disappear (at the onset of the so-called interval III of the emulsion polymerization), a reduced set of equations has to be used, including eq. (48) with $V_d = 0$ and eqs. (49) and (52). At this stage, the solubility laws for the polymer particles–aqueous phase system are required. Due to the lack of experimental data for unsaturated systems, the same relationships for the monomer partition between oil droplets and aqueous phase, f_i, have been assumed for g_i, simply substituting $\phi_i/(\sum_{j=1}^m \phi_j)$ for α_i.

These results can be readily extended to the case of multicomponent systems, under the same approximations mentioned above, leading to the following equilibrium relationships:

$$\phi_i/\alpha_i = \phi_j/\alpha_j, \qquad \sum_{i=1}^m \phi_i = 1 - \phi_p \tag{57}$$

which constitute a system of m linear algebraic equations with m unknowns (ϕ_i or α_i, as desired).

STORTI ET AL.

TABLE II
Monomer Feed Compositions for Binary and Ternary Polymerizations

Run	Monomer feed (wt %)		
	A	S	M
Binary systems			
1	30	70	—
2	50	50	—
3	70	30	—
4	30	—	70
5	50	—	50
6	70	—	30
7	—	30	70
8	—	50	50
9	—	70	30
Ternary systems			
10	33.33	33.33	33.33
11	20	20	60
12	20	60	20
13	60	20	20

Thus summarizing, the simplified multicomponent equilibrium model described above requires only two sets of experimental data: organic phase–water phase solubilities and maximum swelling ratios.

From the experimental side, the ternary system acrylonitrile (A)–styrene (S)–methyl methacrylate (M) has been examined. A batch, isothermal, perfectly mixed glass reactor at constant pressure of nitrogen has been used together with the following operating conditions: stirring = 500 rpm; T = 323 K; P = 1 atm; V_w = 600 cm^3; initial total amount of monomers = 100 g; initiator ($K_2S_2O_8$) = 0.395 g; emulsifier (SDS) = 2.00 g. Polymer conversion and composition values have been measured gravimetrically and through elemental analyzer, respectively. Several experimental runs have been performed at various monomer feed composition both with two and three monomer species, as summarized in Table II.

TABLE III
Numerical Values of the Parameters Considered in the Polymer Composition
Calculations Shown in Figures 5–11 (Experimental Runs of Table II)

Reactivity ratios[16]

$$r_{AS} = 0.04, \qquad\qquad r_{AM} = 0.18$$
$$r_{SA} = 0.41, \qquad\qquad r_{MA} = 1.35$$
$$r_{SM} = 0.52, \qquad\qquad r_{MS} = 0.46$$

Organic phase–water phase solubility laws[14, 17]

$\alpha_A = a_1 M_{wA}/(1 - a_2 M_{wA})$
$\alpha_S = a_3 M_{wS} \quad (a_i = cm^3/mol)$
$\alpha_M = a_4 M_{wM}$
$a_1 = 249.2, \quad a_2 = 429.7, \quad a_3 = 2.7 \times 10^5, \quad a_4 = 6.3 \times 10^3$
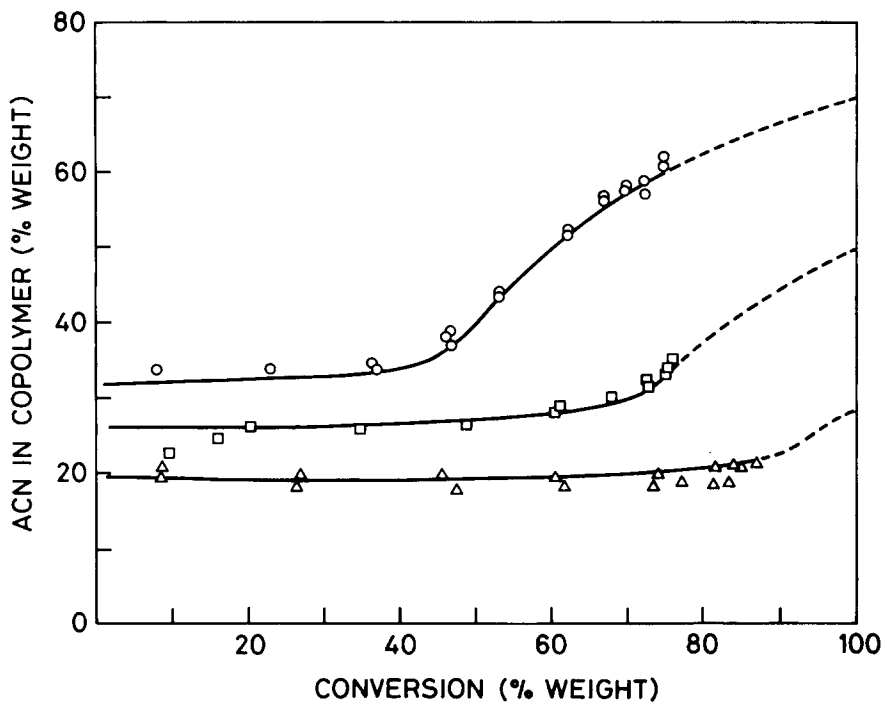
Fig. 5. Copolymer composition vs. conversion for the binary system A–S: (△) run 1; (□) run 2; (○) run 3 of Table II.
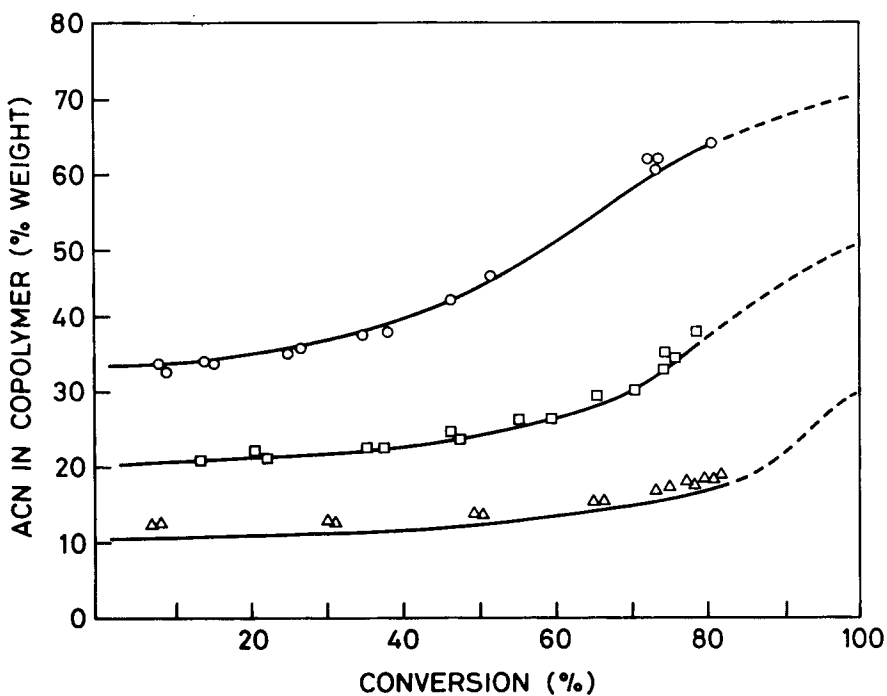

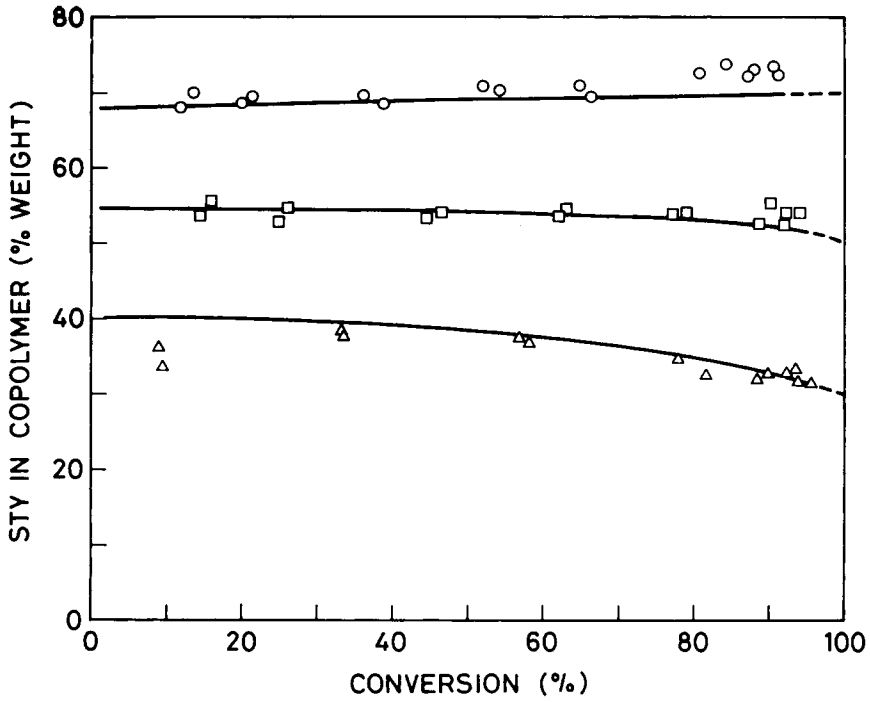Fig. 6. Copolymer composition vs. conversion for the binary system A–M: (△) run 4; (□) run 5; (○) run 6 of Table II.

Fig. 7. Copolymer composition vs. conversion for the binary system S–M: (△) run 7; (□) run 8; (○) run 9 of Table II.
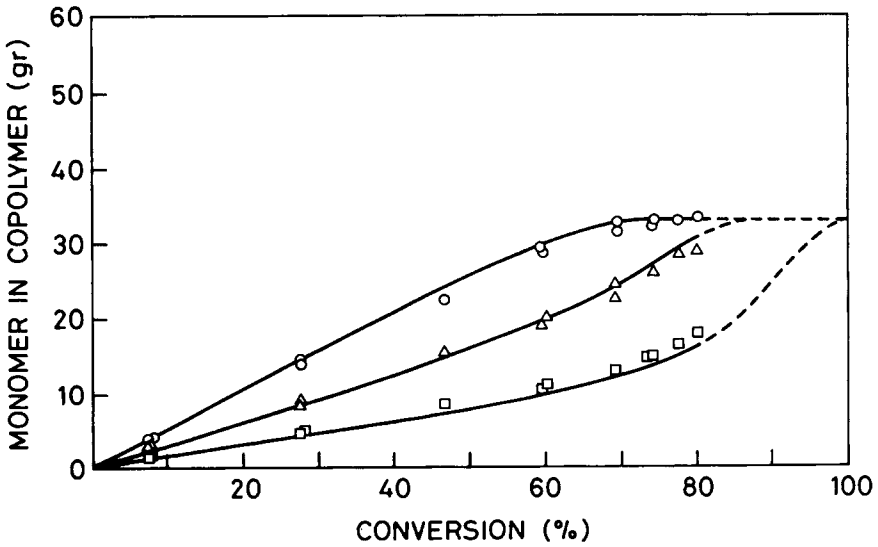

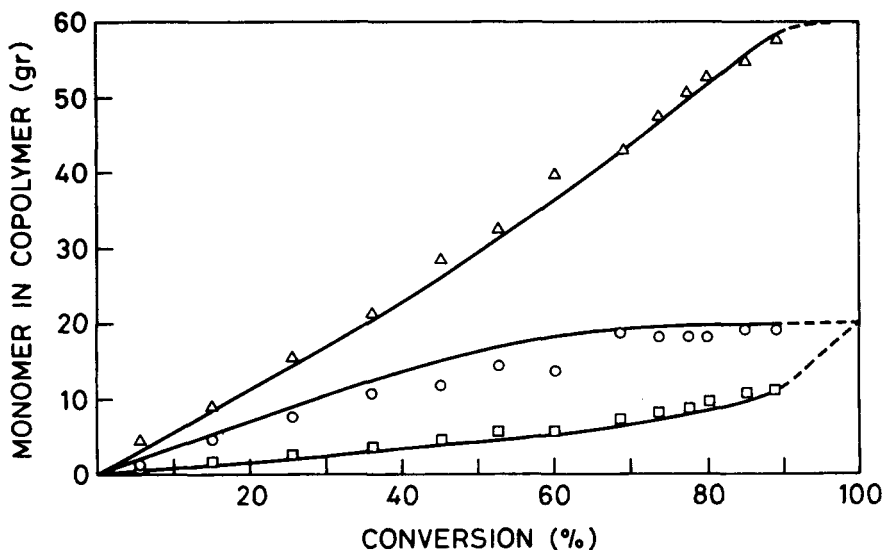Fig. 8. Monomer reacted vs. conversion for the ternary system A (□)–S (○)–M (△); run 10 of Table II.

Fig. 9. Monomer reacted vs. conversion for the ternary system A (□)–S (○)–M (△); run 11 of Table II.

The adopted numerical values of the model parameters, summarized in Table III, have all been taken from the literature without any adjustment: reactivity ratios[16] (bulk values) and binary organic phase–water phase solubility relationships.[14,17] A constant, average value of maximum swelling $(1 - \phi_p)$ has been considered in all runs: $\phi_p = 0.335$.[18,19]

Experimental data and calculated polymer composition vs. conversion values are compared in Figures 5–7 for the three binary systems and in Figures 8–11 for the ternary system at various feed composition values. In all cases
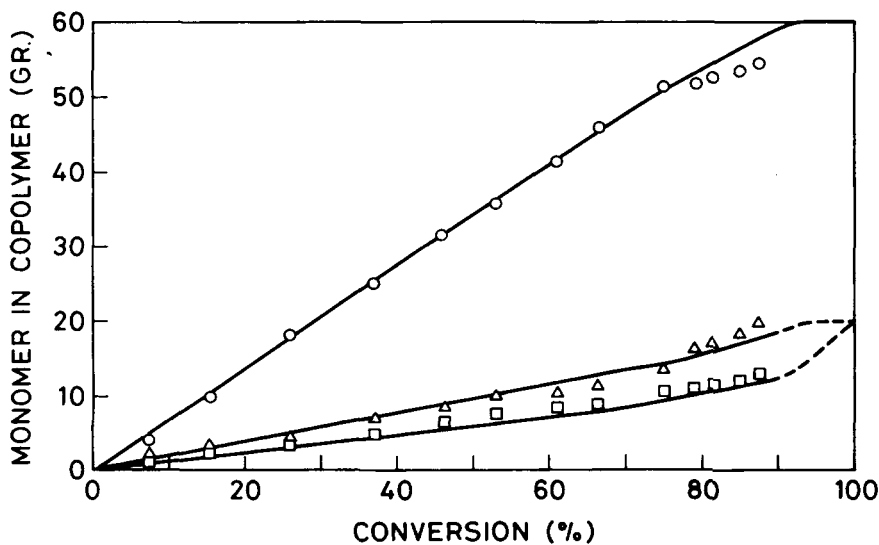

Fig. 10. Monomer reacted vs. conversion for the ternary system A (□)–S (○)–M (△); run 12 of Table II.
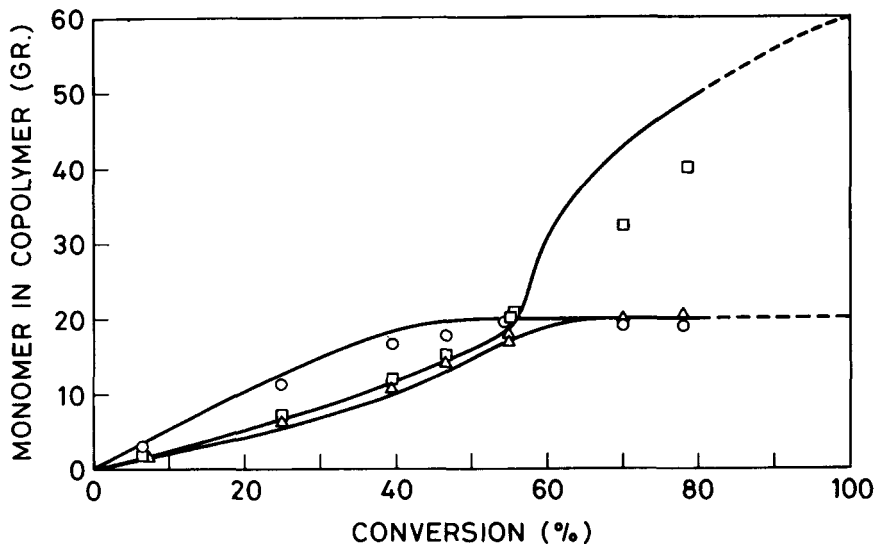
Fig. 11. Monomer reacted vs. conversion for the ternary system A (□)–S (○)–M (△); run 13 of Table II.

the agreement between experimental and calculated values is satisfactory. It is worthwhile pointing out that such an agreement has been obtained using a very simple model, whose parameters have all been taken from independent measurements taken from the literature, without any fitting procedure on the reported experimental data. This result supports the reliability of the pseudo-homopolymerization approach. Moreover, based on the pseudo-homopoly-merization approach it can be argued that a model of the same type could well be used in the case where more than three monomer species are present in the reacting system. It is noticeable that such a model is considerably simpler than the well-known polymer composition equations previously reported in the literature for bulk systems.[16]

CONCLUSION

The kinetic study of a polymerization process where several monomeric species react simultaneously with each other requires the evaluation of the sizes distribution of several particle populations, each characterized by the number and type of radicals contained in each particle. This is obtained through the solution of a set of population balances derived on the basis of the generalized Smith–Ewart theory. In the present work a procedure has been developed for reducing such a set of population balances to a smaller one, where each population is characterized only by the overall number of radicals of any type contained inside each particle. Since the latter is identical to the classical one describing homopolymerization processes, the developed procedure has been called the "pseudo-homopolymerization approach".

The basic approximation is based on the observation that two types of transitions between particles of different populations are possible. The first one involves particles with different overall number of active radicals, and is due to radical entry or exit or termination mechanisms. The second one, instead, is due to propagation reactions and involves particle populations

characterized by the same overall number of active radicals, but of different type. Since in all polymerization systems the transitions of the latter type are much faster, these may be assumed to occur at any time instant under quasi-steady-state conditions with respect to all transitions of the first type.

Since this approximation is quite reasonable for any system of practical interest, the developed pseudo-homogeneous approach is believed to provide a quite accurate description of the true kinetic behavior of multimonomer polymerization systems. Moreover, it reduces the amount of computations to that needed for homopolymerization systems, independently of the number of monomer species involved. This makes possible the detailed kinetic study of such complex reacting systems, resulting in the evaluation of the size distribution function of populations of particles each characterized by the number and type of internal active radicals.

The reliability of the pseudo-homopolymerization approach has been tested by comparison with experimental data relative to binary and ternary systems, involving acrylonitrile styrene, and methyl methacrylate. The reported comparison, in terms of the polymer composition vs. overall conversion data, is not complete, since it does not involve the time evolution of the reacting system. However, the obtained results indicate that the behavior of the ternary system can be predicted from the involved binary polymerization parameters, as it is implied by the pseudo-homopolymerization approach through the relationships defining the pseudo-homopolymerization parameters defined above.

It is worth mentioning that, for some specific systems and particularly in the case of polymer composition vs. conversion behavior, the pseudo-homopolymerization approach produces the same solutions previously reported in the literature. Thus, for example, in the case of a binary system, the ratio of eq. (47) written for component 1 and 2 leads to

$$\frac{dM_{p1}}{dM_{p2}} = \left(\frac{K_{p1}}{k_{p2}} \right) \frac{\overline{M}_1}{\overline{M}_2}$$

which corresponds to the well-known Mayo and Lewis[20] equation for bulk copolymerization. This finding indicates that the copolymer composition vs. conversion behavior is not affected by the compartimentalized nature of the emulsion copolymerization system. In the context of the pseudo-homopolymerization approach this conclusion is apparent for binary systems in eqs. (21)–(22), where it appears that the probability of a particular monomer terminal unit in the chain is independent of all initiation-termination processes. This same result holds true for multicomponent systems, as it appears from eq. (31), which derives from eq. (3), whose reliability in applications has been discussed above.

The value of the pseudo-homopolymerization approach is in the possibility of describing a reacting system involving any number of monomer species, not only as a function of conversion but also of time, using simple mathematical models, i.e., of the same type of those used for homopolymerization systems.

APPENDIX: NOMENCLATURE

a parameter in eq. (38) (see Table I)

A parameter in eq. (55) $= 2\tilde{V}\gamma_p/r_p RT$

b	parameter in eq. (38) (see Table I)
c	parameter in eq. (38) (see Table I)
c_{ij}	rate constant for the bimolecular termination between radical species i and j
c^*	average rate constant for the bimolecular termination, eq. (34)
c'	constant in the expression of c^*, independent on particle size [eq. (40)]
$f(v)$	size (volume) distribution function for the polymer particles
$f_n(v)$	size and total number of active chains distribution function for the polymer particles
$f_{i,j,k}(v)$	size and number of active chains of type i, j, and k distribution function for the polymer particles
f_i	water phase oil droplets solubility law, eq. (51)
g_n^*	average volume growth rate for the polymer particles with n active chains of any type, eq. (35)
g_{ijk}	volume growth rate for the polymer particles, with i, j, and k active chains of type 1, 2, and 3, respectively
g_i	water phase–particle phase solubility law, eq. (52)
k_i	rate constant for the monomolecular termination or desorption of the active chains of type i
k^*	average rate constant for the monomolecular termination, eq. (33)
k'	constant in the expression of k^*, independent on particle size, eq. (40)
k_{pij}	rate constant for the propagation of an active chain of type i with the monomer j
K_{pi}	effective rate constant for the propagation of active chain of any type with the monomer i
$I_\nu(x)$	modified Bessel function of first kind with order ν and argument x
m	number of monomers; ratio between monomolecular and bimolecular termination rates $= k^*/c^*$
m_{ij}	ratio of the number of segments per molecule in species i and j
M_i	total unreacted moles of monomer i in the reactor
M_{pi}	total reacted moles of monomer i in the reactor
M_p	total moles reacted to polymer in the reactor
$\overline{M}_i$	concentration of monomer i within the particles
M_{wi}	concentration of monomer i in aqueous phase
MW_i	molecular weight of monomer i
n	number of active chains of any type within a particle with a particular size
$\bar{n}$	average number of active chains of any type within the particles
n_i	number of active chains of type i within a particle with a particular size
N_p	total number of particles in the reactor per unit volume of aqueous phase
$N_{i,j,k}$	number of particles with any volume containing i, j, and k active chains of type 1, 2, and 3, respectively
N_A	Avogadro's number
P_i	probability of having an active chain with terminal unit of type i
P_{ijk}	probability of having i, j and k active chains of type 1, 2, and 3 within a particle containing $n = i + j + k$ active chains
r_{hi}	rate of homogeneous nucleation by precipitation of an active chains of type i
r_h^*	average rate of homogeneous nucleation, eq. (36)
r_{mi}	rate of micellar nucleation by entry in a micelle of an active chain of type i
r_m^*	average rate of micellar nucleation, eq. (37)
r_d	radius of the oil droplets
r_p	radius of the polymer particles
r_{ij}	reactivity ratio $= k_{pii}/k_{pij}$
R_{pi}	rate of monomer i consumption due to the polymerization reaction
t	time
T	temperature
v	volume of the polymer particle
V_w	total volume of the aqueous phase in the reactor
V_d	total volume of the oil droplets in the reactor
V_p	total volume of the polymer particles in the reactor
$\tilde{V}_i$	molar volume of the monomer i
x	parameter in eq. (39) $= \sqrt{8\alpha}$
y_i	instantaneous mole fraction of monomer i reacted to polymer

Y_i	cumulative mole fraction of monomer i reacted to polymer
α	ratio between radical entry and bimolecular termination rates ρ^*/c^*
α_i	volume fraction of monomer i in the oil droplets
α_{ij}	pseudo-first order rate constant for propagation of the monomer j with the active chains of type i
β_{ij}	$\alpha_{ij}\,MW_j/\rho_p\,N_A$ = rate of polymer volume production for the reaction of propagation of the monomer j with the active chains of type i [see eq. (2)]
γ_d	interfacial tension for the system oil droplets–water
γ_p	interfacial tension for the system polymer particles–water
$\delta(v - \bar{v})$	Dirac function (= 0, except for $v = \bar{v}$)
$\delta_{i,1}$	Kroeneker function (= 0, except for i = 1 where δ = 1)
ϕ_i	volume fraction of monomer i in the polymer particles
ϕ_p	volume fraction of polymer in the polymer particles
μ_i^d	chemical potential of monomer i in the oil droplets
μ_i^p	chemical potential of monomer i in the polymer particles
μ_i^0	chemical potential of monomer i in the reference state
ρ_p	mass density of the polymer
ρ_i	rate of entry in the particles for the active chains of type i
ρ^*	average radical entry in the particles, eq. (32).
ρ'	constant in the expression of ρ^*, independent on particle size, eq. (40)
ξ_{ij}	interaction parameter between component i and component j

References

1. K. W. Min and W. H. Ray, *J. Macromol. Sci., Rev. Macromol. Chem. C*, **11**, 177 (1974).

2. M. J. Ballard, D. H. Napper, R. G. Gilbert, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 939 (1981).

3. M. Nomura and K. Fujita, *Makromol. Chem. Suppl.*, **10–11**, 25 (1985).

4. M. Morbidelli, G. Storti, and E. Giannetti, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2307 (1988).

5. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

6. M. Morbidelli, G. Storti, and S. Carrà, *J. Appl. Polym. Sci.*, **28**, 901 (1983).

7. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1970, p. 823.

8. G. Storti, L. Vitalini, M. Albano, S. Carrà, and M. Morbidelli, IUPAC Symposium SML-87, S. Margherita Ligure (Italy), May 1987.

9. H. M. Hulburt and S. Katz, *Chem. Eng. Sci.*, **19**, 555 (1964).

10. J. T. O'Toole, *J. Appl. Polym. Sci.*, **9**, 129 (1965).

11. G. Buzzi Ferraris and E. Tronconi, *Comput. Chem. Eng.*, **10**(2), 129 (1986).

12. J. Guillot, *Acta Polym.*, **32**(10), 593 (1981).

13. J. Ugelstad, P. C. Mork, I. Nordhuns, H. Mfutakamba, and E. Soleimany, *Makromol. Chem., Suppl.* **10/11**, 215 (1985).

14. *Polymer Handbook*, J. Brandup and E. H. Immergut, Eds., 2nd ed., Wiley, New York, 1975.

15. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

16. G. E. Ham, in *Copolymerization*, High Polymers, Vol. XVIII, G. E. Ham, Ed., Interscience, New York, 1963, p. 42.

17. W. J. Smith, *J. Am. Chem. Soc.*, **70**, 3695 (1948).

18. M. Nomura and K. Fujita, *Makromol. Chem. Suppl.* **10/11**, 25 (1985).

19. C. C. Lin, H. C. Ku, and W. Y. Chiu, *J. Appl. Polym. Sci.*, **26**, 1327 (1981).

20. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **68**, 1594 (1944).