# Kinetics of Long-Chain Branching in Emulsion Polymerization

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ABSTRACT: A mathematical model for the kinetics of long-chain branching in emulsion polymerization systems was developed. The model takes into account the compartmentalization of the reaction system. Large errors were found when the effect of the compartmentalization of the free radicals was ignored. The model predicts that extremely high molecular weights can be reached when termination occurs by combination, and the extent of the chain transfer to polymer reaction is significant. Extensive propagation to terminal double bonds can lead to gel formation irrespective of the type of bimolecular termination. The model was used to analyze the effect of the monomer addition policy on the molecular weights of the copolymers obtained in the emulsion copolymerization of ethyl acrylate and methyl methacrylate.

## Introduction

The prediction of the polymer molecular weight is of paramount importance in the mathematical modeling of emulsion polymerization systems because the mechanical properties of polymers depend on their molecular weight. Mathematical models for the prediction of the molecular weight distribution (MWD) or the corresponding average molecular weights of linear emulsion polymers have been reported.[1-12] However, many emulsion polymerizations are carried out in semicontinuous reactors under starved conditions. Under these circumstances, polymer chain transfer reactions are likely to occur and, hence, branched polymers are produced.

Several mathematical models for the calculation of the molecular weights of branched polymers obtained in bulk and solution polymerizations have been reported.[13-20] However, the kinetics of long-chain branching via chain transfer to the polymer in emulsion polymerization has received much less attention. Tobita[19] extended a mathematical model developed for homogeneous systems to emulsion polymerization. This author considered that the main difference between bulk and emulsion polymerization was the fact that, in emulsion polymerization, the weight fraction of polymer in the polymerization loci (polymer particles) is high from the beginning of the process, whereas in bulk polymerization, the polymer content is zero at the beginning of the process and increases linearly with conversion. This is a simplistic view of the process because the effect of the compartmentalization of the free radicals, which is one of the main features of the emulsion polymerization systems, was ignored.

In the present paper, a mathematical model for the kinetics of long-chain branching in emulsion polymerization systems is presented. The model was used to analyze the effect of the monomer addition policy on the molecular weights of copolymers obtained in the emulsion copolymerization of ethyl acrylate and methyl methacrylate.

## Mathematical Model

In order to develop the mathematical model the following assumptions were made.

(i) The amount of polymer formed in the aqueous phase was negligible when compared with that formed in polymer particles.

(ii) From a kinetic point of view, the whole population of polymer particles could be represented by a monodisperse population of particles.

(iii) The concentrations of the monomers in the monomer-swollen polymer particles, aqueous phase, and monomer droplets were at the thermodynamic equilibrium.

(iv) The free radicals were uniformly distributed (in a statistical sense) in the monomer-swollen polymer particles. This means that the effect of the anchoring of the hydrophilic end group of the growing polymer chain on the surface of the particle was neglected. This is a reasonable assumption for systems in which small mobile radicals are produced by chain transfer reaction and for small polymer particles.[21]

(v) The pseudo steady state for the free radicals applied.

(vi) The growing time of a polymeric chain was less than that required to increase the volume of the polymer particle to an extent that affected the values of the kinetic parameters that control the number of radicals in the polymer particles. Therefore, during the growth of the polymer chain, the distribution of particles containing $j$ radicals remains unchanged. However, the number of radicals in the particle in which the polymer chain is growing can change during the growth of the polymer chain.

(vii) Kinetic parameters were independent of the length of the growing polymer chains. Only single radicals were able to exit to the aqueous phase.

(viii) Radicals entering the polymer particles were considered to be of length one.

(ix) The polymer particles contained a limited number of free radicals, $m$. Therefore, instantaneous termination occurred if a radical entered a polymer particle already containing $m$ radicals.

**Kinetic Mechanisms.** In the presence of a water soluble chemical initiator the emulsion polymerization process can be described by the following reactions and kinetic equations.

Initiation.

$$\mathrm{I} \xrightarrow{f,\,k_\mathrm{I}} 2\mathrm{R}_1 \qquad \text{(R-1)}$$

where $R_1$ represents a single unit radical. The rate of formation of single unit radicals from the initiator is

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$$R_I = 2fk_I I \qquad [\mathrm{mol/(cm^3\,s)}] \tag{1}$$

where $f$ and $k_I$ are the efficiency factor and the rate constant, respectively, for initiator decomposition and $I$ is the amount of initiator present in the reference volume of the reaction medium.

Linear Propagation.

$$R_n + M \xrightarrow{k_p} R_{n+1} \tag{R-2}$$

where $R_n$ represents a radical of length $n$ and M is the monomer. The rate of linear propagation in polymer particles containing $j$ radicals is given by

$$R_p = k_p[M]Y_0^j = k_p[M]jN_j \qquad [\text{monomeric units}/(\mathrm{cm^3\,s})] \tag{2}$$

where $k_p$ is the linear propagation rate constant, [M] is the concentration of monomer in the polymer particles. $Y_0^j$ is the number of radicals present in particles containing $j$ radicals, and $N_j$ is the number of polymer particles containing $j$ radicals in the reference volume.

Propagation to Terminal Double Bonds.

$$M_n(DB) + R_m \xrightarrow{k_p^*} R_{m+n}(LB) \tag{R-3}$$

where $M_n$(DB) denotes an inactive chain of length $n$ containing a terminal double bond and $R_{m+n}$(LB) is a free radical with a length $m + n$ and a long branching point able to grow. The rate of propagation to terminal double bonds in polymer particles containing $j$ radicals is as follows:

$$R_p^* = k_p^*[DB]Y_0^j = k_p^*\frac{Q_0}{N_P N_A v_p}P_{DB}jN_j \qquad [\text{polymer chains}/\mathrm{cm^3\,s}] \tag{3}$$

where $k_p^*$ is the corresponding rate constant, [DB] is the concentration of terminal double bonds, $Q_0$ is the total number of inactive chains in the reference volume, $N_P$ is the number of polymer particles, $v_P$ is the volume of one monomer-swollen polymer particle, $N_A$ is Avogadro's number, and $P_{DB}$ is the probability of finding an inactive chain with a terminal double bond. Implicit in eq 3 is the assumption that both [DB] and $P_{DB}$ are independent of the number of radicals in the polymer particle. This is a reasonable assumption because of the high rate of variation of the number of radicals of a given polymer particle.

Monomer Chain Transfer.

$$R_n + M \xrightarrow{k_{fm}} M_n(DB) + R_1 \tag{R-4}$$

where $M_n$(DB) denotes the terminal double bond created at the end of a macromolecule by the radical deactivation. The rate of this process in polymer particles containing $j$ radicals is

$$R_{fm} = k_{fm}[M]Y_0^j = k_{fm}[M]jN_j \qquad [\text{polymer chains}/(\mathrm{cm^3\,s})] \tag{4}$$

where $k_{fm}$ is the rate constant of the monomer chain transfer reaction.

Polymer Chain Transfer.

$$R_n + M_m \xrightarrow{k_{fp}} M_n + R_m(LB) \tag{R-5}$$

The rate of polymer chain transfer was taken to be proportional to the concentration of units of polymerized monomer. Assuming that the concentration of polymer is the same in all the polymer particles, the rate of polymer chain transfer in the polymer particles containing $j$ radicals is

$$R_{fp} = k_{fp}[Q_1]Y_0^j = k_{fp}\frac{Q_1}{N_P N_A v_P}jN_j \qquad [\text{polymer chains}/(\mathrm{cm^3\,s})] \tag{5}$$

where $k_{fp}$ is the rate constant of the polymer chain transfer reaction and $Q_1$ is the total number of polymerized monomer units in the reference volume.

Termination by Disproportionation.

$$R_n + R_m \xrightarrow{k_{td}} M_n + M_m(DB) \tag{R-6}$$

The rate of termination by disproportionation in polymer particles with $j$ radicals is given by

$$R_{td} = k_{td}\frac{(j-1)j}{v_p N_A}N_j = c_{td}(j-1)jN_j \qquad [\text{termination events}/(\mathrm{cm^3\,s})] \tag{6}$$

where $k_{td}$ is the rate constant of the disproportionation reaction.

Termination by Combination.

$$R_n + R_m \xrightarrow{k_{tc}} M_{n+m} \tag{R-7}$$

The rate of termination by combination in polymer particles containing $j$ radicals is as follows:

$$R_{tc} = k_{tc}\frac{(j-1)j}{v_p N_A}N_j = c_{tc}(j-1)jN_j \qquad [\text{termination events}/(\mathrm{cm^3\,s})] \tag{7}$$

where $k_{tc}$ is the rate constant of the combination reaction.

**Basic Equations.** The goal of the mathematical model is to calculate the average molecular weights in emulsion polymerization systems. Therefore, the material balances for the moments of the molecular weight distribution have to be developed. The so-called tendency model developed by Villermaux and Blavier[13,14] for bulk and solution polymerizations is particularly useful to handle moments of distributions. The details of the model can be found in the corresponding references. To make easier the understanding of the model developed in the present paper, a summary of the tendency model is presented here.

Let us considered a polymer chain distribution, where $f'(n)$ is the number of polymer chains of length $n$. The $k$th order moment of this distribution is

$$Q_k = \sum_{n=1}^{\infty} n^k f'(n) \tag{8}$$

According to eq 8, $Q_0$ is the total number of polymer chains and $Q_1$ is the number of monomeric units in the macromolecules. The distribution $f'(n)$ can be normalized as $f(n) = f'(n)/Q_0$, where $f(n)$ is the fraction of macro-

**Table 1. Moments of the Chain Length Distribution of the Dead Polymer Formed in Polymer Particles Containing *j* Radicals**

| process | $\mu_1'^j$ | $\mu_2'^j$ |
|---|---|---|
| termination by disproportionation | $Y_1^j/Y_0^j$ | $Y_2^j/Y_0^j$ |
| termination by combination | $2Y_1^j/Y_0^j$ | $2Y_2^j/Y_0^j + 2(Y_1^j/Y_0^j)^2$ |
| chain transfer to monomer | $Y_1^j/Y_0^j$ | $Y_2^j/Y_0^j$ |
| propagation to a terminal double bond | $-Q_1/Q_0$ | $-Q_2/Q_0$ |
| transfer to polymer | $Y_1^j/Y_0^j - Q_2/Q_1$ | $Y_2^j/Y_0^j - Q_3/Q_1$ |

molecules that has a length $n$. The moments of this normalized distribution are

$$\mu_k = \sum_{n=1}^{\infty} n^k f(n) = \frac{Q_k}{Q_0} \tag{9}$$

Villermaux and Blavier[13,14] showed that when two polymer samples are mixed, the $k$th order moment of the nonnormalized resulting distribution is given by

$$Q_k = Q_{0_1}\mu_{k_1} + Q_{0_2}\mu_{k_2} \tag{10}$$

During the polymerization process the newly formed polymer is mixed with the existing polymer. The variation of the $k$th order moment of the resulting nonnormalized dead polymer chain length distribution is as follows:[13]

$$\mathrm{d}Q_k/\mathrm{d}t = \sum_i R_i \mu_{ki}' \tag{11}$$

where $R_i$ is the rate of formation of dead polymer chains through the process $i$ and $\mu_{ki}'$ is the $k$th order moment of the normalized chain length distribution of the dead polymer that is produced by the process $i$.

A similar equation can be written for the active polymer:

$$\mathrm{d}Y_k/\mathrm{d}t = 0 = \sum_i R_i \lambda_{ki}' \tag{12}$$

where $Y_k$ is the $k$th order moment of the nonnormalized chain length distribution of the active polymer and $\lambda_{ki}'$ is the $k$th order moment of the normalized distribution of the active polymer formed through process $i$. Notice that in eq 12 the pseudo steady state assumption is made.

According to the kinetic mechanism described before, dead polymer chains are formed by chain transfer to both monomer and polymer and by the bimolecular termination reaction (combination and disproportionation). In addition, they disappear by propagation to terminal double bonds and by chain transfer to polymer. Both the rate of some of these processes and the chain length distribution of the dead macromolecules depend on the number of radicals that are in the polymer particle in which the dead macromolecule is formed at the moment in which it is formed, as well as on the history of the polymer particle while the macromolecule is growing.

The balance for the $k$th order moment of the chain length distribution of dead macromolecules formed in particles containing $j$ radicals is as follows:

$$\frac{\mathrm{d}Q_k^j}{\mathrm{d}t} = 2R_{\mathrm{td}}^j \mu_{k\,\mathrm{td}}'^j + R_{\mathrm{tc}}^j \mu_{k\,\mathrm{tc}}'^j + R_{\mathrm{fm}}^j \mu_{k\,\mathrm{fm}}'^j + R_{\mathrm{p}}^{*j} \mu_{k\mathrm{p}*}'^j + R_{\mathrm{fp}}^j \mu_{k\,\mathrm{fp}}'^j \tag{13}$$

where $R_i^j$ is the rate of formation of dead polymer chains through the process $i$ in polymer particles containing $j$ radicals ($2R_{\mathrm{td}}^j$ for the termination by disproportionation), and $\mu_{ki}'^j$ is the $k$th order moment of the normalized distribution of the dead polymer chains formed through process $i$ in polymer particles containing $j$ radicals.

These moments depend on the moments of the chain length distribution of growing macromolecules. Thus when termination occurs by disproportionation, the moments of the distribution of dead polymer chains are the same as those of the originating growing chains. However, for other termination mechanisms such as combination the relationship between the moments of the growing and dead chains is not that simple. The values of $\mu_{ki}'^j$ adapted from the pioneering work of Villermaux and Blavier[13] are presented in Table 1. Notice that when these values are included in eq 13, this equation presents a closure problem because every moment depends on the next higher.

The balance of the $k$th order moment of the chain length distribution of growing macromolecules in particles containing $j$ radicals is given by eq 14, where $R_{\mathrm{abs}}^j$ and $R_{\mathrm{d}}^j$ are the rates of radical entry and radical desorption, respectively, in polymer particles containing $j$ radicals, $\lambda_{k\mathrm{abs}}'^j$ and $\lambda_{k\mathrm{fm}}'^j$ are the $k$th order moments of the polymer chains resulting from absorbed and monomeric radicals, respectively, $\lambda_{k\mathrm{d}}'^{j+1}$ is the $k$th order moment of the polymer chains that would be formed in particles with $j + 1$ radicals from the single unit monomers if they did not desorb, $\lambda_{k\mathrm{fp}}'^j$ is the $k$th order moment of the active polymer chains formed by chain transfer to polymer, and $\lambda_{k\mathrm{p}*}'^j$ is the $k$th order moment of the growing chains formed by propagation to double terminal bonds. $R_{k\mathrm{abs}}^j$ and $R_{\mathrm{d}}^j$ are given by

$$R_{\mathrm{abs}}^j = k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} N_j \ [\text{radicals}/(\mathrm{cm}^3\ \mathrm{s})] \tag{15}$$

$$R_{\mathrm{d}}^j = k_{\mathrm{d}} j N_j \ [\text{radicals}/(\mathrm{cm}^3\ \mathrm{s})] \tag{16}$$

where $k_{\mathrm{abs}}$ is the entry rate coefficient, $[\mathrm{R}]_{\mathrm{w}}$ is the concentration of radicals in the aqueous phase, and $k_{\mathrm{d}}$ is the desorption rate coefficient.

$\lambda_{k\mathrm{abs}}'^j$ and $\lambda_{k\mathrm{fm}}'^j$ are the $k$th moments of the growing polymer chain distribution resulting from single unit radicals formed by entry and monomer chain transfer reaction, respectively. Assuming that all the single radicals are kinetically equivalent, $\lambda_{k\mathrm{abs}}'^j = \lambda_{k\mathrm{fm}}'^j$. For homogeneous systems, Villermaux and Blavier[13] calculated the first moments of the growing polymer chain distribution from the Schultz–Flory distribution. In the calculation, they assumed that the growing time of the polymeric chain was less than that required for a significant change in the reaction conditions. This is also likely to apply to emulsion polymerization systems, but in these systems, the number of radicals contained in the polymer particle in which the active chain is growing varies during the chain growth due to radical entry, radical desorption, and bimolecular termination of the companion chains. Under these circumstances, the Schultz–Flory distribution cannot be used. Storti et al.[11,12] developed a model for evaluating the instantaneous length distribution of linear polymer in emulsion polymerization systems, based on the mathematics of Markov processes. The first moments of the chain length distribution of linear active chains in particles containing $1 \le j \le m$ radicals are given by

$$\lambda_{0\mathrm{L}} = (\mathbf{I} - \mathbf{Q})^{-1}\mathbf{R} \tag{17}$$

$$\lambda_{1\mathrm{L}} = \mathbf{Q}[(\mathbf{I} - \mathbf{Q})^{-1}]^2\mathbf{R} \tag{18}$$

$$\lambda_{2\mathrm{L}} = \mathbf{Q}^2[(\mathbf{I} - \mathbf{Q})^{-1}]^3\mathbf{R} + \lambda_{1\mathrm{L}} \tag{19}$$

where $\lambda_{k\mathrm{L}}$ is the $(m \times 1)$ column vector containing the $k$th order moment of the chain length distribution of linear

$$\frac{\mathrm{d}\,Y_k^j}{\mathrm{d}t} = 0 = \underbrace{R_{abs}^{j-1}\,(j-1)\,\frac{Y_k^{j-1}}{Y_0^{j-1}}}_{\left(\substack{\text{Growing polymer chains}\\ \text{transferred from polymer}\\ \text{particles with (j-1) radicals}\\ \text{after absorption of one}\\ \text{radical}}\right)} + \underbrace{R_{abs}^{j-1}\,\lambda_{kabs}^{\prime j}}_{\left(\substack{\text{Contribution of the growing}\\ \text{polymer chains resulting}\\ \text{from the absorbed radicals}}\right)} + \underbrace{\delta_{j=m-1}\,R_{abs}^{j+1}\,j\,\frac{Y_k^{j+1}}{Y_0^{j+1}}}_{\left(\substack{\text{Growing polymer chains}\\ \text{transferred from polymer}\\ \text{particles containing m}\\ \text{radicals after absorption}\\ \text{of one radical}}\right)}$$

$$\underbrace{-\,R_{abs}^{j}\,j\,\frac{Y_k^{j}}{Y_0^{j}}}_{\left(\substack{\text{Growing polymer chains}\\ \text{lost when a radical enters}\\ \text{polymer particles with}\\ \text{j radicals}}\right)} + \underbrace{\delta_{j<m}\,R_d^{j+1}\left((j+1)\frac{Y_k^{j+1}}{Y_0^{j+1}} - \lambda_{kd}^{\prime j+1}\right)}_{\left(\substack{\text{Growing polymer chains}\\ \text{transferred from polymer}\\ \text{particles with (j+1) radicals}\\ \text{after exit of one radical}}\right)} - \underbrace{R_d^{j}\,j\,\frac{Y_k^{j}}{Y_0^{j}}}_{\left(\substack{\text{Growing polymer chains}\\ \text{lost when a desorption}\\ \text{reaction occurs in polymer}\\ \text{particles containing j radicals}}\right)}$$

$$+ \underbrace{\delta_{j<m-1}\left(R_{tc}^{j+2} + R_{td}^{j+2}\right) j\,\frac{Y_k^{j+2}}{Y_0^{j+2}}}_{\left(\substack{\text{Growing polymer chains}\\ \text{transferred from polymer}\\ \text{particles with (j+2) radicals}\\ \text{when a bimolecular termi-}\\ \text{nation occurs in these}\\ \text{particles}}\right)} - \underbrace{\left(R_{tc}^{j} + R_{td}^{j}\right) j\,\frac{Y_k^{j}}{Y_0^{j}}\,\delta_{j>1}}_{\left(\substack{\text{Growing polymer chains}\\ \text{lost when a bimolecular}\\ \text{termination occurs in}\\ \text{polymer particles with}\\ \text{j radicals}}\right)}$$

$$+ \underbrace{R_{fm}^{j}\,\lambda_{kfm}^{j}}_{\left(\substack{\text{Contribution of the polymer}\\ \text{chains resulting from the}\\ \text{monomeric radicals formed}\\ \text{after a monomer chain}\\ \text{transfer reaction}}\right)} - \underbrace{R_{fm}^{j}\,\frac{Y_k^{j}}{Y_0^{j}}}_{\left(\substack{\text{Loss of growing}\\ \text{chains by monomer}\\ \text{chain transfer}}\right)} + \underbrace{R_{fp}^{j}\,\lambda_{kfp}^{\prime j}}_{\left(\substack{\text{Growing chains}\\ \text{formed by chain}\\ \text{transfer to polymer}}\right)}$$

$$- \underbrace{R_{fp}^{j}\,\frac{Y_k^{j}}{Y_0^{j}}}_{\left(\substack{\text{Growing chains}\\ \text{lost by chain}\\ \text{transfer to polymer}}\right)} + \underbrace{R_p^{*j}\,\lambda_{kp*}^{\prime j}}_{\left(\substack{\text{Growing chains formed}\\ \text{by propagation to}\\ \text{terminal double bonds}}\right)} - \underbrace{R_p^{*j}\,\frac{Y_k^{j}}{Y_0^{j}}}_{\left(\substack{\text{Growing chains lost}\\ \text{by propagation to}\\ \text{terminal double bonds}}\right)} \tag{14}$$

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active chains in each type of polymer particle (i.e., with a given number of active chains), **Q** is the $(m \times m)$ matrix of the probabilities for the growing chain of adding a new monomeric unit, accounting for all possible events which may change its environment by changing the number or type of the companion chains, **I** is the identity matrix, and **R** is an $(m \times 1)$ column vector containing the probabilities for termination in each type of polymer particle accounting for the changes of environment. **Q** and **R** are given by

$$\mathbf{Q} = (\mathbf{I} - \bar{\mathbf{Q}})^{-1}\bar{\mathbf{S}} \tag{20}$$

$$\mathbf{R} = (\mathbf{I} - \bar{\mathbf{Q}})^{-1}\bar{\mathbf{R}} \tag{21}$$

where $\bar{\mathbf{Q}}$ is the $(m \times m)$ matrix accounting for the changes in the number of radicals in the polymer particles, $\bar{\mathbf{S}}$ is the $(m \times m)$ diagonal matrix accounting for the probability of propagation, and $\bar{\mathbf{R}}$ is the $(m \times 1)$ column vector containing the probabilities of termination. These matrices are summarized in Table 2.

The first moments of the distribution of active polymer chains formed by both chain transfer to polymer and propagation to double terminal bonds can be calculated by operating in the $z$-transformed domain.[13] Application of this method to emulsion polymerization gives

$$\lambda_{1fp}^{\prime j} = \frac{Q_2}{Q_1} + \lambda_{1L}^{j} \tag{22}$$

$$\lambda_{2fp}^{\prime j} = \lambda_{2L}^{j} + 2\lambda_{1L}^{j}\frac{Q_2}{Q_1} + \frac{Q_3}{Q_1} \tag{23}$$

$$\lambda_{1p*}^{\prime j} = \frac{Y_1^j}{Y_0^j} + \frac{Q_1}{Q_0} + \lambda_{1L}^{j} \tag{24}$$

**Table 2. Matrices $\bar{Q}$, $\bar{S}$, and $\bar{R}$ Corresponding to an Emulsion Polymerization System with a Maximum Number of *m* Radicals per Particle**

for $i \geq 1, j \leq m \qquad q_{i,j} = 0$

exception:

$$q_{j,j-2} = \frac{(c_{tc} + c_{td})(j-1)(j-2)}{D_j}$$

$$q_{j,j-1} = \frac{k_d (j-1)}{D_j} + \frac{k_{abs}[R_w]}{D_j}\frac{(j-1)}{j}\,\delta_{n=m}$$

$$q_{j,j+1} = \frac{k_{abs}[R_w]}{D_j}$$

$$\bar{Q} = \left|\begin{array}{cccccccc} 0 & - & & & & & & \\ - & 0 & - & & & & 0 & \\ - & - & 0 & - & & & & \\ & - & - & 0 & - & & & \\ & & q_{j,j-2} & q_{j,j-1} & 0 & q_{j,j+2} & & \\ & & & - & - & 0 & - & \\ & 0 & & & - & - & 0 & - \\ & & & & & - & - & 0 \end{array}\right|$$

for $i \geq 1, j \leq m \qquad s_{i,j} = 0$

exception:

$$s_{j,j} = \frac{k_p[M]}{D_j}$$

$$\bar{S} = \left|\begin{array}{cccccccc} - & & & & & & & \\ & - & & & & & & \\ & & - & & & & 0 & \\ & & & - & & & & \\ & & & & s_{j,j} & & & \\ & & & & & - & & \\ & 0 & & & & & - & \\ & & & & & & & - \end{array}\right|$$

for $1 \leq j \leq m$

$$r_{j,1} = \frac{k_{fm}[M]}{D_j} + \frac{2(c_{tc} + c_{td})(j-1)}{D_j} + \frac{k_{fp}[Q_1]}{D_j} + \frac{k_p^*[DB]}{D_j}$$

$$\bar{R} = \left|\begin{array}{c} - \\ - \\ - \\ - \\ r_{j,1} \\ - \\ - \\ - \end{array}\right|$$

where

$$D_j = \sum_i q_{i,j} + \sum_i s_{i,j} + r_{j,1}$$

$$\lambda'^{j}_{2p*} = \frac{Y_2^j}{Y_0^j} + 2\frac{Y_1^j}{Y_0^j}\frac{Q_1}{Q_0} + \frac{Q_2}{Q_0} + \lambda^j_{2L} + 2\lambda^j_{1L}\left(\frac{Q_1}{Q_0} + \frac{Y_1^j}{Y_0^j}\right) \quad (25)$$

where $\lambda'^{j}_{kL}$ is the *j*th element of the $\lambda_{\mathbf{kL}}$ vector. Notice that eq 23 includes the term $Q_3/Q_1$ that caused a closure problem in eq 13, because the second moment depends on the third moment. This closure problem can be solved by adding eqs 13 and 14 because the terms in the higher moment cancel. Therefore, the moments of the overall polymer chain length distribution are as follows:

$$\frac{dM_k}{dt} = \sum_{j=1}^{m}\frac{dQ_k^j}{dt} + \sum_{j=1}^{m}\frac{dY_k^j}{dt} \quad (26)$$

The instantaneous average molecular weights are

$$\bar{M}_n = \frac{dM_1/dt}{dM_0/dt}P_m \quad (27)$$

**Table 3. Values of Parameters Used in the Illustrative Simulations**

$k_p = 1.5 \times 10^6$ cm$^3$/(mol s)
$k_{fm} = 40$ cm$^3$/(mol s)
$c_{tc} + c_{td} = 180$ s$^{-1}$
$k_{abs} = 7 \times 10^9$ cm$^3$/(mol s)
$k_d = 5 \times 10^{-3}$ s$^{-1}$
$(k_{tc} + k_{td})_w = 2 \times 10^{11}$ cm$^3$/(mol s)
$k_I = 10^{-6}$ s$^{-1}$
$f = 0.5$
$[M]_p = 5.5 \times 10^{-3}$ mol/cm$^3$
$[I] = 5 \times 10^{-5}$ mol/cm$^3$
$N_p = 10^{13}$ part/cm$^3$

$$\bar{M}_w = \frac{dM_2/dt}{dM_1/dt}P_m \quad (28)$$

where $P_m$ is the molecular weight of the monomeric unit.

To solve eqs 27 and 28, the number distribution of polymer particles containing *j* radicals is required. This can be calculated using the approach proposed by Ballard et al.[22] This method is based on the truncation of the Smith–Ewart equations[23] by assuming that the polymer particles can contain a maximum of *m* radicals, i.e., that

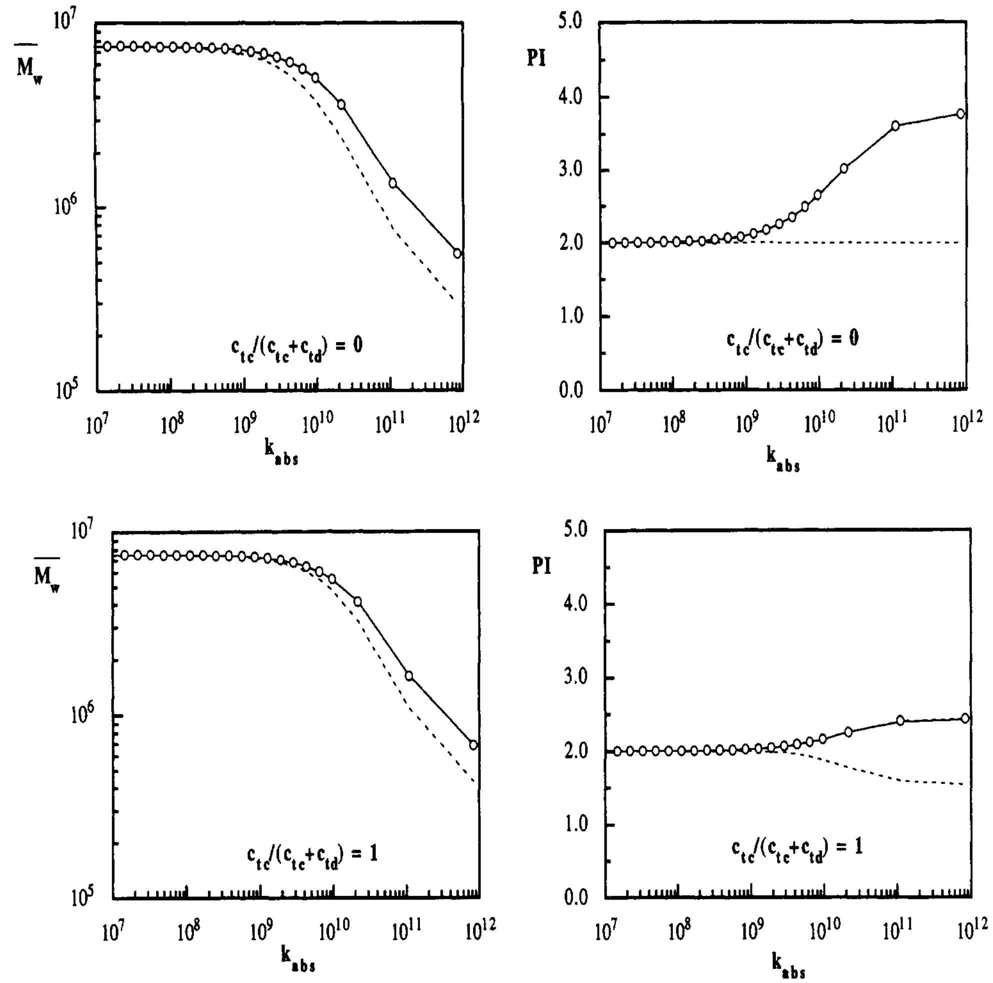

**Figure 1.** Comparison between the predictions of the present model (—), the Forcada and Asua model[10] (○), and the present model neglecting the compartmentalization of the emulsion system (- - -).

the entry of a radical into a particle containing $m$ radicals causes instantaneous bimolecular termination, leaving $(m - 1)$ radicals. Under steady state conditions one obtains

$$N_{m-1} = [k_{abs}[R]_w + mk_d + (c_{tc} + c_{td})m(m-1)]N_m/k_{abs}[R]_w \quad (29)$$

$$N_{m-2} = \{k_{abs}[R]_w + (m-1)k_d + (c_{tc} + c_{td})(m-1)(m-2)N_{m-1} - k_d m N_m - k_{abs}[R]_w N_m\}/k_a[R]_w \quad (30)$$

$$N_j = \{[k_{abs}[R]_w + k_d(j+1) + (c_{tc} + c_{td})(j+1)j]N_{j+1} - k_d(j+2)N_{j+2} - (c_{tc} + c_{td})(j+2)N_{j+3}\}/k_{abs}[R]_w \qquad j = m-3, ..., 2, 1, 0 \quad (31)$$

where $[R]_w$ is the concentration of radicals in the aqueous phase that can be calculated from the balance of radicals in the aqueous phase:

$$0 = 2fk_I I N_A + k_d \bar{n} N_P - k_{abs}[R]_w N_P - 2(k_{tc} + k_{td})_w [R]_w^2 N_A \quad (32)$$

The method of solving eqs 29–32 is to set a value for $m$, assuming $N_m$, and to calculate $N_{m-1}$, ..., $N_1$, $N_0$ from eqs 29–31. The assumed value of $N_m$ is corrected by comparing the actual number of polymer particles, $N_P$, with $\sum N_j$. The calculation is repeated for increasing values of $m$, until convergence is reached. The convergence of this method is very fast.

## Illustrative Simulations

In order to illustrate the effect of the kinetic parameters on the average molecular weights, some simulations were carried out using the reaction conditions and the values of the kinetic parameters given in Table 3. The model was first checked by comparing its predictions (with $k_{fp} = k_{p*} = 0$) and those of the model proposed by Forcada and Asua[10] for linear polymers. Figure 1 shows that a perfect agreement between the two models was achieved. On the other hand, when the moments of the linear growing polymer chains were calculated without taking into consideration the changes in the environment where the chain is growing, the predictions of the present model deviated. This indicates that the kinetic models developed for the calculation of molecular weight distribution in homogeneous systems (bulk and solution polymerization) cannot be used directly in emulsion polymerization systems. On the other hand, it has to be pointed out that the results presented in Figure 1 are just an indirect check for the model, because they only show that the model behaves properly in one of its limits (linear chains).

Figure 2 presents the effect of $k_{fp}$ and the volume fraction of polymer in the polymer particles on the weight average molecular weight for various values of $c_{tc}/(c_{tc} + c_{td})$. It can be seen that an extremely high molecular weight polymer (gel) can be formed when the polymer chain transfer reaction occurs to a significant extent and termination is by combination. On the other hand, termination by disproportionation does not lead to gel formation.

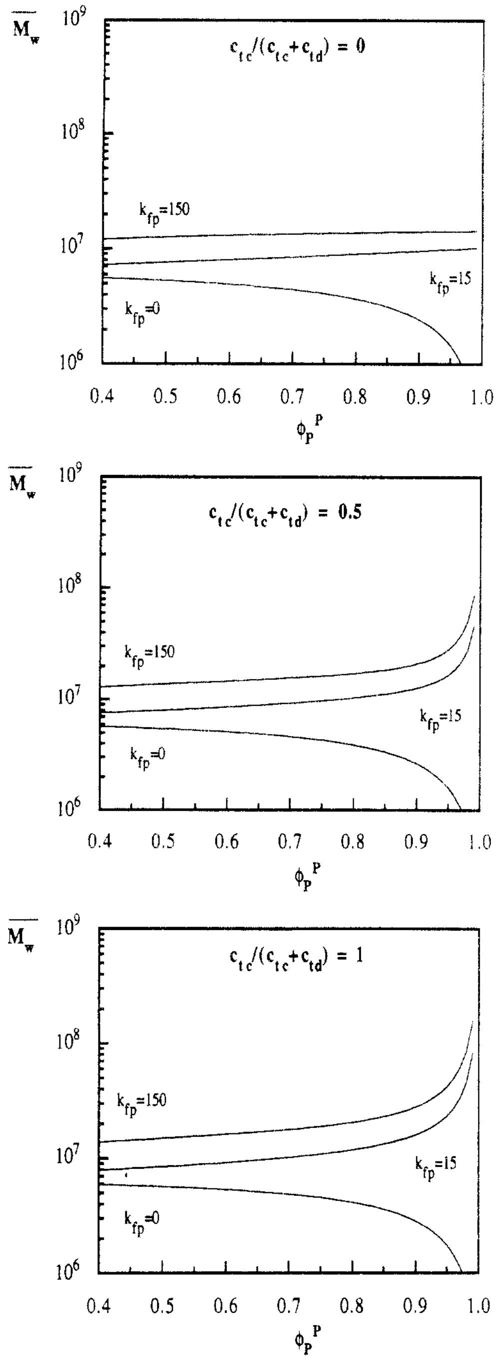

**Figure 2.** Effect of the chain transfer to the polymer and the volume fraction of the polymer in the polymer particles of $\bar{M}_w$ as a function of the type of bimolecular termination.

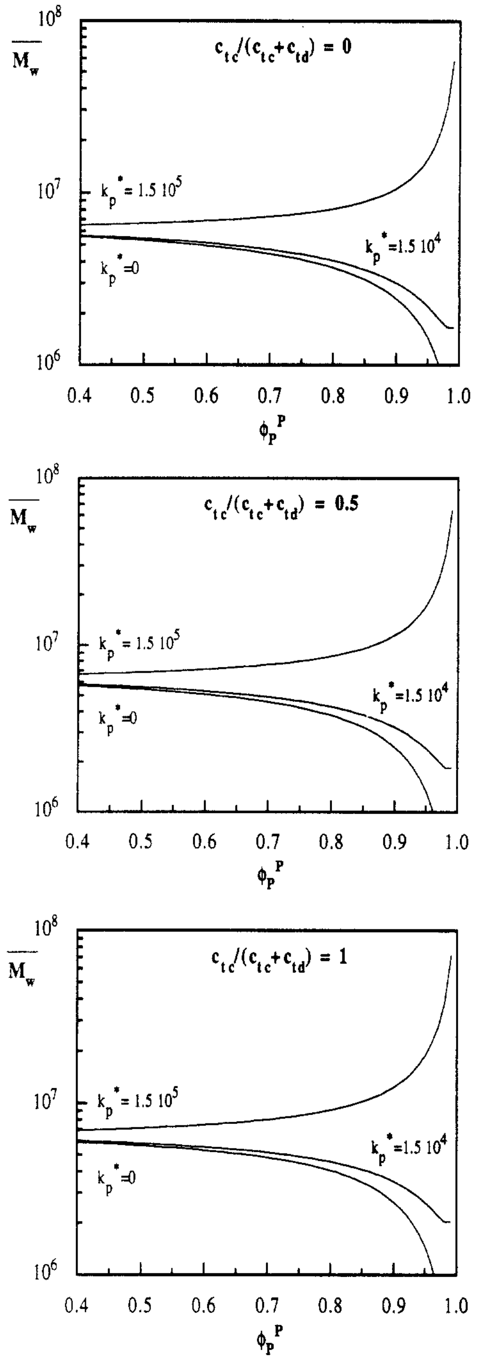

**Figure 3.** Effect of the propagation to terminal double bonds on $\bar{M}_w$ as a function of the type of bimolecular termination.

Figure 3 presents the effect of the propagation to terminal double bonds on $\bar{M}_w$ as a function of the type of bimolecular termination. It can be seen that gel can be formed irrespective of the type of bimolecular termination. When the propagation to terminal double bonds is significant, the terminal double bonds generated by the disproportionation reaction promote reaction R-3 that leads to molecular structures similar to those produced through bimolecular termination by combination.

## Experimental Section

Monomers, ethyl acrylate (EA or A) and methyl methacrylate (MMA or B), were distilled under a reduced pressure of dry nitrogen. The purified monomers were stored at −18 °C until use. The rest of the materials were used as received. Distilled and deionized water (DDI) was used throughout the work. Polymerizations were carried out in a 2 L reactor equipped with stirrer, reflux condenser, sampling device and inlet system for nitrogen. A seed of EA/MMA with a weight ratio of 50/50 was prepared in a batch process using the recipe given in Table 4. The polymerization was carried out at 70 °C for 3 h. Then the latex was heated to 90 °C and this temperature maintained for 15 h to decompose all of the initiator. A seed of 71 nm in diameter was obtained. Four polymerizations were carried out in order to investigate the effect of the monomer feed rate on the molecular weights. These were as follows.

(i) A seeded batch emulsion copolymerization was carried out using the recipe given in Table 4 (run 1).

(ii) A semistarved process was carried out using the recipe given in Table 4 (run 2). The seed, all of the ethyl acrylate (less reactive monomer), initiator, and buffer, and a fraction of the methyl methacrylate (more reactive monomer), surfactant, and water were initially charged into the reactor. An aqueous emulsion of the remaining MMA was fed using a computer controlled metering pump. Figure 1 presents the feed rate used in this reaction that was calculated by means of the method proposed by Arzamendi et al.[24-28]

**Table 4. Recipe Used for the Polymerizations**

| | seed $T = 70$ °C | seeded batch (run 1) $T = 60$ °C | semistarved process (run 2) $T = 60$ °C | | starved process (runs 3, 4) $T = 60$ °C | |
|---|---|---|---|---|---|---|
| | | | initial charge | feed | initial charge | feed |
| ethyl acetate (g) | 300 | 157 | 157 | | | 157 |
| methyl methacrylate (g) | 300 | 157 | 53.8 | 103.2 | | 157 |
| $K_2S_2O_8$ (g) | 3.33 | 0.4 | 0.4 | | 0.4 | |
| sodium lauryl sulfate (g) | 26.0 | 11 | 7.38 | 3.62 | | 11.0 |
| $NaHCO_3$ (g) | 4.24 | 0.75 | 0.75 | | 0.75 | |
| DDI water (g) | 1200 | 941 | 632.4 | 308.7 | 50 | 891 |
| seed | | 238 | 238 | | 238 | |

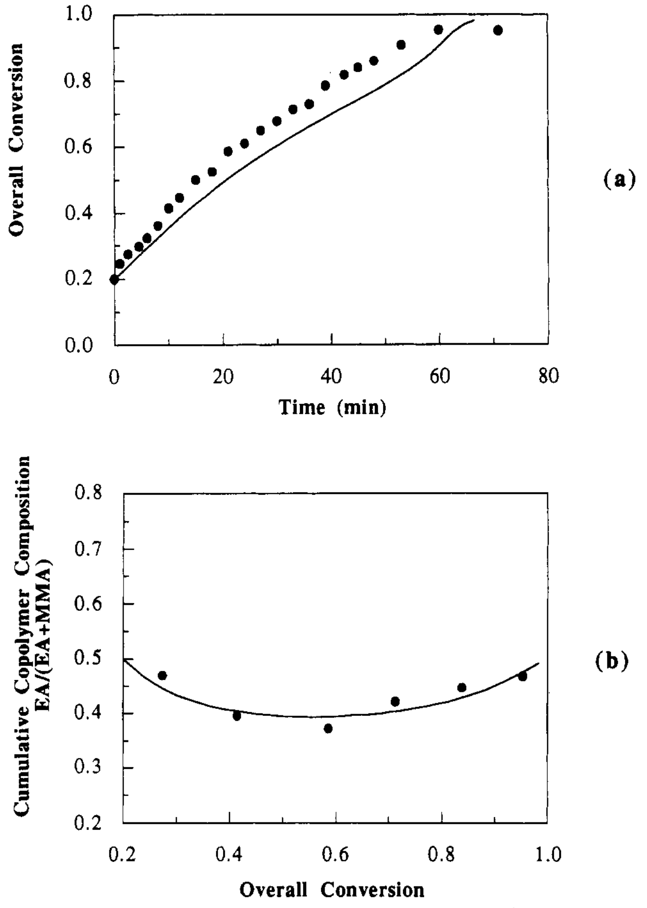

**Figure 4.** Evolution of the overall conversion and cumulative copolymer composition for the seeded batch emulsion copolymerization. Legend: (●) experimental data; (—) model.

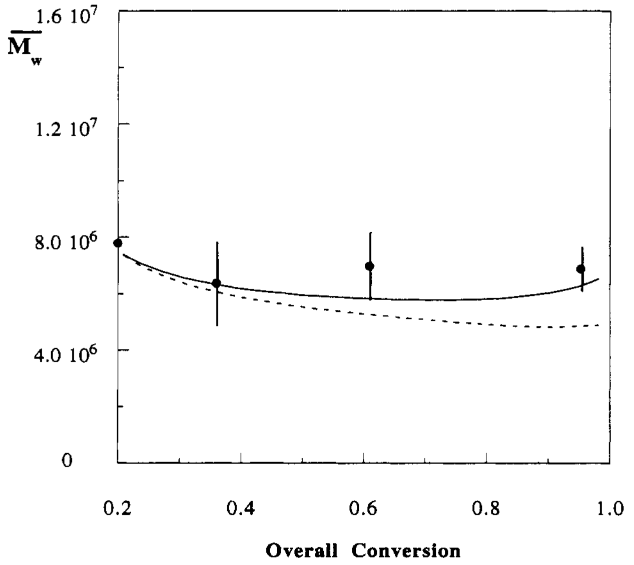

**Figure 5.** Evolution of the weight average molecular weight for the batch emulsion polymerization. Legend: (●) experimental data; (—) model including polymer transfer reactions ($k_{fpEA}$ = 10, $k_{fpMMA}$ = 5.73); (- - -) model considering $k_{fp}$ = 0.

(iii) Two starved processeses were carried out using the recipe given in Table 4. Neat monomer addition was used, and an aqueous solution of surfactant was added in a separate stream. In the first of these experiments (run 3), the feed rate was adjusted to obtain the same total feed time as in the case of the semistarved process. In the second, a feed time double that of the semistarved process was used (run 4).

Samples were withdrawn during the reaction, the polymerization was short stopped with hydroquinone, the overall conversion was measured gravimetrically, and the copolymer composition was determined by $^1H$ NMR and gas chromatography. The particle size was measured by dynamic light scattering.

High molecular weight polymers as expected in emulsion polymerization when long-chain branching occurs are difficult to characterize by GPC. Therefore, the weight average molecular weights were measured by light scattering using a Malvern 4700 dynamic light scattering apparatus at 25 °C and with an incident light of wavelength 514.5 nm. The EA/MMA copolymers were dissolved in tetrahydrofuran (THF) and the specific refractive index increment ($dn/dc$) determined using LDC Analytical KMX-16, a differential refractometer. Toluene was used as a reference to calibrate the light scattering photometer. The light scattering measurements were carried out over a range of polymer concentrations from $1 \times 10^{-4}$ to $1 \times 10^{-3}$ g/cm$^3$, varying the observation angle from 30 to 140°. These data were fitted with the following equation by means of a nonlinear regression method.

$$\frac{Kc}{R(q,c)} = \frac{1}{\bar{M}_w\left(1 - c_1 \sin^2 \frac{\theta}{2} + c_2 \sin^4 \frac{\theta}{2}\right)} + 2\bar{A}_2 c \tag{33}$$

where $K$ is an optical constant that depends on the refractive index, $c$ is the polymer concentration, $R(q,c)$ is the Rayleigh ratio, and $\bar{A}_2$ is the second virial coefficient. The values of $\bar{M}_w$, $c_1$, $c_2$, and $\bar{A}_2$ were estimated to fit the experimental data.

It should be noted that eq 33 results from the truncation of two series.[29] This limits the maximum values of $c$ and $\theta$ that can be used. In order to determine the optimal range of both $c$ and $\theta$, commercial standards of polystyrene dissolved in toluene were analyzed. It was found that for a polymer concentration range from $1 \times 10^{-4}$ to $1 \times 10^{-3}$ g/cm$^3$, $\theta$ has to be lower than 60° when the molecular weight is greater than $10 \times 10^6$ whereas it can be as high as 140° for molecular weights lower than $1 \times 10^6$.

## Results and Discussion

Figure 4 presents the evolution of the overall conversion and the cumulative copolymer composition during the seeded batch emulsion copolymerization. The overall conversion was defined as follows:

$$X = \frac{\text{total amount of polymer in the reactor}}{\text{total amount of both monomers in the recipe + amount of polymer seed}} \tag{34}$$

It can be seen that a heterogeneous copolymer was obtained. Because of the larger MMA reactivity ratio, a MMA-rich copolymer was obtained at the beginning of the reaction. Figure 5 presents the evolution of the weight

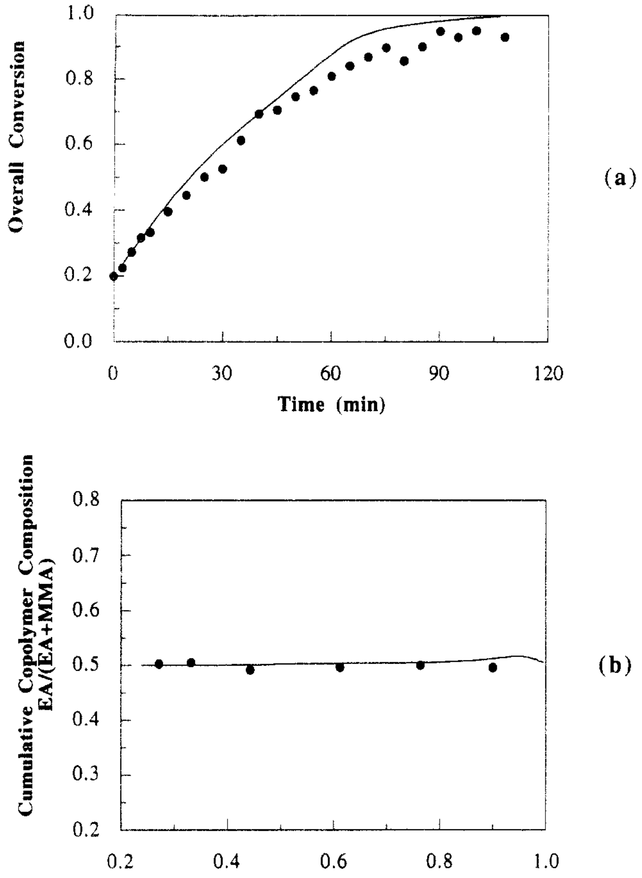

**Figure 6.** Evolution of the overall conversion and cumulative copolymer composition for the semistarved emulsion copolymerization. Legend: (●) experimental data; (—) model.

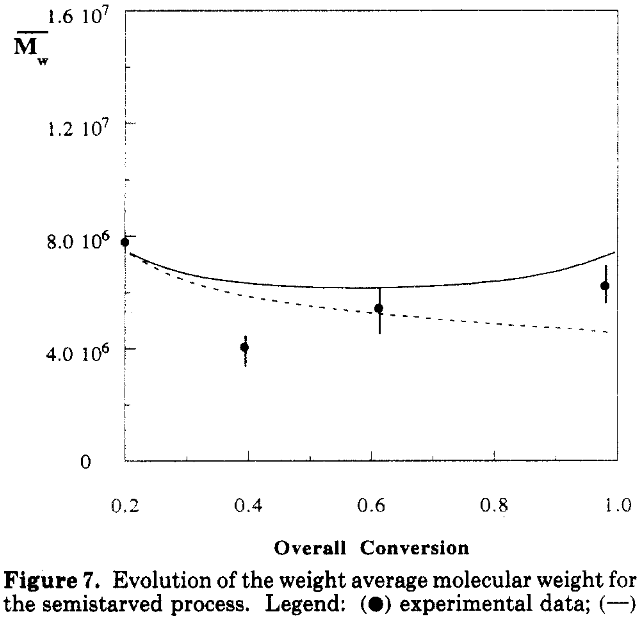

**Figure 7.** Evolution of the weight average molecular weight for the semistarved process. Legend: (●) experimental data; (—) model including polymer transfer reactions ($k_{fpEA}$ = 10, $k_{fpMMA}$ = 5.73); (- - -) model considering $k_{fp}$ = 0.

average molecular weight during the seeded batch emulsion copolymerization measured by light scattering. The 95% confidence intervals are included in this figure. It can be seen that $\bar{M}_w$ was roughly constant during the process.

Figure 6 shows the evolution of the overall conversion and the cumulative copolymer composition during the semistarved emulsion copolymerization. It can be seen that a homogeneous copolymer was obtained. Figure 7 presents the evolution of the weight average molecular

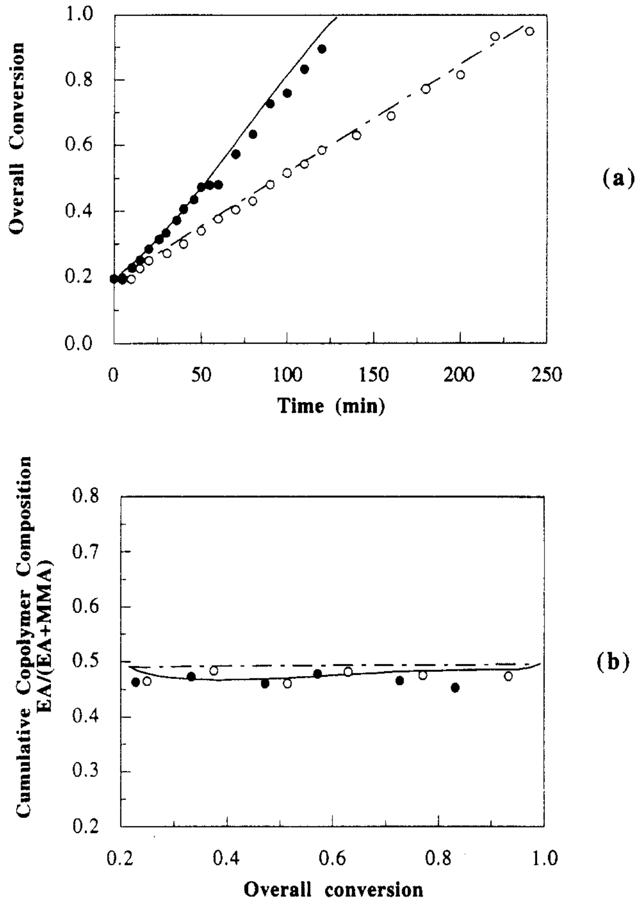

**Figure 8.** Evolution of the overall conversions and cumulative copolymer compositions for the starved processes. Run 3: (●) experimental data; (—) model. Run 4: (○) experimental data; (– · –) model.

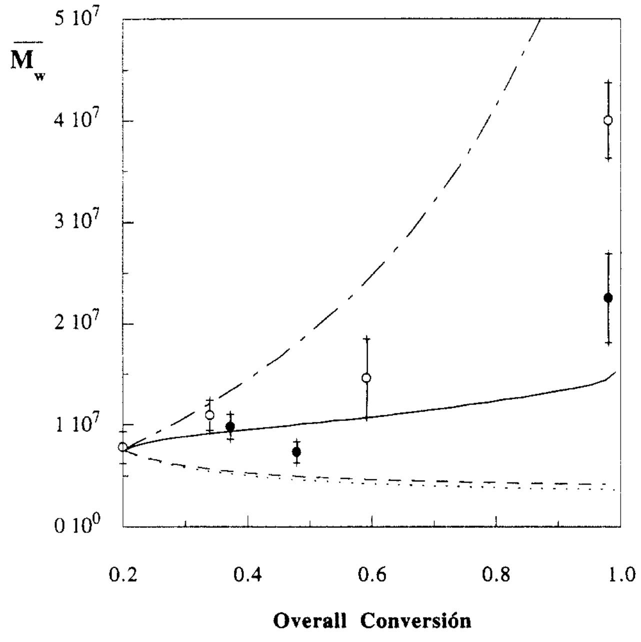

**Figure 9.** Evolution of the weight average molecular weight for the starved processes. Run 3: (●) experimental data; (—) model ($k_{fpEA}$ = 10, $k_{fpMMA}$ = 5.73); (- - -) model ($k_{fp}$ = 0). Run 4: (○) experimental data; (– · –) model ($k_{fpEA}$ = 10, $k_{fpMMA}$ = 5.73); (···) model ($k_{fp}$ = 0).

weight for the semistarved process. It can be seen that $\bar{M}_w$ increased during the process. In addition, the molecular weights were slightly lower than those obtained in the batch process.

**Table 5. Values of the Nonadjustable Parameters**

| | | | | |
|---|---|---|---|---|
| $k_{pAA}$[34], $k_{pBB}$[35] [cm$^3$/(mol s)] | $1.5 \times 10^6$ | $5.73 \times 10^5$ | | |
| $r_A$, $r_B$[34] | 0.24 | 2.03 | | |
| $k_{tcAA}$, $k_{tcBB}$, $k_{tdAA}$, $k_{tdBB}$[34,36] [cm$^3$/(mol s)] | $3.06 \times 10^{10}$ | 0 | 0 | $2.5 \times 10^{10}$ |
| $k_{fAA}$, $k_{fBB}$[35,37] [cm$^3$/(mol s)] | 40 | 20 | | |
| $\chi_{Aw}$, $\chi_{Bw}$, $\chi_{AB}$, $\chi_{BA}$[38] | 4.20 | 4.15 | $6.26 \times 10^{-3}$ | $6.13 \times 10^{-3}$ |
| $\chi_{wA}$, $\chi_{wB}$[38] | 4.468 | 4.77 | | |
| $(1 - m_{Aw})$, $(1 - m_{Bw})$, $(1 - m_{AB})$, $(1 - m_{BA})$[38] | 0.06 | 0.13 | −0.0216 | −0.0212 |
| $(1 - m_{Ap})$, $(1 - m_{Bp})$, $(1 - m_{wA})$, $(1 - m_{wB})$[38] | 1 | 1 | −0.0638 | −0.1494 |
| $\chi_{ApA}$, $\chi_{BpB}$, $\chi_{ApB}$, $\chi_{BpA}$[39] | 0.44 | 0.373 | 0.409 | 0.395 |
| $f$, $k_I$[40] (s$^{-1}$) | 0.5 | $5.78 \times 10^{-6}$ | | |
| $\sigma$[41] (dyn cm$^{-1}$), $T$ (K) | 4 | 333 | | |
| $k_{fpMMA}$[42] [cm$^3$/(mol s)] | 5.73 | | | |

Figure 8 presents the evolution of the overall conversions and the copolymer compositions obtained in the starved processes. Comparison with Figure 6 shows that the semistarved process gave a copolymer which was more homogeneous than that obtained by means of the starved processes even when a double process time was used.

Figure 9 presents the evolution of $\bar{M}_w$ during the starved processes. It can be seen that $\bar{M}_w$ increased during the process and that the longer the process time, the higher the molecular weight.

The results present in Figures 4–9 were analyzed by means of the mathematical model described above combined with the material balances for the reactor.[26] No nucleation mechanism was included in the model, but the experimental values of $N_p$ were used. The following average coefficients were used.

Propagation

$$\sum_{i=A,B} (k_{p_{Ai}} P_A^P + k_{p_{Bi}} P_B^P)[i]_P \quad \text{is used instead of } k_p[M] \tag{35}$$

Monomer Chain Transfer

$$\sum_{i=A,B} (k_{f_{Ai}} P_A^P + k_{f_{Bi}} P_B^P)[i]_P \quad \text{is used instead of } k_{f_m}[M] \tag{36}$$

Termination by Disproportionation

$$\bar{k}_{t_d} = k_{t_{dAA}} P_A^{P2} + 2k_{t_{dAB}} P_A^P P_B^P + k_{t_{dBB}} P_B^{P2} \quad \text{is used instead of } k_{t_d} \tag{37}$$

Termination by Combination

$$\bar{k}_{t_c} = k_{t_{cAA}} P_A^{P2} + 2k_{t_{cAB}} P_A^P P_B^P + k_{t_{dBB}} P_B^{P2} \quad \text{is used instead of } k_{t_c} \tag{38}$$

Chain Transfer to Polymer

$$(k_{fpA} Y_A + k_{fpB}(1 - Y_A))[Q_1] \quad \text{is used instead of } k_{fp}[Q_1] \tag{39}$$

where $P_i^P$ is the time averaged probability of finding a free radical with an ultimate unit of type i in the polymer particles given by[30]

$$P_A^P = k_{pBA}[A]_P/(k_{pBA}[A]_P + k_{pAB}[B]_P) \tag{40}$$

$$P_B^P = 1 - P_A^P \tag{41}$$

An average gel effect was used:

$$\bar{k}_t = \bar{k}_{t0} \exp(a_1 \phi_P^P + b_1 \phi_P^P) \tag{42}$$

where $k_{t0}$ is the average termination rate constant at zero polymer content and $a_1$ and $b_1$ are adjustable parameters.

On the other hand, although approaches to calculate the average desorption rate coefficients in emulsion copolymerization systems have been proposed,[31,32] in this work $k_d$ was considered to be an adjustable parameter.

The mathematical model assumes uniform monomer concentration in the polymer particles. Because of the low $T_g$ (≃27 °C) of the polymer as compared with the reaction temperature (60 °C), this is a reasonable assumption even under starved conditions.[33]

The mathematical model involves a rather large number of parameters. Table 5 presents the values of the parameters taken from the literature. In addition, the radical entry rate coefficient, $k_{abs}$, the desorption rate coefficient, $k_d$, the parameters of the gel effect factor, $a_1$ and $b_1$, and the rate constant of the polymer chain transfer reaction, $k_{fpEA}$, were estimated by means of the Nelder and Mead method of direct search. $k_p^*$ was considered to be zero. The objective function was the best fit of all experimental data, namely, evolution of overall conversion, copolymer composition, and weight average molecular weight. The estimated values for the adjustable parameters were

$$k_{abs} = 6.43 \times 10^9 \text{ cm}^3/(\text{mol s})$$

$$k_d = 9.6 \times 10^{-3} \text{ s}^{-1}$$

$$a_1 = -3.6$$

$$b_1 = -7.6$$

$$k_{fpEA} = 10 \text{ cm}^3/(\text{mol s})$$

This value of the entry rate coefficient is between that reported by Asua and de la Cal[43] for the batch emulsion polymerization of styrene [$k_{abs} = 7 \times 10^8$ cm$^3$/(mol s)] and those obtained by Urquiola et al.[44] for semicontinuous emulsion polymerization of vinyl acetate and methyl acrylate [$k_{abs} = 1.10 \times 10^{10}$ cm$^3$/(mol s)] and by Forcada and Asua[31] for the batch emulsion polymerization of styrene and methyl methacrylate [$k_{abs} = 3.8 \times 10^{10}$ cm$^3$/(mol s)]. Taking into account the water solubities of the monomers, the value of the exit rate coefficient agrees well with those obtained by Asua and de la Cal[43] for the emulsion polymerization of styrene (less water soluble monomer) ($k_d = 6 \times 10^{-4}$ s$^{-1}$) and by Urquiola et al.[44] for the emulsion polymerization of vinyl acetate and methyl acrylate (more water soluble monomers) ($k_d = 4.5 \times 10^{-2}$ s$^{-1}$). Due to the influence of the ethyl acrylate, the gel effect factor estimated in this work is less pronounced than that of MMA.[45] The value of $k_{fpEA}$ was twice that reported in the literature for MMA[42] [$k_{fpMMA} = 5.73$ cm$^3$/(mol s)].

A comparison between experimental results and model predictions is presented in Figures 4–9. It can be seen that, in agreement with the experimental results, the model predicted that the molecular weights of the batch and semistarved processes were lower than those of the starved process. In addition, the molecular weight of the polymer produced in the starved processes increased when the monomer feed rate decreased, i.e., when the starved character of the polymerization increased. These results show that, in spite of the low value of $k_{\mathrm{fpEA}}$, chain transfer to polymer occurred to a significant extent at high polymer concentrations. Figures 5, 7, and 9 show that when simulations were carried out with $k_{\mathrm{fp}} = 0$, contrary to that found experimentally, the molecular weights of the starved processes were smaller than those of the batch and semistarved process. These results show that the monomer addition policy has a marked effect on the molecular weight of the polymer. Taking into account the effect of the molecular weights on the mechanical properties of the polymer, this is a factor that has to be taken into consideration when optimal policies for polymer quality control are developed.

## Conclusions

A mathematical model for the kinetics of long-chain branching in emulsion polymerization systems was developed. The model accounts for all the reactions leading to this molecular structure as well as for the compartmentalization of the reaction system. The outputs of the model are the moments of the molecular weight distribution. From these moments, $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$ can be obtained readily. The model was checked in the limit of the linear chains with a well established model, a perfect agreement between the predictions of both models being found. On the other hand, when the changes in the environment where the chain is growing were not taken into account, the present model deviated. It was found that gel can be formed when the extent of the chain transfer to polymer is significant and termination occurs by combination. Extensive propagation to terminal double bonds can lead to gel formation irrespective of the type of bimolecular termination.

The model was used to analyze the effect of the monomer addition policy on the molecular weights of the copolymer obtained in the emulsion copolymerization of ethyl acrylate and methyl methacrylate. The batch process, semistarved optimal process and two starved processes with different feed times were considered. It was found that the molecular weights of the polymers produced in the batch and semistarved processes were smaller than those obtained in the starved processes. On the other hand, the more starved the process the higher the molecular weight. When these results were analyzed by means of the mathematical model, it was concluded that chain transfer to the polymer was responsible for the observed effects. These results have to be taken into consideration when optimal policies for polymer quality control are developed.

**Acknowledgment.** The financial support by the CICYT (Grant MAT 91-0195) is greatly appreciated.

## Nomenclature

| | |
|---|---|
| $a_1$, $b_1$ | gel effect parameters, eq 42 |
| $\bar{A}_2$ | second virial coefficient estimated by light scattering |
| $c$ | polymer concentration (g cm$^{-3}$) |
| $c_{\mathrm{tc}}$ | rate coefficient for termination by combination (s$^{-1}$) |
| $c_{\mathrm{td}}$ | rate coefficient for termination by disproportionation (s$^{-1}$) |
| $c_1$, $c_2$ | adjustable parameters, eq 33 |
| [DB] | concentration of terminal double bonds |
| $f$ | efficiency factor of the initiator radical generation |
| $I$ | amount of initiator present in the reaction medium (mol cm$^{-3}$) |
| $\mathbf{I}$ | identity matrix |
| $k_{\mathrm{abs}}$ | absorption rate coefficient (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{d}}$ | desorption rate coefficients (s$^{-1}$) |
| $k_{\mathrm{fm}}$ | monomer chain transfer rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{fp}}$ | polymer chain transfer rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{I}}$ | rate constant for initiator decomposition (s$^{-1}$) |
| $k_{\mathrm{p}}$ | propagation rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{I}}$ | rate constant for initiator decomposition (s$^{-1}$) |
| $k_{\mathrm{p}}$ | propagation rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{p}}^*$ | rate constant for propagation to terminal double bonds (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{tc}}$ | termination by combination rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $k_{\mathrm{td}}$ | termination by disproportionation rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$) |
| $K$ | optical constant, eq 33 |
| $m$ | maximum number of radicals per particle |
| $m_{\mathrm{ij}}$ | ratio of the equivalent number of segments of components j and i |
| [M] | concentration of monomer in polymer particles (mol cm$^{-3}$) |
| $M_{\mathrm{k}}$ | $k$th order moment of the overall polymer chain distribution |
| $\bar{M}_{\mathrm{n}}$ | number average molecular weight |
| $\bar{M}_{\mathrm{w}}$ | weight average molecular weight |
| $\bar{n}$ | average number of radicals per particle |
| $N_{\mathrm{A}}$ | Avogadro's number |
| $N_j$ | number of polymer particles containing $j$ radicals (cm$^{-3}$) |
| $N_{\mathrm{P}}$ | total number of polymer particles in the reactor |
| $P_{\mathrm{DB}}$ | probability of finding an inactive chain with a terminal double bond |
| $P_{\mathrm{i}}^{\mathrm{p}}$ | time averaged probability of finding a free radical with an ultimate unit of type $i$ in the polymer particles |
| $P_{\mathrm{M}}$ | molecular weight of the monomeric unit |
| $\mathbf{Q}$ | ($m \times m$) matrix of the probabilities for the growing chain of adding a new monomeric unit taking into account the environmental changes |
| $\bar{\mathbf{Q}}$ | ($m \times m$) matrix accounting for the changes in the number of radicals in the polymer particles |
| $Q_k$ | $k$th order moment of the overall chain length distribution of inactive polymeric chains |
| $Q_k^j$ | $k$th order moment of the chain length distribution of inactive polymeric chains in particles containing $j$ radicals |
| $\mathbf{R}$ | ($m \times 1$) column vector containing the probabilities of termination accounting for the environmental changes |
| $\bar{\mathbf{R}}$ | ($m \times 1$) column vector containing the probabilities of termination |
| $r_{\mathrm{i}}$ | reactivity ratio of the monomer $i$ |
| $R_{\mathrm{i}}$ | production rate of the $i$ process |
| $[\mathrm{R}]_{\mathrm{w}}$ | concentration of radicals in the aqueous phase (mol cm$^{-3}$) |
| $\mathrm{R}_1$ | single unit radicals |
| $R(q,c)$ | Rayleigh ratio |
| $\bar{\mathbf{S}}$ | ($m \times m$) diagonal matrix accounting for the probability of propagation |
| $t$ | time (s) |
| $T$ | temperature (K) |

| | |
|---|---|
| $X$ | overall conversion defined by eq 34 |
| $Y_k^j$ | $k$th order moment of the nonnormalized chain length distribution of the active polymer in polymer particles containing $j$ radicals |
| $Y_A$ | copolymer composition |

## Greek Symbols

| | |
|---|---|
| $\delta$ | Dirac delta function |
| $\theta$ | observation angle in the light scattering measurements |
| $\chi_{jk}$ | interaction parameters |
| $\lambda_{ki}^{\prime j}$ | $k$th order moment of the instantaneous normalized chain length distribution of active polymeric chains formed or consumed through process $i$ in polymer particles containing $j$ radicals |
| $\lambda_{\mathbf{kL}}$ | $(m \times 1)$ column vector containing the $k$th order moment of the chain length distribution of linear active chains in each type of polymer particle |
| $\mu_{\mathrm{ki}}^{\prime}$ | $k$th order moment of the normalized chain length distribution of inactive polymeric chains formed through process $i$ |
| $\phi_P{}^P$ | volume fraction of polymer in the polymer particles |
| $\sigma$ | interfacial tension (dynes cm$^{-1}$) |

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