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Modeling Gelation and Sol Molecular Weight Distribution in Emulsion Polymerization

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ABSTRACT: A mathematical model for the computation of the molecular weight distribution (MWD) of the sol, the gel fraction, and the gel point in emulsion polymerization systems was developed. The model accounts for the compartmentalization of the free radicals in the reaction system and for the changes in the environment where the chain was growing. An improved numerical fractionation technique that allows a better description of the MWD of the sol was used. A parametric sensitivity analysis was carried out and a comparison between the batch and the semicontinuous processes is presented.

Introduction

Because of heat transfer limitations or in order to avoid compositional drift, emulsion polymerizations are often carried out under starved conditions. Under these circumstances, the polymer/monomer ratio in the polymerization loci is very high and polymer chain transfer reactions are likely to occur. In addition, gel can be formed in systems in which there is chain transfer to polymer and termination occurs through combination.[1] Several mathematical models for the calculation of the molecular weights of branched polymers and the gel fraction in bulk and solution systems have been reported.[2−8] However, the kinetics of long chain branching and gelation in emulsion polymerization systems has received much less attention. Tobita[7,9−11] extended a mathematical model developed for homogeneous systems to emulsion polymerization. In the first papers[7,9−10] 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. More recently, Tobita et al.[11] have applied Monte Carlo simulations to determine the molecular weight distribution in emulsion polymerization considering the compartmentalization of the free radicals. The authors applied their method for linear and branched polymers resulting from propagation to terminal double bonds. The gelation was not considered. The compartmentalization of the free radicals was also accounted for in the model developed by Arzamendi et al.[12] for the kinetics of the long chain branching in emulsion polymerization. However, this model provides only the overall average molecular weights, and hence neither the MWD nor the gelation (the second moment diverges at the gel point) can be calculated.

In the present paper a mathematical model for the computation of the molecular weight distribution of the sol, the gel fraction, and the gel point in emulsion polymerization systems is presented. The model uses a variation of the "numerical fractionation" technique developed by Teymour and Campbell[4,5] and accounts for the compartmentalization of the free radicals in emulsion polymerization.

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.[13]

(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 1.

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(ix) The polymer particles are allowed to contain 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

$$\mathcal{R}_1 = 2fk_\mathrm{I}I \quad [\mathrm{mol/(cm^3\ s)}] \qquad (1)$$

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

$$\mathrm{R}_n + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{R}_{n+1} \qquad \text{(R-2)}$$

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

$$\mathcal{R}_\mathrm{p} = k_\mathrm{p}[\mathrm{M}]Y_0^j = k_\mathrm{p}[\mathrm{M}]jN_j \quad [\text{monomeric units/(cm}^3\ \text{s)}] \qquad (2)$$

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

$$\mathrm{M}_n(\mathrm{DB}) + \mathrm{R}_m \xrightarrow{k_\mathrm{p}^*} \mathrm{R}_{m+n}(\mathrm{LB}) \qquad \text{(R-3)}$$

where $\mathrm{M}_n(\mathrm{DB})$ denotes an inactive chain of length n containing a terminal double bond and $\mathrm{R}_{m+n}(\mathrm{LB})$ 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:

$$\mathcal{R}_\mathrm{p}^* = k_\mathrm{p}^*[\mathrm{DB}]Y_0^j = k_\mathrm{p}^*\frac{Q_0}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}P_\mathrm{DB}jN_j \quad [\text{polymer chains/(cm}^3\ \text{s)}] \qquad (3)$$

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 the Avogadro 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

$$\mathrm{R}_n + \mathrm{M} \xrightarrow{k_\mathrm{fm}} \mathrm{M}_n(\mathrm{DB}) + \mathrm{R}_1 \qquad \text{(R-4)}$$

where $\mathrm{M}_n(\mathrm{DB})$ 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

$$\mathcal{R}_\mathrm{fm} = k_\mathrm{fm}[\mathrm{M}]jN_j \quad [\text{polymer chains/(cm}^3\ \text{s)}] \qquad (4)$$

where k_fm is the rate constant of the monomer chain transfer reaction.

Polymer Chain Transfer

$$\mathrm{R}_n + \mathrm{M}_m \xrightarrow{k_\mathrm{fp}} \mathrm{M}_n + \mathrm{R}_m(\mathrm{LB}) \qquad \text{(R-5)}$$

The rate of polymer chain transfer was taken to be proportional to the concentration of units of polymerized monomer. If it is assumed 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

$$\mathcal{R}_\mathrm{fp} = k_\mathrm{fp}[Q_1]Y_0^j = k_\mathrm{fp}\frac{Q_1}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}jN_j \quad [\text{polymer chains/(cm}^3\ \text{s)}] \qquad (5)$$

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

$$\mathrm{R}_n + \mathrm{R}_m \xrightarrow{k_\mathrm{td}} \mathrm{M}_n + \mathrm{M}_m(\mathrm{DB}) \qquad \text{(R-6)}$$

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

$$\mathcal{R}_\mathrm{td} = k_\mathrm{td}\frac{(j-1)}{N_\mathrm{A}v_\mathrm{p}}jN_j = c_\mathrm{td}(j-1)jN_j \quad [\text{termination events/(cm}^3\ \text{s)}] \qquad (6)$$

where k_td is the rate constant of the disproportionation reaction.

Termination by Combination

$$\mathrm{R}_n + \mathrm{R}_m \xrightarrow{k_\mathrm{tc}} \mathrm{M}_{n+m} \qquad \text{(R-7)}$$

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

$$\mathcal{R}_\mathrm{tc} = k_\mathrm{tc}\frac{(j-1)}{N_\mathrm{A}v_\mathrm{p}}jN_j = c_\mathrm{tc}(j-1)jN_j \quad [\text{termination events/(cm}^3\ \text{s)}] \qquad (7)$$

where k_tc is the rate constant of the combination reaction.

Numerical Fractionation. Teymour and Campbell[4,5] proposed to divide the overall polymer chain population into different classes according to their size. They distinguished between linear polymer and branched polymer and the latter was further subdivided into various generations that were composed by polymer chains of similar sizes. Polymer chains were transferred from linear to the first-generation branched when they suffer a polymer chain transfer reaction. Transfer from the first to the second generation occurred when two first-generation chains reacted together (for instance by means of a termination by combination or by propagation to terminal double bonds), forming a single chain. This means that polymer chains can add branches without being transferred to the next generation. The same rules applied for the transfer to higher generations. This process allowed for a geometrical growth in size of the different generations. Therefore, the size of the polymer chains in generations higher than a critical one, n_c, were large enough to be considered gel. A set of ordinary differential equations for the moments of the polymer chain length distribution of each generation were developed. The amount of gel was calculated by the difference between the total amount of polymerized monomer and the monomer units in the polymer chains in linear polymer and in branched generations up to n_c. The molecular weight distribution of both the linear polymer and each branched generation was calculated from the corresponding moments by assuming that the Schultz distribution[14] applied. The overall MWD of the sol polymer was calculated by adding the MWDs of all the classes.

The numerical fractionation technique developed by Teymour and Campbell[4,5] was mainly focused on the dynamics of gelation, and hence stress was placed on a geometrical growth in size of the different generations. However, this is a disadvantage for a detailed description of the molecular weight distribution of the sol fraction as well as for the MWD of the low and medium branched polymer that often appears in polymerization systems in which chain transfer to polymer but neither termination by combination nor propagation to terminal double bonds occurs. Therefore, in the present paper a slight variation of the approach developed by Teymour and Campbell[4,5] was used. The overall polymer chain population was also divided into linear and branched polymer but the latter was subdivided as follows: Each of the first n_e generations was composed of polymer chains having the same number of branching points, and for generations higher than $n_e + 1$ the geometrical growth of Teymour and Campbell[4,5] was adopted. Table 1 presents the transfer reactions between classes. Q(n) and Y(n) represent the inactive and the active polymer chains, respectively, of generation n.

Linear polymer ($n = 0$) is transferred to the first branched generation by chain transfer to polymer and by propagation to terminal double bonds. For the first n_e generations, the transfer from one generation to a higher one occurred by polymer chain transfer reaction (to the next higher generation) and by termination by combination and propagation to terminal double bonds (to the generation having the corresponding branching points or to generation $n_e + 1$ if the number of branching points exceeds n_e). For the generations higher than n_e, transfer to the next higher generation occurred when two chains of the same generation reacted together by termination by combination or by propagation to terminal double bonds.

In order to apply this numerical fractionation technique to emulsion polymerization systems, the effect of the compartmentalization of free radicals has to be taken into account. Therefore, distinction was made between the inactive polymer chains of each generation formed in particles with a different number of radicals per particle. Also, the active chains belonging to each generation that are in particles with j radicals should be taken into account. Therefore, the material balances for the moments of the chain length distribution of both active polymer in particles with j radicals and inactive polymer formed in particles with j radicals have to be developed.

Table 1. Transfer Reactions between Generations

linear polymer (0)

$$\mathrm{Y}(0) + \mathrm{M} \xrightarrow{k_{\mathrm{fm}}} \mathrm{Q}(0) + \mathrm{Y}(0)$$

$$\mathrm{Y}(0) + \mathrm{Y}(0) \xrightarrow{k_{\mathrm{td}}} \mathrm{Q}(0) + \mathrm{Q}(0)$$

$$\mathrm{Y}(0) + \mathrm{Y}(0) \xrightarrow{k_{\mathrm{tc}}} \mathrm{Q}(0)$$

$$\mathrm{Y}(0) + \mathrm{Q}(0) \xrightarrow{k_{\mathrm{fp}}} \mathrm{Q}(0) + \mathrm{Y}(1)$$

$$\mathrm{Y}(0) + \mathrm{Q}(0) \xrightarrow{k_{\mathrm{p}}^{*}} \mathrm{Y}(1)$$

branched polymer ($1 \le i$ and $j \le n_e$)

$$\mathrm{Y}(i) + \mathrm{M} \xrightarrow{k_{\mathrm{fm}}} \mathrm{Q}(i) + \mathrm{Y}(0)$$

$$\mathrm{Y}(i) + \mathrm{Y}(j) \xrightarrow{k_{\mathrm{td}}} \mathrm{Q}(i) + \mathrm{Q}(j)$$

$$\mathrm{Y}(i) + \mathrm{Y}(j) \xrightarrow{k_{\mathrm{tc}}} \mathrm{Q}(i+j)\ \delta_{(i+j)\le n_e} + \mathrm{Q}(n_e+1)\ \delta_{(i+j)>n_e}$$

$$\mathrm{Y}(i) + \mathrm{Q}(j) \xrightarrow{k_{\mathrm{fp}}} \mathrm{Q}(i) + \mathrm{Y}(j+1)$$

$$\mathrm{Y}(i) + \mathrm{Q}(j) \xrightarrow{k_{\mathrm{p}}^{*}} \mathrm{Y}(i+j+1)\ \delta_{(i+j+1)\le n_e} + \mathrm{Y}(n_e+1)\ \delta_{(i+j+1)>n_e}$$

branched polymer ($n_e \le i \le n_c$ and $0 < j \le n_c$)

$$\mathrm{Y}(i) + \mathrm{M} \xrightarrow{k_{\mathrm{fm}}} \mathrm{Q}(i) + \mathrm{Y}(0)$$

$$\mathrm{Y}(i) + \mathrm{Y}(j) \xrightarrow{k_{\mathrm{td}}} \mathrm{Q}(i) + \mathrm{Q}(j)$$

$$\mathrm{Y}(i) + \mathrm{Y}(j) \xrightarrow{k_{\mathrm{tc}}} \mathrm{Q}(i)\ \delta_{i>j} + \mathrm{Q}(j)\ \delta_{i<j} + \mathrm{Q}(i+1)\ \delta_{i=j}$$

$$\mathrm{Y}(i) + \mathrm{Q}(j) \xrightarrow{k_{\mathrm{fp}}} \mathrm{Q}(i) + \mathrm{Y}(j+1)$$

$$\mathrm{Y}(i) + \mathrm{Q}(j) \xrightarrow{k_{\mathrm{p}}^{*}} \mathrm{Y}(i)\ \delta_{i>j} + \mathrm{Y}(j)\ \delta_{i<j} + \mathrm{Y}(i+1)\ \delta_{i=j}$$

Basic Equations. The aim of the mathematical model is to calculate the MWD of the sol, the gel fraction, and the gel point from the moments of the different generations. Therefore, the material balances for these moments have to be developed. The so-called tendency model developed by Villermaux and Blavier[2,3] 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 consider a polymer chain length distribution, where $f'(x)$ is the number of polymer chains of length x. The kth-order moment of this distribution is

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

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 $f'(x)$ can be normalized as $f(x) = f'(x)/Q_0$, where $f(x)$ is the fraction of macromolecules that has a length x. The moments of this normalized distribution are

$$\mu_k = \sum_{x=1}^{\infty} x^k f(x) = Q_k/Q_0 \qquad (9)$$

Villermaux and Blavier[2,3] showed that when two polymer samples are mixed, the *k*th-order moment of the non-normalized resulting distribution is given by

$$Q_k = Q_{0_1}\mu_{k_1} + Q_{0_2}\mu_{k_2} \qquad (10)$$

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 non-normalized dead polymer chain length distribution is as follows:[2]

$$\frac{\mathrm{d}Q_k}{\mathrm{d}t} = \sum_i \mathcal{R}_i \mu'_{ki} \qquad (11)$$

where $\mathcal{R}_i$ is the rate of formation of dead polymer chains through the process *i* and μ'_{ki} is the *k*th-order moment of the normalized chain length distribution of the dead polymer that is produced by the process *i*.

In order to apply this concept to the present case, the subdivision of the overall MWD into classes and the compartmentalization of the free radicals have to be taken into account. Thus, the balances for the chain length distribution moments should include terms that represent: (i) the transfer between active and inactive chains, (ii) the transfer between generations, and (iii) also the transfer between particles containing a different number of radicals.

The balance for the *k*th-order moment of the chain length distribution of inactive macromolecules of generation *n* (for $0 < n < n_e$) formed in particles with *j* radicals is

$$\begin{aligned}\frac{\mathrm{d}Q^j_k(n)}{\mathrm{d}t} = {} & 2c_{\mathrm{td}}(j-1)\, Y^j_0(n)\, \mu^j_{k_{\mathrm{td}}}(n) + \\ & c_{\mathrm{tc}}\frac{(j-1)}{jN_j}(Y^j_0(n))^2\, \mu^j_{k_{\mathrm{tc}}}(n,n)\, \delta_{n=0} + \\ & c_{\mathrm{tc}}\frac{(j-1)}{jN_j}\sum_{h=0}^{n} Y^j_0(h)\, Y^j_0(n-h)\, \mu^j_{k_{\mathrm{tc}}}(h,n-h)\, \delta_{n>0} + \\ & k_{\mathrm{fm}}[\mathrm{M}]Y^j_0(n)\, \mu^j_{k_{\mathrm{fm}}}(n) + k_{\mathrm{fp}}\frac{Q_1}{N_{\mathrm{p}}N_{\mathrm{A}}v_{\mathrm{p}}}Y^j_0(n)\, \mu^j_{k_{\mathrm{fp}}1}(n) - \\ & k_{\mathrm{fp}}\frac{Q_1(n)}{N_{\mathrm{p}}N_{\mathrm{A}}v_{\mathrm{p}}}jN_j\mu^j_{k_{\mathrm{fp}}2}(n) - k^*_{\mathrm{p}}\frac{Q_0(n)}{N_{\mathrm{p}}N_{\mathrm{A}}v_{\mathrm{p}}}P_{\mathrm{DB}}jN_j\mu^j_{k_{\mathrm{p}}*}(n)\end{aligned}$$
$$\text{for } 0 \le n \le n_e \qquad (12)$$

where the first term of the right-hand member accounts for the formation of inactive chains by termination by disproportionation; the second and third account for the formation of inactive linear and branched, respectively, polymer by combination; the fourth includes the effect of the monomer chain transfer; the fifth and sixth account for the formation and consumption, respectively, of inactive chains by chain transfer to polymer; and the last one represents the effect of the propagation of terminal double bonds.

Table 2. Moments of the Chain Length Distribution of the Inactive Polymer of Generation *n* ($0 < n < n_c$) Formed in Polymer Particles with *j* Radicals

process	μ^j_1	μ^j_2
termination by disproportionation		
$\mu^j_{\mathrm{ktd}}(\mathrm{n})$	$\dfrac{Y^j_1(n)}{Y^j_0(n)}$	$\dfrac{Y^j_2(n)}{Y^j_0(n)}$
termination by combination		
$\mu^j_{\mathrm{ktc}}(\mathrm{h,k})$	$\dfrac{Y^j_1(h)}{Y^j_0(h)} + \dfrac{Y^j_1(k)}{Y^j_0(k)}$	$\dfrac{Y^j_2(h)}{Y^j_0(h)} + \dfrac{Y^j_2(k)}{Y^j_0(k)} + 2\dfrac{Y^j_1(h)}{Y^j_0(h)}\dfrac{Y^j_1(k)}{Y^j_0(k)}$
chain transfer to monomer		
$\mu^j_{\mathrm{kfm}}(\mathrm{n})$	$\dfrac{Y^j_1(n)}{Y^j_0(n)}$	$\dfrac{Y^j_2(n)}{Y^j_0(n)}$
chain transfer to polymer		
formation		
$\mu^j_{\mathrm{kfp1}}(n)$	$\dfrac{Y^j_1(n)}{Y^j_0(n)}$	$\dfrac{Y^j_2(n)}{Y^j_0(n)}$
consumption		
$\mu^j_{\mathrm{kfp2}}(n)$	$\dfrac{Q_2(n)}{Q_1(n)}$	$\dfrac{Q_3(n)}{Q_1(n)}$
propagation to a terminal double bond		
$\mu^j_{\mathrm{kp*}}(n)$	$\dfrac{Q_1(n)}{Q_0(n)}$	$\dfrac{Q_2(n)}{Q_0(n)}$

$\mu^j_{ki}(n)$ is the *k*th-order moment of the normalized distribution of the dead polymer chains of generation *n* formed through process *i* in polymer particles containing *j* radicals and $\mu^j_{ki}(h,n-h)$ is the *k*th-order moment of the normalized distribution of the dead polymer chains coming from the combination of one radical of generation *h* and one radical of generation $n - h$. These moments depend on the moments of the distribution of the growing macromolecules, $Y^j_k(n)$. Thus, when termination occurs by disproportionation, the moments of distribution of dead polymer chains are the same as those of the original growing chains. However, for other termination mechanisms such as combination, the relationship between the moments of growing and dead chains is not that simple. Table 2 presents the values of $\mu^j_{ki}(n)$ and $\mu^j_{ki}(h,k)$ for the different termination mechanisms. Notice that when these values are included in eq 12, a closure problem appears because every moment depends on the next higher. For the overall chain length distribution this closure problem can be solved by adding the balances of active and dead polymer.[12] However, this is not possible when the overall MWD is subdivided. Therefore, following Teymour and Campbell[5] the Saidel and Katz[15] approximation for the third moment was used:

$$Q_3(n) = 2\frac{Q_2(n)^2}{Q_1(n)} - \frac{Q_2(n)\,Q_1(n)}{Q_0(n)} \qquad (13)$$

The balance of the *k*th-order moment of the chain length distribution of inactive macromolecules of generation *n* (for $n_e < n < n_c$) formed in particles with *j* radicals is

$$\begin{aligned}\frac{\mathrm{d}Q^j_k(n)}{\mathrm{d}t} &= 2c_{\mathrm{td}}(j-1)\,Y^j_0(n)\,\mu^j_{k_{\mathrm{td}}}(n) + \\ &c_{\mathrm{tc}}\frac{(j-1)}{jN_j}\Big[\sum_{h=0}^{n_\mathrm{e}+1} Y^j_0(h) \sum_{k=n_\mathrm{e}+1-h}^{n_\mathrm{e}+1} Y^j_0(k)\,\mu^j_{k_{\mathrm{tc}}}(h,k) - \\ &(Y^j_0(n_\mathrm{e}+1))^2\mu^j_{k_{\mathrm{tc}}}(n_\mathrm{e}+1,n_\mathrm{e}+1)\Big] + \\ &c_{\mathrm{tc}}\frac{(j-1)}{jN_j}\Big[Y^j_0(n)\sum_{h=0}^{n-1} 2Y^j_0(h)\,\mu^j_{k_{\mathrm{tc}}}(n,h) + \\ &(Y^j_0(n-1))^2\,\mu^j_{k_{\mathrm{tc}}}(n-1,n-1)\Big]\delta_{n>n_\mathrm{e}+1} + \\ &k_{\mathrm{fm}}[\mathrm{M}]Y^j_0(n)\,\mu^j_{k_{\mathrm{fm}}}(n) + k_{\mathrm{fp}}\frac{Q_1}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}Y^j_0(n)\,\mu^j_{k_{\mathrm{fp}}1}(n) - \\ &k_{\mathrm{fp}}\frac{Q_1(n)}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}jN_j\mu^j_{k_{\mathrm{fp}}2}(n) - k^*_\mathrm{p}\frac{Q_0(n)}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}P_{\mathrm{DB}}jN_j\mu^j_{k_\mathrm{p}{}^*}(n) \\ &\qquad \text{for } n_\mathrm{e} \le n \le n_\mathrm{c} \quad (14)\end{aligned}$$

The evolution of the probability of finding an inactive chain with a terminal double bond can be calculated as follows:

$$P_{\mathrm{DB}} = \mathrm{DB}/Q_0 \qquad (15)$$

where DB is the total number of double bonds and Q_0 is the total number of macromolecules are given by

$$\frac{\mathrm{dDB}}{\mathrm{d}t} = \sum_{j=1}^{m}\sum_{n=0}^{n_\mathrm{c}} \frac{\mathrm{dDB}^j(n)}{\mathrm{d}t} \qquad (16)$$

$$\frac{\mathrm{d}Q_0}{\mathrm{d}t} = \sum_{j=1}^{m}\sum_{n=0}^{n_\mathrm{c}} \frac{\mathrm{d}Q^j_0(n)}{\mathrm{d}t} \qquad (17)$$

where

$$\frac{\mathrm{dDB}^j(n)}{\mathrm{d}t} = c_{\mathrm{td}}(j-1)\,Y^j_0(n) + k_{\mathrm{fm}}[\mathrm{M}]Y^j_0(n) - k^*_\mathrm{p}\frac{Q_0(n)}{N_\mathrm{p}N_\mathrm{A}v_\mathrm{p}}P_{\mathrm{DB}}jN_j \qquad (18)$$

The moments of the chain length distribution of the inactive polymer chains ($Q^j_k(n)$) depend on the moments of the active macromolecules ($Y^j_k(n)$) given by eq 19 (see Scheme 1). Where k_{abs} and k_d are the rate coefficients for radical entry and exit, respectively, $[\mathrm{R}]_\mathrm{w}$ is the concentration of free radicals in the aqueous phase, λ^j_k is the kth-order moment of an active linear chain in polymer particles with j radicals, $\lambda^j_{k_{\mathrm{fp}}i}(n)$ is the kth-order moment of the active polymer chains formed by chain transfer polymer. $\lambda^j_{k_\mathrm{p}{}^*i}(n,h)$ is the kth-order moment of the growing chains formed by propagation to double terminal bonds.

Term 1 in eq 19 accounts for the active macromolecules formed from the absorbed radicals. Terms 2−7 account for the transfer of active chains from one class of polymer particles to another when the number of radicals in the particles varies by entry and exit of free radicals. Thus, when a radical enters a particle containing $j-1$ radicals, the particle becomes part of the class of particles with j radicals and the $j-1$ radicals present in the particle prior the radical entry are transferred to the class of particles j (term 2 in eq 19). Similarly, the class of particles with j radicals loses j radicals when a radical enters into one of these particles (term 4). Implicit in term 3 is the assumption that instantaneous termination occurs when a free radical enters a polymer particle already containing m radicals. Term 5 represents the j active macromolecules transfer from particles of class $j+1$ to class j when a free radical desorbs from a particle with $j+1$ radicals. Terms 6 and 7 account for the loss of active chains from particles j by desorption. Term 6 takes into account that the desorbing radical is always linear and term 7 accounts for the contribution of the $(j-1)$ nondesorbing radicals. Terms 8 and 9 represent the gain and loss, respectively, of free radicals by bimolecular termination. Terms 10 and 11 refer to the formation and deactivation, respectively, of active macromolecules by the monomer chain transfer reaction. Term 12 represents the loss of active macromolecules by chain transfer to polymer, and terms 13 and 14 account for the formation of active chains by this process. Notice that both terms are used when $n = n_\mathrm{e}+1$. The reason is that, according to the division of the MWD into classes used in this work, an active macromolecule of the class $n_\mathrm{e}+1$ is produced when a radical is transferred to an inactive chain of class n_e (term 13). In addition, active chains of the class $n_\mathrm{e}+1$ are also produced when radicals are transferred to inactive chains of class $n_\mathrm{e}+1$ (term 14) because the transfer from class $n_\mathrm{e}+1$ to class $n_\mathrm{e}+2$ is only produced by combination and propagation to terminal double bonds. For $n \le n_\mathrm{e}$, when an active chain of generation $(n-h-1)$ propagates to a terminal double bond located on an inactive chain of generation h, a growing chain of generation n is produced (term 15). An active chain of class $n_\mathrm{e}+1$ is produced when a propagation to terminal double bonds between chains of lengths h and k (being $h+k=n_\mathrm{e}$) occurs (term 16). The negative part of this term counteracts the term $h = n_\mathrm{e}+1/k = n_\mathrm{e}+1$ that appears in the summations. If $n > n_\mathrm{e}+1$, the transfer only occurs when both the active and the inactive chains belong to the same generation (term 17). Term 18 accounts for the loss of active macromolecules by propagation to terminal double bonds.

In order to evaluate the instantaneous length moments of linear polymer (λ^j_k) the approach developed by Storti et al.[16,17] was applied. This approach accounts for the fact that in emulsion polymerization the number of the radicals contained in the polymer particle in which the active chain is growing varies during the chain growth due to radical entry, radical exit, and bimolecular termination of the companion chains. For linear polymers, Arzamendi et al.[12] showed that when the effect of the changes of the environment in which the polymer chains was growing was not taken into account, the prediction of the model deviated. In the present paper, the moments of the distribution of active chains were calculated by taking into account the influence of the changes of the environment where the polymer chains were growing. For the sake of the brevity, the equations are not reproduced here, but the reader is referred to ref 12. Table 3 presents the values of $\lambda^j_{k_{\mathrm{fp}}i}(n)$ and $\lambda^j_{k_\mathrm{p}{}^*i}(n,h)$ calculated by operating in the z-transformed domain.[3]

Scheme 1

$$\frac{dY_k^j(n)}{dt} = k_{abs}[R]_w N_{j-1}(n)\,\lambda_k^j \delta_{n=0} + k_{abs}[R]_w Y_k^{j-1}(n) + k_{abs}[R]_w \frac{m-1}{m} Y_k^m(n)\,\delta_{j=m-1}$$

1 Contribution of the growing polymer chains resulting from the absorbed radicals

2 Growing polymer chains transferred from particles with j - 1 radicals after absorption of one radical

3 Growing polymer chains transferred from particles containing m radicals after absorption of one radical

$$-k_{abs}[R]_w Y_k^j(n) + k_d\, j\, Y_k^{j+1}(n) - k_d\, j\, N_j\, \lambda_k^j\, \delta_{n=0}$$

4 Growing polymer chains lost when a radical enters in polymer particles with j radicals

5 Growing polymer chains transferred from particles with j + 1 radicals after the exit of one radical

6 Linear growing polymer chains lost when a desorption reaction occurs in polymer particles containing j radicals

$$-k_d(j-1)Y_k^j(n) + (c_{tc}+c_{td})(j+1)\,j\,Y_k^{j+2}(n)\,\delta_{j<m-1} - (c_{tc}+c_{td})\,j\,(j-1)Y_k^j(n)\,\delta_{j>1}$$

7 Growing polymer chains transferred when a desorption reaction occurs in particles with j radicals

8 Growing polymer chains transferred from particles with j + 2 radicals after a bimolecular termination

9 Growing polymer chains lost when a termination reaction occurs in polymer particles containing j radicals

$$+k_{fm}[M]\,j\,N_j\,\lambda_k^j(n)\,\delta_{n=0} - k_{fm}[M]\,Y_k^j(n) - k_{fp}\frac{Q_1}{N_p N_A v_P} Y_k^j(n)$$

10 Contribution of the polymer chains resulting from the monomeric radicals formed by monomer chain transfer

11 Loss of growing polymer chains by monomer chain transfer

12 Growing polymer chains lost by chain transfer to polymer

$$+ k_{fp}\frac{Q_1(n-1)}{N_p N_A v_P}\,j\,N_j\,\lambda_{kfp}^j(n-1)\,\delta_{n\le n_e+1} + k_{fp}\frac{Q_1(n)}{N_p N_A v_P}\,j\,N_j\,\lambda_{kfp}^j(n)\,\delta_{n\ge n_e+1}$$

13 Growing polymer chains formed by chain transfer to polymer when $n \le n_e + 1$

14 Growing polymer chains formed by chain transfer to polymer when $n \ge n_e + 1$

$$+ k_p^* \sum_{h=0}^{n-1} \frac{Q_0(h)}{N_p N_A v_P} P_{DB}\, Y_0^j(n-h-1)\,\lambda_{kp*1}^j(h, n-h-1)\,\delta_{n\le n_e}$$

15 Growing polymer chains formed by propagation to terminal double bonds when $n \le n_e$

$$+ k_p^* \frac{P_{DB}}{N_p N_A v_P}\left(\sum_{h=0}^{n_e+1} Q_0(h) \sum_{k=n_e-h}^{n_e+1} Y_0^j(k)\lambda_{kp*1}^j(h,k)\delta_{k\ge 0} - Q_0(n)Y_0^j(n)\lambda_{kp*1}^j(n,n)\right)\delta_{n=n_e+1}$$

16 Growing polymer chains formed by propagation to terminal double bonds when $n = n_e + 1$

$$+ k_p^* \frac{P_{DB}}{N_p N_A v_P}\Big(\sum_{h=0}^{n-1} Q_0(h)\,Y_0^j(n)\,\lambda_{kp*1}^j(h,n) + \sum_{h=0}^{n-1} Q_0(n)\,Y_0^j(h)\,\lambda_{kp*1}^j(n,h) +$$

$$+ Q_0(n-1)\,Y_0^j(n-1)\,\lambda_{kp*1}^j(n-1,n-1)\Big)\,\delta_{n>n_e+1} - k_p^* \frac{Q_0}{N_p N_A v_P} P_{DB}\, Y_0^j(n)\,\lambda_{kp*2}^j(n)$$

17 Growing polymer chains formed by propagation to terminal double bonds when $n > n_e + 1$

18 Growing polymer chains lost by propagation to terminal double bonds

(19)

Table 3. Moments of the Chain Length Distribution of the Active Polymer of Generation n ($0 < n < n_c$) Formed in Polymer Particles with j Radicals

process	λ_1^j	λ_2^j
chain transfer to polymer		
$\lambda^j_{\mathrm{kfp}}(n)$	$\lambda_1^j + \dfrac{Q_2(n)}{Q_1(n)}$	$\lambda_2^j + 2\lambda_1^j\dfrac{Q_2(n)}{Q_1(n)} + \dfrac{Q_3(n)}{Q_1(n)}$
propagation to a terminal double bond *formation*		
$\lambda^j_{\mathrm{kp*1}}(n,h)$	$\lambda_1^j + \dfrac{Y_1^j(n)}{Y_0^j(n)} + \dfrac{Q_1(h)}{Q_0(h)}$	$\lambda_2^j + \dfrac{Y_2^j(n)}{Y_0^j(n)} + 2\dfrac{Y_1^j(n)}{Y_0^j(n)}\dfrac{Q_1(h)}{Q_0(h)} + \dfrac{Q_2(h)}{Q_0(h)} + 2\lambda_1^j\left(\dfrac{Q_1(h)}{Q_0(h)} + \dfrac{Y_1^j(n)}{Y_0^j(n)}\right)$
comsumption		
$\lambda^j_{kp*2}(n)$	$\dfrac{Q_1(n)}{Q_0(n)}$	$\dfrac{Q_2(n)}{Q_0(n)}$

The moments of the MWD of the sol polymer are as follows:

$$\frac{\mathrm{d}M_{k,\mathrm{sol}}}{\mathrm{d}t} = \sum_{j=1}^{m}\sum_{n=0}^{n_c}\frac{\mathrm{d}Q_k^j(n)}{\mathrm{d}t} + \sum_{j=1}^{m}\sum_{n=0}^{n_c}\frac{\mathrm{d}Y_k^j(n)}{\mathrm{d}t} \tag{20}$$

The amount of gel can be calculated as the difference between the first moment of overall distribution and the first moment of sol polymer distribution, with the first moment of the overall MWD calculated by the following equation:

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = \sum_j k_p[\mathrm{M}]_p jN_j \tag{21}$$

The equations derived by Arzamendi and Asua[12] for the moments of the overall MWD can be used to check the present model up to the gel point by comparing the sum of the individual moments with the moments of the overall MWD.

On the other hand, although the complete MWD of the sol can be obtained by expanding the moments M_k in Laguerre and Hermite polynomials,[18] in this paper a different approach was used. It was assumed that the instantaneous molecular weight distribution of the polymer formed by each process follows the Schultz distribution.

The Schultz distribution is a two-parameter distribution defined by the number and weight average chain lengths. Thus, the instantaneous weight fraction of chains of length x in the polymer of generation n formed in polymer particles with j radicals through the process i is

$$w(x,n,j,i) = \frac{y(n,j,i)[xy(n,j,i)]^{z(n,j,i)}\exp[-xy(n,j,i)]}{\Gamma[z(n,j,i)+1]} \tag{22}$$

where

$$z(n,j,i) = \frac{1}{\left[\dfrac{\bar{X}_{\mathrm{w}}(n,j,i)}{\bar{X}_{\mathrm{n}}(n,j,i)} - 1\right]} \tag{23}$$

$$y(n,j,i) = \frac{z(n,j,i)+1}{\bar{X}_{\mathrm{w}}(n,j,i)} \tag{24}$$

where $\bar{X}_{\mathrm{n}}(n,j,i)$ and $\bar{X}_{\mathrm{w}}(n,j,i)$ are the number and weight average chain lengths of the polymer of generation n formed in polymer particles with j radicals through the process i.

The instantaneous chain length distribution of generation n can be obtained taking into account the contribution of each process according to the ratio of its instantaneous first moment and the instantaneous overall first moment,

$$W(x,n) = \sum_{j=1}^{m}\sum_{i=1}^{n_p}\frac{\mathrm{d}Q_1^j(n,i)/\mathrm{d}t}{\mathrm{d}M_1/\mathrm{d}t}w(x,n,j,i) \tag{25}$$

where n_p is the number of processes leading to inactive macromolecules.

By integration of the instantaneous distribution, the cumulative chain length distribution of each n generation can be obtained.

$$\bar{W}(x,n) = \frac{1}{X}\int_0^X W(x,n)\,\mathrm{d}X \tag{26}$$

where X is the conversion. Equation 26 can be transformed into the following differential equation:

$$\frac{\mathrm{d}\bar{W}(x,n)}{\mathrm{d}t} = \frac{1}{M_1}(W(x,n) - \bar{W}(x,n))\frac{\mathrm{d}M_1}{\mathrm{d}t} \tag{27}$$

where $\mathrm{d}M_1/\mathrm{d}t$ is given by eq 21. The overall cumulative chain length distribution is given by the sum of the contribution of each generation:

$$\bar{W}(x) = \sum_{n=0}^{n_c}\bar{W}(x,n) \tag{28}$$

To solve the model, the number distribution of polymer particles containing j radicals is required. This can be calculated using the approach proposed by Ballard et al.[19] This method is based on the truncation of the Smith–Ewart equations[20] by assuming that the polymer particles can contain a maximum of m radicals, i.e., that 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:

$$N_{m-1} = (k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} + mk_{\mathrm{d}} + (c_{\mathrm{tc}} + c_{\mathrm{td}})m(m - 1))N_m/k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} \tag{29}$$

$$N_{m-2} = \{(k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} + (m-1)k_{\mathrm{d}} + (c_{\mathrm{tc}} + c_{\mathrm{td}})(m-1)(m-2))N_{m-1} - mk_{\mathrm{d}}N_m - k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}}N_m\}/k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} \tag{30}$$

$$N_j = \{(k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} + (j+1)k_{\mathrm{d}} + (c_{\mathrm{tc}} + c_{\mathrm{td}})(j+1)j)N_{j+1} - (j+2)k_{\mathrm{d}}N_{j+2} - (c_{\mathrm{tc}} + c_{\mathrm{td}})(j+3)(j+2)N_{j+3}\}/k_{\mathrm{abs}}[\mathrm{R}]_{\mathrm{w}} \quad j = m-3, ..., 2, 1, 0 \tag{31}$$

Table 4. Values of Parameters Used in the Illustrative Simulations

$k_p = 2.3 \times 10^6$ cm^3/(mol s)
$k_{fm}/k_p = 1 \times 10^{-4}$
$k_{fp}/k_p = 1 \times 10^{-3}$
$k_p{}^*/k_p = 0$
$(c_{tc} + c_{td}) = 0.2$ s^{-1}
$k_{abs} = 7 \times 10^9$ cm^3/(mol s)
$k_d = 5 \times 10^{-3}$ s^{-1}
$(k_{tc} + k_{td})_w = 2.9 \times 10^{10}$ cm^3/(mol s)
$k_I = 5.78 \times 10^{-6}$ s^{-1}
$f = 0.5$

$[M] = 2.9 \times 10^{-3}$ mol/cm^3 water
$[I] = 5 \times 10^{-5}$ mol/cm^3 water
$N_p = 4 \times 10^{13}$ part/cm^3 water
$d_p = 100$ mm
$\bar{M}_{n,seed} = 1.25 \times 10^6$
$\bar{M}_{w,seed} = 1.25 \times 10^6$

Table 5. "Recipes" for the Simulated Seeded Emulsion Polymerizations

	seeded batch	starved process	
	initial charge	initial charge	feed rate
monomer	0.73 mol		2×10^{-5} mol/s
initiator (mol)	0.0125	0.0125	
water (cm^3)	250	250	
seed (particles/cm^3 water) ($d_p = 100$ nm)	4×10^{13}	4×10^{13}	

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

Simulations were carried out using the mathematical model described above combined with the material balances for the reactor[21] and the values of the kinetic parameters given in Table 4. Both seeded batch emulsion polymerizations and seeded semicontinuous emulsion polymerization were considered. The "recipes" for these processes are given in Table 5. Because seeded processes were simulated, the initial conversions were greater than zero.

First, the model was checked by studying the effect of the choice of n_e on the evolution of the gel fraction (fraction of the polymer that is in the gel form). The value of n_e only influences the description of the sol fraction and hence should not have any effect on the gel fraction. Figure 1 shows that this is the case for a seeded batch emulsion polymerization using widely different values of n_e. Teymour and Campbell[4,5] showed that the gel fraction predicted by the numerical fractionation technique became independent of the value of n_c provided that large enough values of n_c were used. In the present work, the algorithm automatically chooses a value of n_c high enough to make the gel fraction independent of n_c by making the mass fraction of polymer in generation n_c with respect to the mass of polymer in the sol less than 10^{-3}. Figure 1 also shows that the amount of gel increases sharply at the end of the process because of the increase of the polymer chain transfer. It has to be pointed out that in these simulations k_{tc} was kept constant during the polymerization; namely, no gel effect was considered. The effect of the gel effect will be analyzed below.

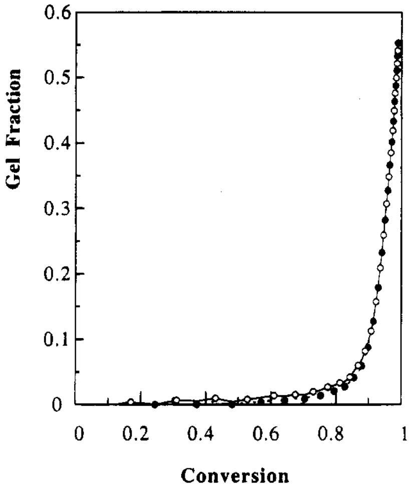

Figure 1. Effect of n_e on the evolution of the gel fraction for the seeded batch emulsion polymerization simulated using the parameters given in Table 4. Termination by combination. Legend: (●) $n_e = 0$ ($n_c = 7$); (○) $n_e = 16$ ($n_c = 20$).

The present approach was also checked by comparing up to the gel point the sum of the individual moments with the moments of the overall MWD calculated using the approach proposed by Arzamendi and Asua.[12] An excellent agreement was found between the predictions of both models.

Figure 2 presents the effect of the value of n_e on the MWD of the sol fraction. For each value of n_e, Figure 2 presents the MWD of each generation as well as the overall MWD. It can be seen that the numerical fractionation method proposed by Teymour and Campbell[4,5] ($n_e = 0$) led to a bimodal MWD. However, this is an artifact of the method because the second peak decreased when the value of n_e increased. A large enough value of n_e will eventually lead to the disappearance of the second peak. Unfortunately, the computer time also increased sharply. Therefore, $n_e = 16$ was used for the simulations presented in this paper. This value provided a reasonably good description of the MWD of the sol fraction with affordable computer time. However, a small peak of high molecular weights still remained in the predicted MWD. This is considered to be an artifact of the method because of the different transfer rules that apply up to n_e and from $n_e + 1$ and will not be shown in the MWDs presented below, but its contribution to the average molecular weights was always taken into account. It is worthwhile to point out that large shoulders or even bimodal MWDs can eventually appear if extensive chain transfer to polymer occurs.

Figure 3 presents the evolution of the MWD of the sol during a seeded batch emulsion polymerization. It can be seen that the molecular weights decreased during the process and a shoulder appeared in the MWD. The MWD shifted toward lower molecular weights because large macromolecules became gels more easily than the small ones. In addition, the shoulder was due to the chain transfer to polymer.

Figure 4 presents the effect of k_{tc} on the gel fraction during a seeded batch emulsion polymerization. The maximum values of $\bar{n}$, m, and n_c calculated for each case are included. It can be seen that for some range of k_{tc} values, the higher k_{tc} the larger the gel fraction.

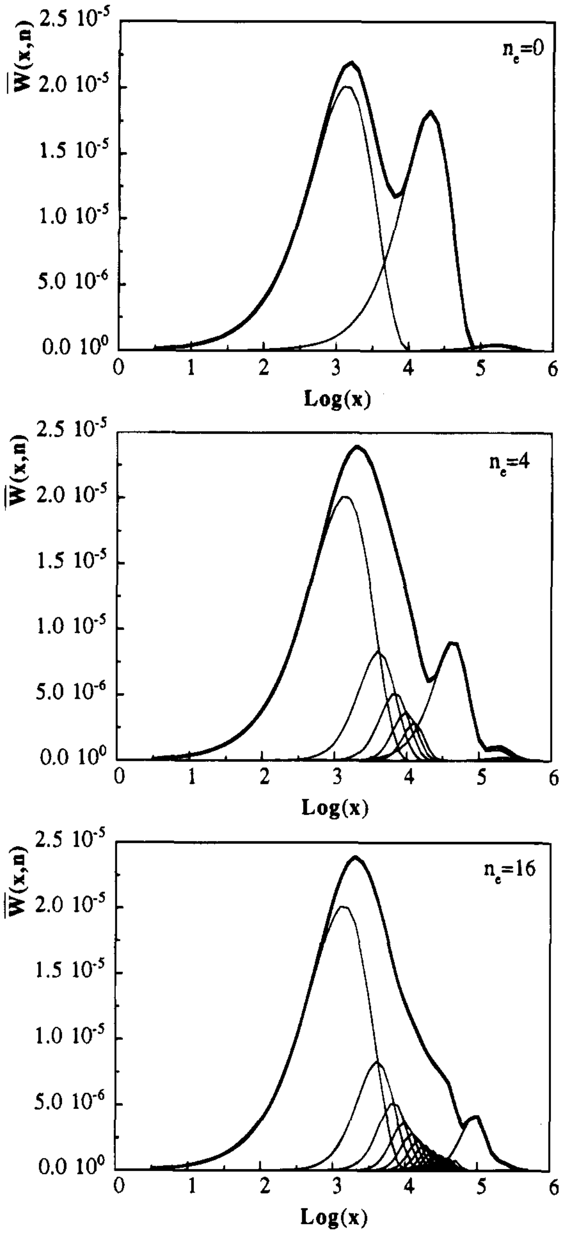

Figure 2. Effect of the value of n_e on the MWD of the sol fraction ($X = 0.4$). Termination by combination.

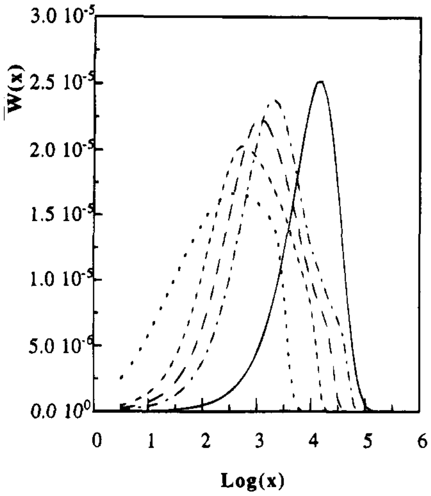

Figure 3. Evolution of the MWD of the sol during the seeded batch emulsion polymerization simulated using the parameters given in Table 4 ($\bar{n} = 0.58$; $m = 4$; $n_e = 16$; $n_c = 20$). Termination by combination. Legend: (—) $X = 0.09$; (—·—) $X = 0.4$; (– –) $X = 0.6$; (- - -) $X = 0.8$; (···) $X = 0.99$.

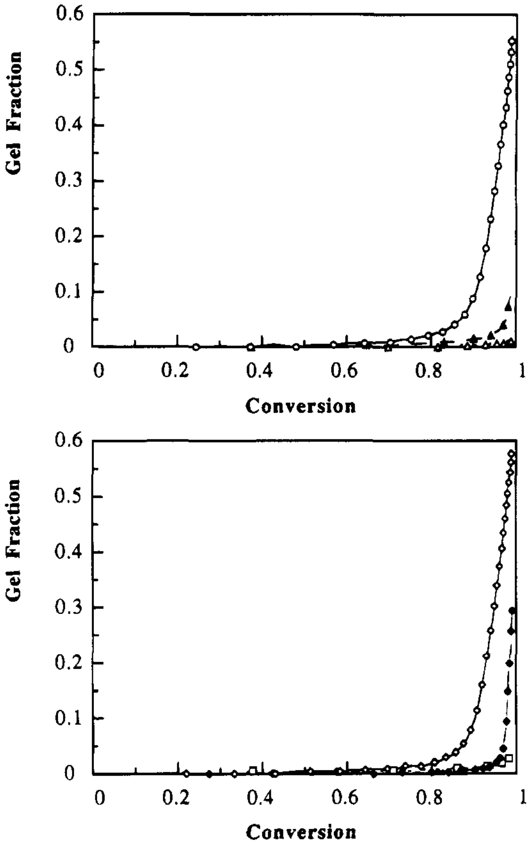

Figure 4. Effect of c_{tc} on the evolution of the gel fraction during the seeded batch emulsion polymerization simulated using the parameters given in Table 4. Termination by combination. Legend: (△) 0.002 s^{-1}, $\bar{n} = 3.13$, $m = 10$, $n_c = 20$; (▲) 0.02 s^{-1}, $\bar{n} = 1.18$, $m = 6$, $n_c = 21$; (○) 0.2 s^{-1}, $\bar{n} = 0.58$; $m = 4$, $n_c = 23$; (◇) 2 s^{-1}, $\bar{n} = 0.49$, $m = 4$, $n_c = 22$; (◆) 20 s^{-1}, $\bar{n} = 0.47$, $m = 4$, $n_c = 22$; (□) 200 s^{-1}, $\bar{n} = 0.47$, $m = 4$, $n_c = 21$.

However, further increases in k_{tc} led to lower amounts of gel because the average number of radicals per particle decreased toward $\bar{n} = 0.5$, and under these circumstances (system 0−1), termination between long active chains could not occur. On the other hand, simulations not presented here showed that for a given value of k_{tc}, the gel fraction increased when k_{fp} increased.

Figure 5 presents the evolution of the gel fraction during a seeded batch emulsion polymerization for various values of k_p^* with $k_{tc} = 0$ and $k_{fp}/k_p = 1 \times 10^{-3}$. It can be seen that no gel is formed if $k_{tc} = k_p^* = 0$. On the other hand, Figure 5 shows that gel is formed for $k_p^* > 0$ even if $k_{tc} = 0$.

The simulations discussed above were carried out for a seeded batch emulsion polymerization. However, most emulsion polymerizations are conducted in a semicontinuous way under starved conditions to control either the heat generation rate or the polymer characteristics. Therefore, it is interesting to compare the predictions of the model for batch and semicontinuous starved processes. Simulations were carried out using the parameters given in Table 4 but including the following gel effect factor:

$$k_{tc} = k_{tc}^0 \exp(-0.44x_p - 6.753{x_p}^2 - 0.3495{x_p}^3) \quad (33)$$

where k_{tc}^0 was taken as 2.9×10^{10} cm^3/(mol s) and x_p is the equivalent conversion in the polymer particles.

Figure 6a presents the evolution of the conversions for both processes. For the starved process two conver-

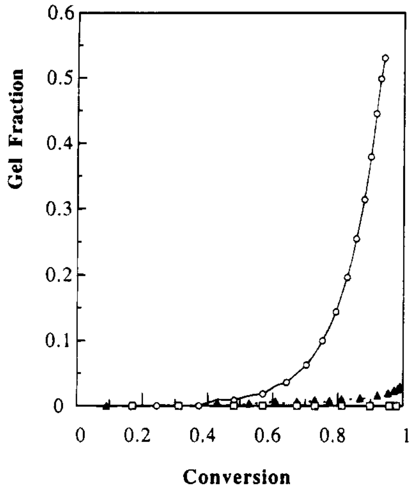

Figure 5. Effect of k_p^* on the evolution of the gel fraction during the seeded batch emulsion polymerization simulated using the parameters given in Table 4. Termination by disproportionation. Legend: (□) $k_p^* = 0$ ($n_c = 17$); (▲) $k_p^* = k_p/10$ ($n_c = 21$); (○) $k_p^* = k_p$ ($n_c = 23$).

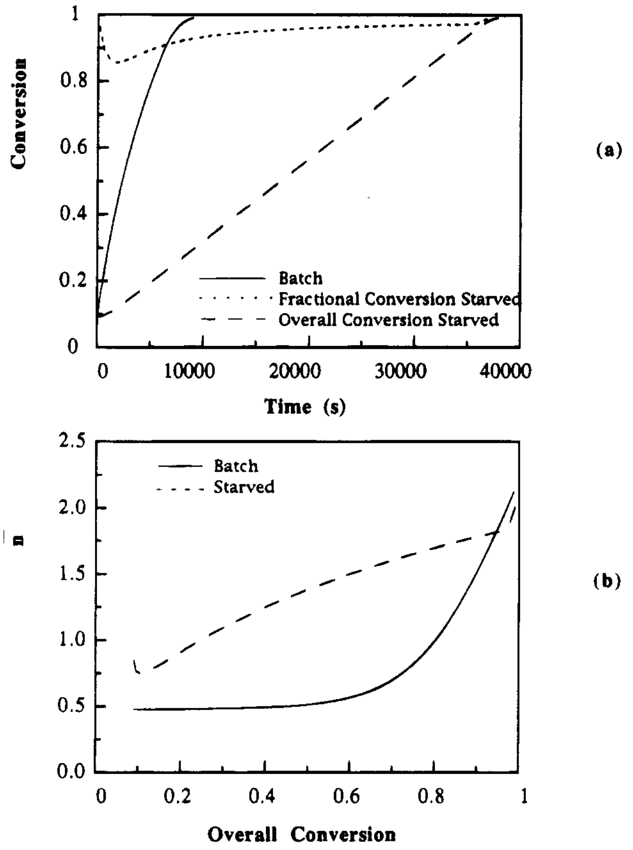

Figure 6. Evolution of the conversions and $\bar{n}$ for both batch and semicontinuous seeded emulsion polymerization. Termination by combination.

sions were defined: fractional conversion which is the fraction of the monomer already fed into the reactor converted to polymer, and the overall conversion that is based on the total amount of monomer in the recipe. Both conversions are the same for the batch process. The initial conversions were not zero because both were seeded processes. The fractional conversion gives the ratio polymer/(polymer + monomer) in the polymer particles that significantly affects both the rate of chain transfer to polymer and the extent of the gel effect. It can be seen that the polymer concentration in the polymer particles in the starved process was much

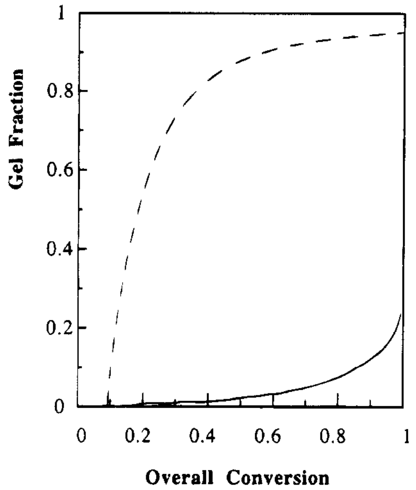

Figure 7. Gel fraction evolution for both batch and semicontinuous seeded emulsion polymerizations. Termination by combination (n_c = 20). Legend: (—) batch process; (- - -) starved process.

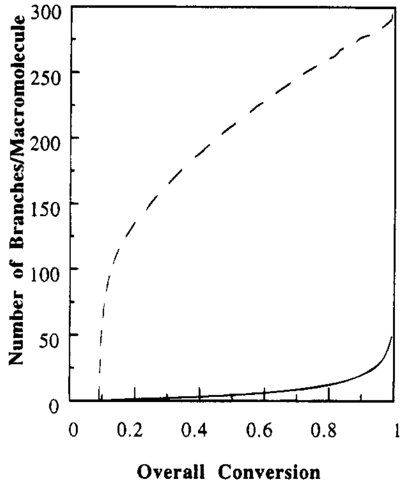

Figure 8. Evolution of the number of branches per macromolecule for both batch and semicontinuous seeded emulsion polymerizations. Termination by combination. Legend: (—) batch process; (- - -) starved process.

higher than in the batch process. Therefore, the gel effect was more pronounced in the starved process, leading to a higher average number of radicals per particle (Figure 6b).

Figure 7 presents the evolution of the gel fraction of both processes. It can be seen that in the starved process, gel was formed soon in the process because of the combined effect of high polymer concentration (that promotes the polymer chain transfer) and high $\bar{n}$ (that favors the bimolecular termination). On the other hand, almost no gel was formed in the batch reactor for $X < 0.6$. In addition, the amount of gel was lower than in the previous examples because an evolution of k_{tc} (gel effect) was considered in this simulation. Similar results were obtained for the number of branches per macromolecule (Figure 8).

Figure 9 presents the evolution of the MWD of the sol fraction for both processes. The first chart describes the polymer contained in the initial seed. It can be seen that the sol produced in the starved process had a lower molecular weight than that of the batch process. The reason is that in the starved process the long chains were more easily swept up by the gel, and hence the larger the amount of gel the lower the molecular weight of the sol fraction. Also, it can be seen that the MWD

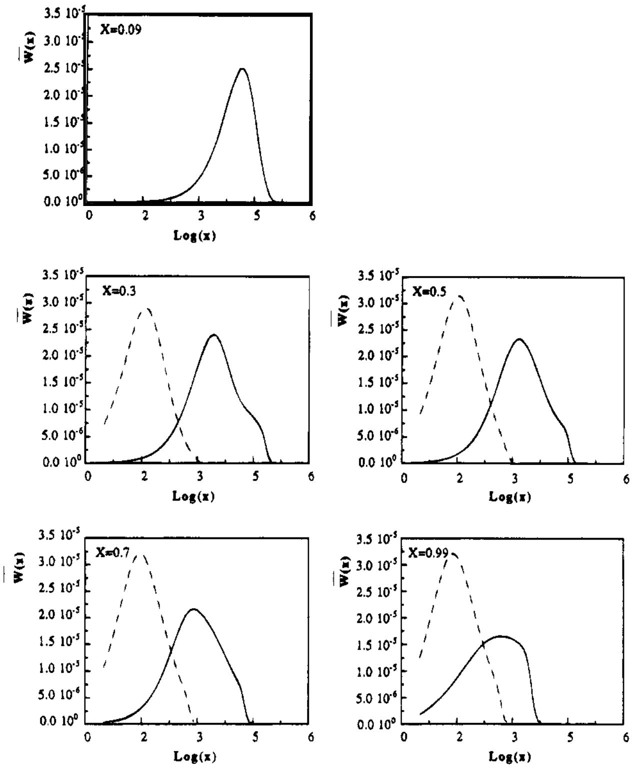

Figure 9. Evolution of the MWD of the sol fraction for both batch and semicontinuous seeded emulsion polymerizations. Termination by combination. Legend: (—) batch process; (- - -) starved process.

of the batch process is broader than that of the starved process, because the conditions of the polymer particles vary more for the batch process than for the starved process, and hence a more heterogeneous polymer is produced in batch polymerization.

Conclusions

A mathematical model for the computation of the molecular weight distribution of the sol, the gel fraction, and the gel point in emulsion polymerization systems was developed. The model uses a variation of the numerical fractionation technique developed by Teymour and Campbell[4,5] and accounts for both the compartmentalization of the free radicals in the reaction system and the changes in the environment where the chain was growing. The numerical fractionation technique used in the present work allows a better description of the MWD of the sol fraction than the original approach.[4,5] Illustrative simulations of seeded batch emulsion polymerizations carried out using the model showed that gel can be formed when the extent of the chain transfer to polymer is significant and termination occurs by combination. It was found that for some range of k_{tc} values, the higher k_{tc} the larger the gel fraction. However, further increases in k_{tc} led to lower amounts of gel because the probability of finding two or more radicals in a polymer particle became negligible. Extensive propagation to terminal double bonds can lead to gel formation irrespective of the type of bimolecular termination. The comparison between batch and semicontinuous starved emulsion polymerizations showed that, because of the combined effect of high polymer concentration and high $\bar{n}$, the amount of gel formed in the starved process was higher than for the batch system. On the other hand, the molecular weights of the sol fraction produced in the starved process was lower than that of the batch process because the long chains were more easily swept up by the gel.

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Nomenclature

c_{tc}	rate coefficient for termination by combination (s^{-1})
c_{td}	rate coefficient for termination by disproportionation (s^{-1})
[DB]	concentration of terminal double bonds
d_p	particle diameter (nm)
f	efficiency factor of the initiator radical generation
I	amount of initiator present in the reaction medium (mol cm^{-3})
k_{abs}	absorption rate coefficient ($cm^3\ mol^{-1}\ s^{-1}$)
k_d	desorption rate coefficient (s^{-1})
k_{fm}	monomer chain transfer rate constant ($cm^3\ mol^{-1}\ s^{-1}$)
k_{fp}	polymer chain transfer rate constant ($cm^3\ mol^{-1}\ s^{-1}$)
k_I	rate constant for initiator decomposition (s^{-1})
k_p	propagation rate constant ($cm^3\ mol^{-1}\ s^{-1}$)
k_p^*	rate constant for propagation to terminal double bonds ($cm^3\ mol^{-1}\ s^{-1}$)
k_{tc}	termination by combination rate constant ($cm^3\ mol^{-1}\ s^{-1}$)
k_{td}	termination by disproportionation rate constant ($cm^3\ mol^{-1}\ s^{-1}$)
m	maximum number of radicals per particle
[M]	concentration of monomer in polymer particles (mol cm^{-3})
M_k	kth-order moment of the overall polymer chain distribution
$M_{k,sol}$	kth-order moment of the sol polymer chain distribution
$\bar{n}$	average number of radicals per particle
n_e	boundary generation (generations lower than n_e are characterized by the number of branching points. Generations higher than n_e are characterized by a geometrical growth.)
n_c	critical generation to sol description
n_p	number of processes leading to inactive macromolecules
N_A	Avogadro's number
N_j	number of polymer particles containing j radicals (cm^{-3})
N_p	total number of polymer particles in the reactor
P_{DB}	probability of finding an inactive chain with a terminal double bond
Q_k	kth-order moment of the overall polymer chain distribution of inactive polymeric chains
$Q_k^j(n)$	kth-order moment of the chain length distribution of inactive polymeric chains in particles containing j radicals of generation n
$\mathscr{R}_i$	production rate of process i
$[R]_w$	concentration of radicals in the aqueous phase (mol cm^{-3})
R_1	single unit radicals
t	time (s)
T	temperature (K)

$w(x,n,j,i)$	instantaneous weight fraction of chains of length x in the polymer of generation n formed in polymer particles with j radicals through the process i
$W(x,n)$	instantaneous chain length distribution of generation n
$\bar{W}(x)$	overall cumulative chain length distribution
$\bar{W}(x,n)$	cumulative chain length distribution of generation n
x_p	equivalent conversion in the polymer particles
X	overall conversion
$\bar{X}_n(n,j,i)$	number average chain length of the polymer of generation n formed in polymer particles with j radicals through the process i
$\bar{X}_w(n,j,i)$	weight average chain length of the polymer of generation n formed in polymer particles with j radicals through the process i
$Y^j_k(n)$	kth-order moment of the non-normalized chain length distribution of the active polymer in polymer particles containing j radicals of generation n

Greek symbols

δ	Dirac delta function
Γ	gamma function
λ^j_{ki}	kth-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
μ'_{ki}	kth-order moment of the normalized chain length distribution of inactive polymeric chains formed through process i
ϕ^P_p	volume fraction of polymer in the polymer particles

References and Notes

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