A New Look at Kinetic Modeling of Nonlinear Free Radical Polymerizations with Terminal Branching and Chain Transfer to Polymer

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ABSTRACT: The authors' previously developed method for the general kinetic analysis of nonlinear irreversible polymerizations based on moment generating functions is used for simulating free radical polymerization systems in which terminal branching and chain transfer to polymer are present, leading possibly to gel formation. The numerical solution of the equations needed for postgel predictions of sol fraction and average molecular weights (a major difficulty) is discussed with some detail. Finally, some different combinations of kinetic parameters were tested in order to assess their influence on the molecular weight development in a batch reactor.

Introduction

It is well-known that in free radical polymerizations long chain branching can occur due to propagation on terminal double bonds and transfer to polymer. Vinyl acetate polymerization is one of the most representative systems in which transfer to monomer creates a terminal double bond and a radical located in the methyl substituent group. Subsequent addition on the terminal double bond leads to branched polymer molecules. In addition, this system is also characterized by transfer to polymer via the reaction of chain radicals with active centers in the polymer, namely, a tertiary hydrogen on the substituted chain carbon or a methylenic hydrogen in the methyl acetate group. As a result, trifunctional units are formed in the structure of the polymer.[1,2]

In other systems, such as ethylene, methyl acrylate, vinylidene fluoride, and vinylidene chloride polymerizations, branching also occurs involving other or a subset of the mechanisms related with terminal double bond branching and transfer to polymer.[3] In some cases, termination by disproportionation is also an indirect source of branching. If the terminal double bonds generated by this mechanism have some tendency to propagate, then additional branching occurs in the polymer.

Free-radical polymerization is kinetically controlled. As the condition for random branch points in a statistical gelation process cannot be applied, with errors becoming important as soon as substitution effects are present,[4] this fact invalidates the mathematical treatment of these systems by the theory of branching processes.

Following Bamford and Tompa's pioneering work,[5] some derivations for kinetic models taking into account terminal double bond polymerization and transfer to polymer have been done,[6,7] in particular for the vinyl acetate polymerization.

These models were derived using some mathematical approximations which became widespread:

(A) Quasi-steady state for radical concentrations.

(B) Negligible presence of multiple radical centers.

(C) Negligible initiation and termination reactions relative to the propagation and transfer mechanisms.

Additionally, a closure condition is needed for solving the equations for the moments. In more recent works, the need for approximation C was avoided, but the other two simplifications are used.[8,9]

Many key features of kinetic modeling of nonlinear free radical polymerizations have been acknowledged by Kuchanov and Pis'men,[10] namely the need of avoiding quasi-steady-state hypothesis for radical concentrations and the usefulness of consideration of multiple radical centers. Nevertheless, in current methods used to describe this kind of systems some of these approximations have been kept: published works using the method of moments,[11] the numerical fractionation technique,[12] and Galerkin finite-elements method[13] have made use of approximations A and B above.

Monte Carlo simulation has the advantage of providing a detailed view of molecular structure and is a possible alternative way for dealing with these problems. Successful use with polycondensations has been known since long ago,[4] but widely different time scales in free radical polymerization make its straightforward application very time-consuming, and so it has never been carried out. Approximate Monte Carlo simulation of these same systems (and many others) has been extensively used by H. Tobita and collaborators.[14−16] It also relies on quasi-steady-state approximation and Flory's theory of branching.

The authors have been developing a more rigorous kinetic approach for modeling irreversible nonlinear polymerizations,[17] with full success for nonlinear polycondensations and nonradical polyadditions.[20] The method thus presented can be used for the prediction of average molecular weights and molecular weight distributions before and after gelation. In addition, it has been shown that elastic properties of the gel can also be calculated. Meanwhile, this approach was ex-

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Table 1. Notation Used for Describing Group Counts

variable	meaning
N_A	no. of chemical groups
N_P	no. of chemical groups belonging to polymer molecules
N_{A_P}	no. of chemical groups belonging to polymer molecules which can be consumed by chemical reaction

Table 2. Notation Used for Describing Reactions

variable	meaning
N_R	no. of reactions creating connections between repeating units
N_{R_P}	no. of reactions creating connections between repeating units involving only polymer molecules
N_R^{**}	no. of bimolecular reactions which do not create connections between repeating units
N_{RP}^{**}	no. of bimolecular reactions which do not create connections between repeating units involving only polymer molecules
N_{RS}^{**}	no. of bimolecular reactions which do not create connections between repeating units involving a polymer molecule and a small molecule
N_R^{*}	no. of unimolecular reactions
N_I	no. of bimolecular reactions involving small molecules and leading to polymer creation
N_M	no. of reactions of transfer to monomer (creating a new polymer species)

tended to the prediction of average radius of gyration of branched polymers in nonradical polyadditions.[21]

Further progress has been delayed on account of severe numerical difficulties in the application of the method to the systems after gelation in nonlinear free radical polymerizations. Only very recently those difficulties have been overcome and the method has been applied with success to the free radical mono/divinyl monomers copolymerizations,[18] complex anionic mono/divinyl monomers copolymerizations and free radical copolymerization of monovinyl and conjugated divinyl monomers.[19]

In this paper, the general method proposed by the authors is applied to nonlinear free radical polymerizations with terminal branching and transfer to polymer. This requires, to begin with, a careful consideration of the intervening groups, reactions and their stoichiometry in order to find a model according to this approach. On leaving aside the above-described classical approximations, appreciable gains in accuracy and reliability of predicted molecular weights result, with possible further use in obtaining better estimates of chemical parameters.[22] It is also interesting to use simulation to assess the influence of the different branching reactions on the average molecular weights before and after gelation, which is done toward the end of this presentation.

Kinetic Scheme

Keeping in mind that one of the main objectives of this work is to show the flexibility of this treatment of nonlinear free radical polymerizations, we select a kinetic scheme as generic as possible and avoid sticking to some particular chemical system. In previous works, the authors have analyzed the particular case of vinyl acetate polymerization in batch and continuous reactors.[22,23] The results obtained in those simulations demonstrate a fairly good agreement with experimental results of several other previous works.[9,24−27] In those cases, we have considered the situation where transfer to polymer can occur in two different sites in the molecules. Then the formation of saponified and nonsaponified branches can also be simulated.

On the other hand, in this system there is no evidence for polymerization of terminal double bond derived from termination by disproportionation. Notice that in the experimental conditions used by the above-mentioned authors no gelation was observed and our simulations were in agreement with this finding. One of the advantages of this approach is the possibility of adding new reactions and/or chemical groups and easily modifying the kinetic scheme.

In this paper we will consider a kinetic scheme consisting in the following generic steps:

- Initiator decomposition.
- Initiation of monomer and terminal double bonds.
- Propagation of monomer and terminal double bonds with creation of active centers for transfer to polymer.
- Termination by combination.
- Termination by disproportionation with formation of terminal double bonds.
- Transfer to polymer.
- Transfer to monomer with formation of terminal double bonds.

It is a kinetic scheme close to that considered in related recent works in this subject,[11−13] but in addition, we opt for distinguishing the terminal double bonds created in termination by disproportionation from the terminal double bonds originated in the transfer to monomer reaction because they can have very different reactivities.

The simplest description of the system considers the following nine groups: free radicals, which we represent by A_1, terminal double bonds originated by transfer to monomer (A_2), terminal double bonds originated by termination by disproportionation (A_3), transfer to polymer center (A_4), monomer (A_5), primary radicals (A_6), initiator (A_7), polymerized monomer unity (A_8), and the fragment from initiator (A_9).

The general treatment of irreversible polymerization[19] greatly helps in establishing the mathematical description of the kinetic model, and so we will now start to gather the information needed by that approach. A summary of the notations used is present in Tables 1 and 2. For instance, variable N_A, counting the number of chemical groups, is thus 9.

Only six chemical groups belong to the polymer. In the context of the forementioned method,[19] this is variable $N_P = 6$. To each chemical group A_j belonging to polymer, an incidence value $\delta_{P_j} = 1$ is defined, otherwise this variable will have a nil value: $\delta_{P_j} = 0$.

Seven groups are consumed by chemical reaction. In a similar way, another incidence value will be introduced, a group A_j with $\delta_{A_j} = 1$ is consumed by chemical reaction, otherwise $\delta_{A_j} = 0$.

The first 4 groups are present in the polymer, $N_{A_P} = 4$. Three groups are active but not present in the

Table 3. Description of Groups in a Free Radical Polymerization with Terminal Double Bonds Branching and Transfer to Polymer

group description	n	δ_{P_n}	δ_{A_n}	chemical formula (example)
free radical	1	1	1	$-HYC^{\bullet}$
terminal double bond originated by transfer to monomer	2	1	1	$CH_2{=}CH-$
terminal double bond originated by termination by disproportionation	3	1	1	$CHY{=}CH-$
transfer to polymer center	4	1	1	$-CH_2-C\mathit{H}Y-CH_2-$
monomer	5	0	1	$CH_2{=}CHY$
primary radical	6	0	1	$(CH_3)_2(CN)C^{\bullet}$
initiator	7	0	1	$(CH_3)_2(CN)CN{=}NC(CN)(CH_3)_2$
polymerized monomer unit	8	1	0	$-CH_2-CHY-$
initiator fragment	9	1	0	$(CH_3)_2(CN)C-$

Table 4. Reaction Scheme in a Free Radical Polymerization with Terminal Double Bonds Branching and Transfer to Polymer

reaction name	chemical equation
initiator decomposition	$A_7 \xrightarrow{k_1^* = k_d} 2fA_6$
monomer initiation	$A_5 + A_6 \xrightarrow{k_{I_1} = k_{i_1}} A_1 + A_8 + A_9$
propagation of terminal double bond originated from transfer to monomer	$A_1 + A_2 \xrightarrow{k_1 = k_{P_2}} A_4 + A_1$
propagation of terminal double bond originated from termination by disproportionation	$A_1 + A_3 \xrightarrow{k_2 = k_{P_3}} A_4 + A_1$
termination by combination	$A_1 + A_1 \xrightarrow{k_3 = k_{tc}} A_4 + A_4$
propagation of monomer	$A_1 + A_5 \xrightarrow{k_4 = k_{P_1}} A_4 + A_1 + A_8$
transfer to polymer	$A_1 + A_4 \xrightarrow{k_1^{**} = k_{fp}} A_1$
termination by disproportionation	$A_1 + A_1 \xrightarrow{k_2^{**} = k_{td}} A_3$
initiation of terminal double bond originated from transfer to monomer	$A_2 + A_6 \xrightarrow{k_3^{**} = k_{i_2}} A_1 + A_9$
initiation of terminal double bond originated from termination by disproportionation	$A_3 + A_6 \xrightarrow{k_4^{**} = k_{i_3}} A_1 + A_9$
transfer to monomer	$A_1 + A_5 \xrightarrow{k_{M_1} = k_{fm}} A_1 + A_2 + A_8$

polymer ($\delta_{P_j} = 0$). This description of groups is presented in Table 3.

If the goal is only the prediction of average degrees of polymerization, the group corresponding to the fragment from the initiator can be eliminated, but if its small effect on average molecular weights is to be taken into account, it should also be considered.

Notice that for simplicity, A_1 represents a lumped set of different kinds of free radicals (radical from the monomer and radical from the substituent of the monomer, for example). If a more detailed description is needed (taking into account the possible difference of reactivities between radicals), more groups shall have to be added to this set. This is likely to occur owing to the sensitivity of radical reactions to steric effects.

The kinetic scheme consists also in 11 elementary reactions (see Table 4) that can be divided into five different classes according to the general model basis.[19] A total number of $N_R = 4$ reactions create connections between repeating units and among these $N_{R_P} = 3$ involve only groups present in polymer molecules (propagation of terminal double bonds and termination by combination) and $N_R - N_{R_P} = 1$ involve a group in the polymer and a nonpolymeric molecule (propagation of monomer). Notice that all of these reactions generate centers for transfer to polymer.

A total number of $N_R^{**} = 4$ bimolecular reactions do not create connections between repeating units, $N_{R_P}^{**} = 2$ of these involve two polymer molecules (transfer to polymer and termination by disproportionation) and $N_{R_S}^{**} = 2$ involve a polymer molecule and a small molecule (terminal double bonds initiation).

The other reactions are $N_R^* = 1$ unimolecular reactions (initiator decomposition), $N_I = 1$ bimolecular involving groups not present in the polymer with polymer creation (monomer initiation) and $N_M = 1$ transfers to monomer also with polymer formation.

As we have already mentioned, the increase in the degree of complexity of the kinetic scheme considered can be automatically taken into account in the model equations by increasing the number of groups and/or the number of elementary reactions between them.

Mathematical Description of the Polymer

The set of polymer species with same numbers of groups, described by vector $\mathbf{a}_m$ of size N_A is named $P(\mathbf{a}_m)$ and its correspondent mole concentration is $P(\mathbf{a}_m)$.

On considering that vector $\mathbf{a}_m$ has size N_A and not simply N_P (which would be possible since this is the number of different groups in polymer) an arbitrary labeling of the groups becomes possible: there will be no need to specify that the groups belonging to polymer molecules have to be the first N_P of the total count N_A. This is especially advantageous if different kinetic schemes with growing complexity (implying the consideration of new groups) are used for describing a polymerization system. Different numbering schemes of groups would be extremely confusing.

As a consequence, if any component a_{m_j} of $\mathbf{a}_m$ such that $\delta_{P_j} = 0$ and $a_{m_j} \neq 0$ (from Table 3 they are a_{m_5}, a_{m_6} and a_{m_7} with the chemical system here discussed), then there will be no polymer species with that group count: $P(\mathbf{a}_m) = 0$.

The vectorial moment generating function of $P(\mathbf{a}_m)$ with the respect to the group counts is the key for an easier calculation of average chain lengths and other polymer properties. It will depend on a vector of complex numbers $\mathbf{s}$ of size N_A. In fact, no dependence will be observed on the components corresponding to groups not present in polymer (s_5, s_6, and s_7 for this chemical scheme).

The general definition of that vectorial moment generating function is

$$G(\mathbf{s}) = \sum_{a_1=0}^{\infty} ... \sum_{a_{1_{N_A}}=0}^{\infty} {s_1}^{a_1} ... {s_{N_A}}^{a_{N_A}} P(a_1, ..., a_{N_A}) \quad (1)$$

Following the methods we have already presented[17,19] it is possible to write the generating function of the rate equations of formation of polymer species by chemical reaction, taking advantage of the simplification of convolution terms made possible by eq 1. For a batch reactor with negligible volume change, the mass balance equation in Laplace domain describing this polymerization scheme is

$$\begin{aligned} \frac{\partial G}{\partial t} = {} & k_{p_2}\left(\frac{s_4}{s_2}\frac{\partial G}{\partial \log s_1}\frac{\partial G}{\partial \log s_2} - A_2\frac{\partial G}{\partial \log s_1} - A_1\frac{\partial G}{\partial \log s_2}\right) + \\ & k_{p_3}\left(\frac{s_4}{s_3}\frac{\partial G}{\partial \log s_1}\frac{\partial G}{\partial \log s_3} - A_3\frac{\partial G}{\partial \log s_1} - A_1\frac{\partial G}{\partial \log s_3}\right) + \\ & k_{tc}\left[\frac{{s_4}^2}{{s_1}^2}\left(\frac{\partial G}{\partial \log s_1}\right)^2 - 2A_1\frac{\partial G}{\partial \log s_1}\right] + \\ & k_{p_1}A_5\frac{\partial G}{\partial \log s_1}(s_4 s_8 - 1) + \\ & k_{fp}\left[A_4\frac{\partial G}{\partial \log s_1}\left(\frac{1}{s_1} - 1\right) + A_1\frac{\partial G}{\partial \log s_4}\left(\frac{s_1}{s_4} - 1\right)\right] + \\ & k_{td}\left[A_1\frac{\partial G}{\partial \log s_1}\left(\frac{1}{s_1} - 1\right) + A_1\frac{\partial G}{\partial \log s_1}\left(\frac{s_3}{s_1} - 1\right)\right] + \\ & k_{i_1}A_5A_6s_1s_8s_9 + k_{i_2}A_6\frac{\partial G}{\partial \log s_2}\left(\frac{s_1 s_9}{s_2} - 1\right) + \\ & k_{i_3}A_6\frac{\partial G}{\partial \log s_3}\left(\frac{s_1 s_9}{s_3} - 1\right) + \\ & k_{fm}A_5\left[A_1s_1s_2s_8 + \frac{\partial G}{\partial \log s_1}\left(\frac{1}{s_1} - 1\right)\right] \end{aligned} \quad (2)$$

The mathematical treatment presented avoids the need of considering approximations like the quasi-steady-state hypothesis for radical concentrations and negligible presence of multiple radical centers (in our notation these are the polymer species for which $a_1 > 1$). Moments with respect to the counts of groups are obtained through the differentiation of eq 2 with respect to log s_i, and in addition, rate equations for the moments are obtained; there is no need for moment closure conditions.

The solution of eq 2 is obtained by the method of characteristics[29] and a system of ordinary differential equations results, the resolution of which is discussed in the next section.

Numerical Integration of the Characteristics

Integration of the characteristics is one crucial point in this method. If one is interested only in the prediction of average molecular weights before gelation, the problem is much easier because the characteristics follow from a trivial solution. But if there is a gel, a nontrivial solution for the characteristics has to be found, and this can be a very difficult problem. For this reason it is presented in this section a detailed discussion about the way of circumventing those numerical difficulties.

Following the techniques presented by us,[17,19] the mass balance equations in Laplace domain describing this polymerization system in batch reactor share the characteristic lines, which are obtained from the system of ordinary equations below:

$$\frac{dA_1}{dt} = k_{i_1}A_5A_6 + k_{i_2}A_2A_6 + k_{i_3}A_3A_6 - 2k_{tc}{A_1}^2 - 2k_{td}{A_1}^2 \quad (3)$$

$$\frac{dA_2}{dt} = k_{fm}A_1A_5 - k_{i_2}A_2A_6 - k_{p2}A_1A_2 \quad (4)$$

$$\frac{dA_3}{dt} = k_{td}{A_1}^2 - k_{i_3}A_3A_6 - k_{p_3}A_1A_3 \quad (5)$$

$$\frac{dA_4}{dt} = k_{p_1}A_1A_5 + k_{p2}A_1A_2 + k_{p_3}A_1A_3 + 2k_{tc}{A_1}^2 - k_{fp}A_1A_4 \quad (6)$$

$$\frac{dA_5}{dt} = -k_{i_1}A_5A_6 - k_{p1}A_1A_5 - k_{fm}A_1A_5 \quad (7)$$

$$\frac{dA_6}{dt} = 2fk_dA_7 - k_{i_1}A_5A_6 - k_{i_2}A_2A_6 - k_{i_3}A_3A_6 \quad (8)$$

$$\frac{dA_7}{dt} = -\, k_dA_7 \quad (9)$$

The system of ordinary differential equations eqs 3−9 simply represents the mass balances of active groups in the batch reactor. Other equations could be added for the groups which are only produced but not consumed by chemical reaction (A_8 and A_9).

At the start of the polymerization only monomer and initiator are present, and so, the initial conditions for eqs 3−9 are

$$A_{j|t=0} = 0; \quad j = 1, 2, 3, 4, 6 \quad (10)$$

$$A_{5|t=0} = M_0 \quad (11)$$

$$A_{7|t=0} = I_0 \quad (12)$$

To estimate chain length distributions (full or marginal), the solution of eq 2 for a vector **s** over spherical surfaces of up to $N_P = 6$ dimensions of radius close to 1 and centered in the origin would be needed.[28] The much simpler problem of predicting average degrees of polymerization requires only the values of $G(\mathbf{s})$ and its derivatives for $\mathbf{s} = \mathbf{1}$ (a vector of N_A components all equal to 1). Laplace parameters related to the groups which are not consumed by chemical reaction can in that case be immediately set to 1 ($s_8 = s_9 = 1$).

Defining $G_i = \partial G/\partial \log s_i$, the characteristics are the solution of the system below:

$$\frac{\mathrm{d}G_1}{\mathrm{d}t} = k_{\mathrm{i}_1} s_1 A_5 A_6 + k_{\mathrm{i}_2} \frac{s_1}{s_2} G_2 A_6 + k_{\mathrm{i}_3} \frac{s_1}{s_3} G_3 A_6 - 2k_{\mathrm{tc}} \frac{{s_4}^2}{{s_1}^2} {G_1}^2 - k_{\mathrm{td}} \frac{1 + s_3}{s_1} A_1 G_1 + k_{\mathrm{fp}} \left(\frac{s_1}{s_4} A_1 G_4 - \frac{1}{s_1} A_4 G_1 \right) + k_{\mathrm{fm}} A_5 \left(s_1 s_2 A_1 - \frac{1}{s_1} G_1 \right) \quad (13)$$

$$\frac{\mathrm{d}G_2}{\mathrm{d}t} = k_{\mathrm{fm}} s_1 s_2 A_1 A_5 - k_{\mathrm{p}_2} \frac{s_4}{s_2} G_1 G_2 - k_{\mathrm{i}_2} \frac{s_1}{s_2} A_6 G_2 \quad (14)$$

$$\frac{\mathrm{d}G_3}{\mathrm{d}t} = k_{\mathrm{td}} \frac{s_3}{s_1} A_1 G_1 - k_{\mathrm{p}_3} \frac{s_4}{s_3} G_1 G_3 - k_{\mathrm{i}_3} \frac{s_1}{s_3} A_6 G_3 \quad (15)$$

$$\frac{\mathrm{d}G_4}{\mathrm{d}t} = k_{\mathrm{p}_1} s_4 A_5 G_1 + k_{\mathrm{p}_2} \frac{s_4}{s_2} G_1 G_2 + k_{\mathrm{p}_3} \frac{s_4}{s_3} G_1 G_3 + 2k_{\mathrm{tc}} \frac{{s_4}^2}{{s_1}^2} {G_1}^2 - k_{\mathrm{fp}} \frac{s_1}{s_4} A_1 G_4 \quad (16)$$

Since in the beginning of the reaction there is no polymer in the system, the initial conditions for eqs 13–16 are

$$G_{\mathrm{j}|t=0} = 0; \quad j = 1...4 \quad (17)$$

The system allowing to compute the characteristics becomes complete with the following set of equations:

$$\frac{\mathrm{d}(\log s_1)}{\mathrm{d}t} = k_{\mathrm{p}_2} \left(A_2 - \frac{s_4}{s_2} G_2 \right) + k_{\mathrm{p}_3} \left(A_3 - \frac{s_4}{s_3} G_3 \right) + 2k_{\mathrm{tc}} \left(A_1 - \frac{{s_4}^2}{{s_1}^2} G_1 \right) + k_{\mathrm{p}_1} A_5 (1 - s_4) + k_{\mathrm{fp}} A_4 \left(1 - \frac{1}{s_1} \right) + k_{\mathrm{fm}} A_5 \left(1 - \frac{1}{s_1} \right) + k_{\mathrm{td}} A_1 \left(2 - \frac{1 + s_3}{s_1} \right) \quad (18)$$

$$\frac{\mathrm{d}(\log s_2)}{\mathrm{d}t} = k_{\mathrm{p}2} \left(A_1 - \frac{s_4}{s_2} G_1 \right) + k_{\mathrm{i}_2} A_6 \left(1 - \frac{s_1}{s_2} \right) \quad (19)$$

$$\frac{\mathrm{d}(\log s_3)}{\mathrm{d}t} = k_{\mathrm{p}_3} \left(A_1 - \frac{s_4}{s_3} G_1 \right) + k_{\mathrm{i}_3} A_6 \left(1 - \frac{s_1}{s_3} \right) \quad (20)$$

$$\frac{\mathrm{d}(\log s_4)}{\mathrm{d}t} = k_{\mathrm{fp}} A_1 \left(1 - \frac{s_1}{s_4} \right) \quad (21)$$

The initial values of $N_{\mathrm{A_P}} = 4$ components of the vector of Laplace parameters **s** (the ones related to groups which are consumed by chemical reaction) are unknown and must be found as a function of its final value, $\mathbf{s}_{\mathrm{f}}$, which is prescribed for a certain time of polymerization $t = t_{\mathrm{f}}$. So, the initial conditions for the system eqs 18–21 are

$$s_{j|t=0} = s_{j_0}; \quad j = 1...4 \quad (22)$$

The problem to be solved consists of the system of ordinary differential eqs 3–9, 13–16, and eqs 18–21, together with initial conditions given by eqs 10, 11, 12, 17, and 22. In practice, one has to solve a two-point boundary value problem with the conditions at the right point $t = t_{\mathrm{f}}$:

$$s_{j|t=t_{\mathrm{f}}} = s_{j_{\mathrm{f}}}; \quad j = 1...4 \quad (23)$$

Since the goal is only to compute the moments of the chain length distribution, $\mathbf{s}_{\mathrm{f}} = \mathbf{1}$.

With a simple inspection of the characteristics problem one can easily conclude that a possible solution is: $G_i = A_i$ with $\mathbf{s}_0 = \mathbf{1}$. This is the *trivial* solution and is also the physically meaningful solution before gelation. It means that all groups belong to *finite* polymer molecules.

Gelation is defined by a bifurcation point where a second branch with at least some $s_{j_0} < 1$ intersects the trivial solution, $t = t_{\mathrm{g}}$ being the gel time. For $t > t_{\mathrm{g}}$, the physically meaningful solution is the *nontrivial* solution branch. Notice that $G_i(\mathbf{1})$ represents the concentration of groups in *finite* polymer molecules, and then, after gelation for some cases $G_i(\mathbf{1}) < A_i$ because some groups belong to *infinite* polymer molecules (gel).

If only average properties of the polymer before gelation are needed, integration of the system of ordinary differential equations leads to a problem of initial conditions, relatively straightforward as will be later shown. However, finding the *nontrivial* solution branch for the gel region (a class of boundary value problems of the “timelike” variety[30]) can be a very difficult task.

Because of the high relative values of termination rate constants relative to propagation, the system in either case becomes extremely “stiff”. This can verified in a number of ways, for instance, computing the product of the end value of the time t_{f} by the absolute value of the real part of the eigenvalues of the jacobian of the right-hand sides of the system of eqs 3–9, 13–16, and 18–21.

Well-known code for “stiff” systems of ordinary differential equations RADAU5[31] can successfully solve the system for the end groups mass balances, eqs 3–9, but on trying to use it to solve the entire problem of the characteristics, numerical values “blow out”, even with the exact solution (*trivial* solution branch) for s_{j_0} (Figure 1). We are in the presence of very ill-conditioned problems.

It is also well-known that this kind of problems must be solved by parallel multiple shooting.[33,35,36] Unfortunately, due to the extreme numerical sensitivity almost currently available codes we have tried fail the solution, with the exception of the integrator present in Cash, Moore, and Wright’s automatic continuation code ACDC,[37–39] available in http:/www.netlib.org/ode/acdc.f. We have observed that its continuation procedure (along some parameter, such as the propagation rate constant) usually leads to the trivial solution branch instead of the physically meaningful solution. Fortunately, its implicit Runge–Kutta integrator based on Lobatto quadrature can be used to find the solution for every

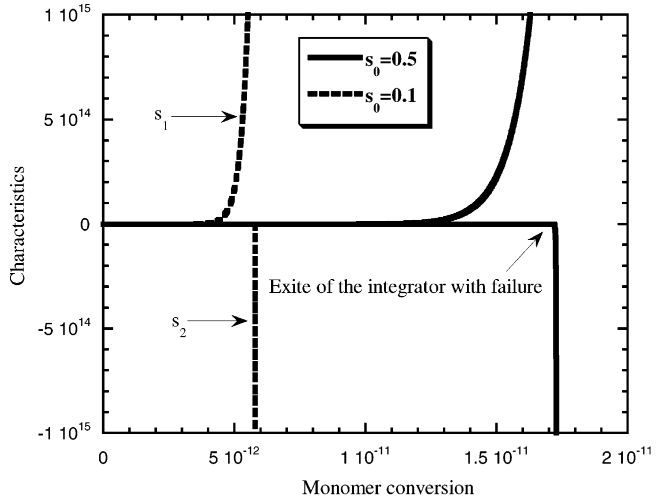

Figure 1. Numerical “blow-up” of solution of characteristics system of differential equations.

Table 5. Representative Set of Kinetic Parameters in a Free Radical Polymerization with Terminal Double Bonds Branching and Transfer to Polymer

kinetic parameter	relative value	absolute value
k_{p_1}		1.17×10^4 dm^3 mol^{-1} s^{-1}
k_t		2.5×10^8 dm^3 mol^{-1} s^{-1}
k_d		9×10^{-6} s^{-1}
f		0.5
k_{p_2}	$K_2 = k_{p_2}/k_{p_1} = 0.8$	9.36×10^3 dm^3 mol^{-1} s^{-1}
k_{p_3}	$K_3 = k_{p_3}/k_{p_1} = 0.8$	9.36×10^3 dm^3 mol^{-1} s^{-1}
k_{i_1}	$C_{i_1} = k_{i_1}/k_{p_1} = 1.0$	1.17×10^4 dm^3 mol^{-1} s^{-1}
k_{i_2}	$C_{i_2} = k_{i_2}/k_{p_2} = 1.0$	9.36×10^3 dm^3 mol^{-1} s^{-1}
k_{i_3}	$C_{i_3} = k_{i_3}/k_{p_3} = 1.0$	9.36×10^3 dm^3 mol^{-1} s^{-1}
k_{fm}	$C_M = k_{fm}/k_{p_1} = 1.9 \times 10^{-4}$	2.223 dm^3 mol^{-1} s^{-1}
k_{fp}	$C_P = k_{fp}/k_{p_1} = 1.2 \times 10^{-4}$	1.404 dm^3 mol^{-1} s^{-1}
k_{td}	$C_{td} = k_{td}/k_t = 0.5$	1.25×10^8 dm^3 mol^{-1} s^{-1}
k_{tc}	$C_{tc} = k_{tc}/k_t = 0.5$	1.25×10^8 dm^3 mol^{-1} s^{-1}

value of final time, and the whole procedure can be started over for the next value of final time (something which must be improved in the future).

In Table 5, a representative set of kinetic parameters for the system under study is presented. The propagation rate constant for the monomer is a recently published value for vinyl acetate[40] and the values for relative transfer constant to monomer, transfer constant to polymer and propagation of terminal double bonds were taken from earlier works also for the vinyl acetate polymerization.[6,34] To keep this analysis applicable to other (generic) chemical systems with a similar chemistry, other parameters were assumed to have similar values (as a basis). It is the case of the rate constants for polymerization of terminal double bonds originated by termination by disproportionation. In this first set of kinetic parameters, it was assumed that termination occurs in a ratio of 0.5 for each mechanism. In the simulations that will be presented some perturbations about this basic set will be done in order to analyze its effect on the properties of the polymer. Initial concentrations of monomer and initiator were fixed in $M_0 = 10.83$ mol dm^{-3} and $I_0 = 1 \times 10^{-3}$ mol dm^{-3}. Molecular masses of monomer and initiator fragment were taken as the correspondent values (86 and 68) for vinyl acetate and AIBN.

The first task in every simulation is predicting gel time. This was done by integration of the equations for the second-order moments along the trivial solution branch until divergence to infinity, which is a relatively easy initial value problem. When this integration ends, a table of average molecular weights before gelation is also obtained.

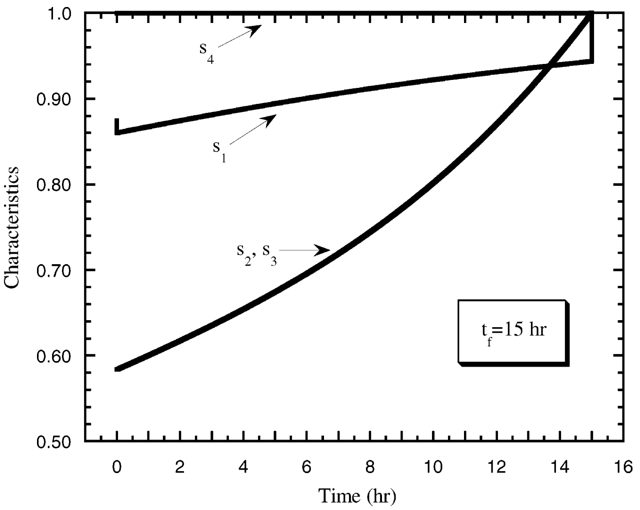

Figure 2. Solution of characteristics **s** as a function of the time for a prescribed final value $t_f = 15$ h.

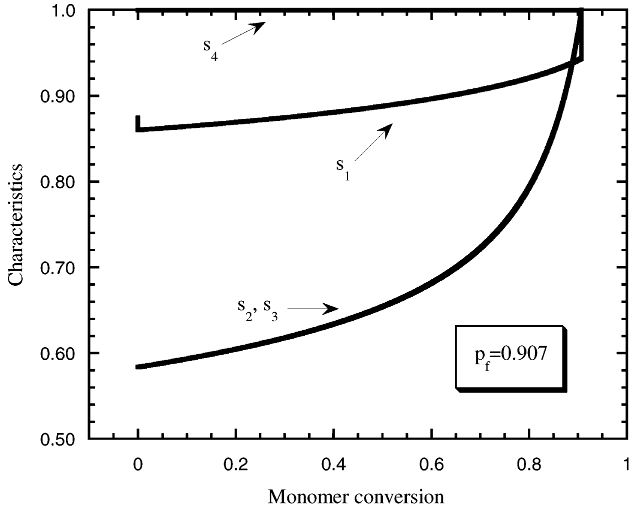

Figure 3. Solution of characteristics **s** as a function of monomer conversion for a prescribed final value $p_f = 0.907$.

A vector of final times (in each case $t_f > t_g$) is then chosen in order to obtain the properties of the polymer after gelation. Code ACDC computes iteratively the characteristics in a mesh of intermediate values between $t = 0$ and $t = t_f$ with mesh adaptation. A good initial definition of the number and placement of the grid is the crux for the convergence of the method. For this system, in most cases, if the interval is divided in a fairly large number of grid points and a proper initial estimate of the vectors of unknowns $\mathbf{G} = [G_i]$ and **s** is provided, convergence is obtained. The division of integration interval into three sections works well because the solution presents two boundary layers in each side of the interval as can be seen in Figure 2, Figure 3, and especially Figure 4 for the characteristic s_1. Good choices were 2000, 20000, and 2000 grid points for each section. The end time of the first section is on the order of the time needed to reach a slowly changing in radical concentration and in these simulations 200 s was used. In the grid points, the exact values of concentrations of active groups must be fed in order to accelerate convergence. Initial estimates for **G** in the

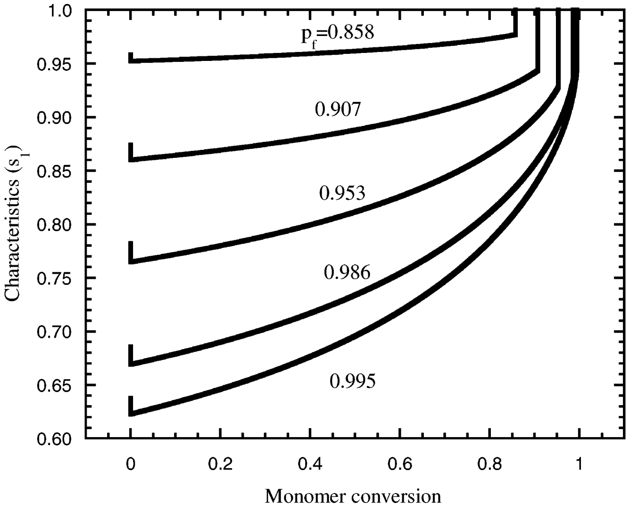

Figure 4. Solution of characteristic s_1 for different prescribed monomer conversions (p_f).

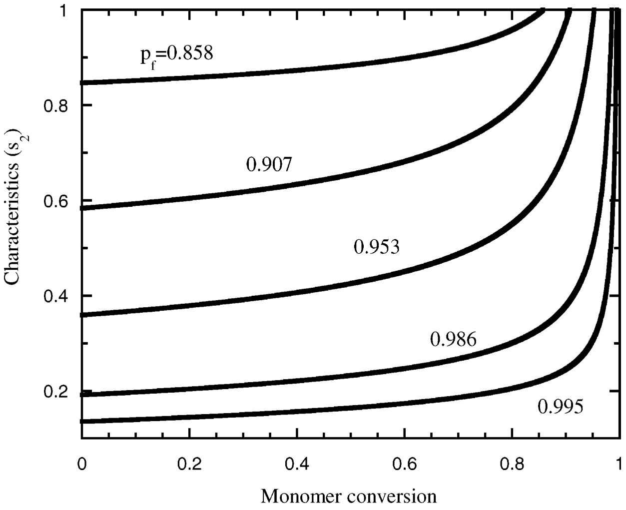

Figure 5. Solution of characteristic s_2 for different prescribed monomer conversions (p_f).

grid points are some fraction of the correspondent vector **A** and 0.01 usually gave good results. The initial estimate for **s** must also be divided in 3 sections with a starting value on the order of 10^{-2} in the left, 10^{-1} in the middle, and 1 in the right boundary.

These indications are useful for obtaining convergence but do not guarantee it. Some changes in the number and location of the grid points, and initial estimates must be carried out in failed attempts. In some cases, several trials must be done over these parameters to obtain convergence. The accuracy of the solution can be tested comparing the values of the concentrations of active groups obtained with RADAU5 and ACDC, and relative errors on the order of or less than 10^{-8} were obtained.

The results that are presented for the integration of the system of the characteristics (Figures 2−9) were calculated using the kinetic parameters presented in Table 5. The computations were carried out in a workstation with a double Xeon 2.8 GHz processor with 4 Gb memory, running Red Hat Linux 9.0 (kernel version 2.4.20-8). Fortran sources were compiled using GNU compiler g77 based on gcc 3.2.2. Typically the CPU time spent for solve each problem of characteristics is on the order of 380 s and final solutions with a number of grid points on the order of 50000 can be obtained.

It is important to discuss the profiles of characteristics obtained. The results presented in Figure 2 clearly show that the profiles for the components of **s** have different behaviors. Characteristic s_1 has two sharp, nearly vertical, boundary layers in each side of the interval of integration. This is a common result for characteristics related to the free radicals and is one of the sources of the difficulty of the problem. Characteristics s_2, s_3, and s_4 follow smooth paths of low slope (s_4 is near, but not exactly over, the trivial solution branch). This can also be seen in Figure 3 where monomer conversion is used as the independent variable of the plot for easier comparison between different kinetic systems. In Figures 4 and 5, are presented profiles of the characteristics for increasing final prescribed conversions (times). It should be noticed that the boundary layers for s_1 become narrower with increasing conversions, making the numerical problem also more difficult.

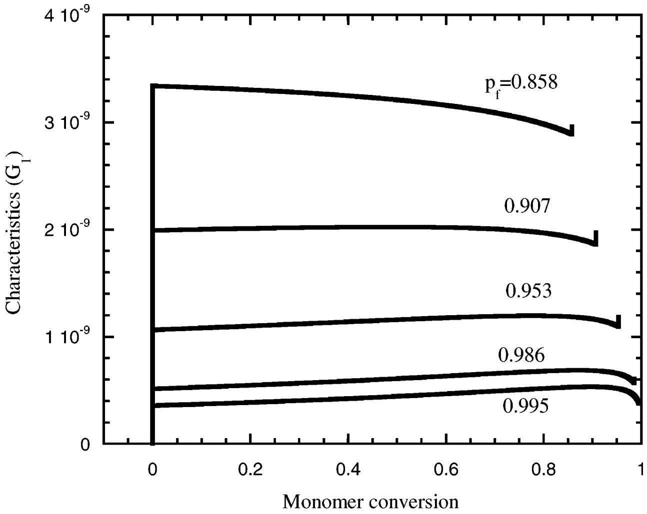

Figure 6. Solution of characteristic G_1 for different prescribed monomer conversions (p_f).

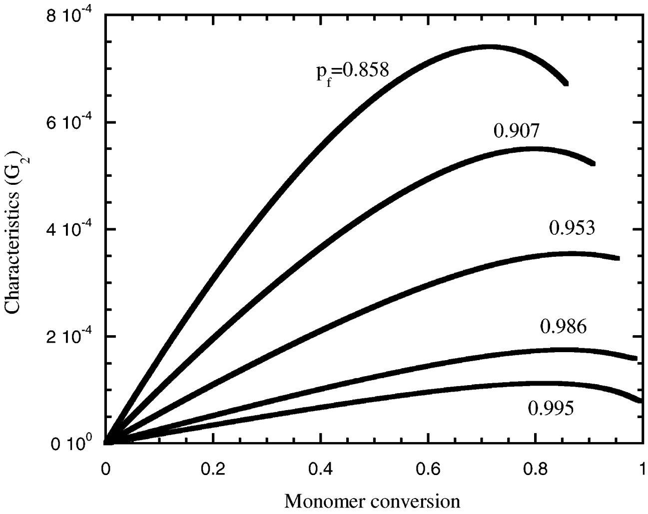

Figure 7. Solution of characteristic G_2 for different prescribed monomer conversions (p_f).

It must be remembered that, after gelation, the values of G_i have also to be iteratively computed. In Figures 6−8 are presented profiles of the characteristics for G_1, G_2, and G_4 for increasing final prescribed conversions. Again, the characteristic of G_1 has two narrow boundary layers in each extremity of the interval of integration and G_2, G_3, and G_4 follow smooth curves. In Figure 9

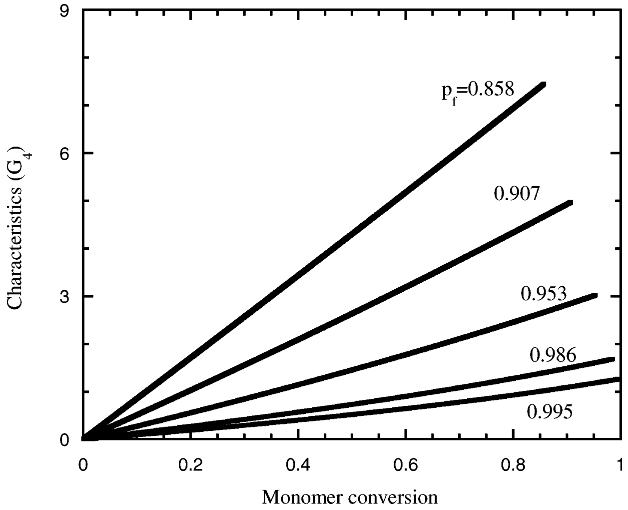

Figure 8. Solution of characteristic G_4 for different prescribed monomer conversions (p_f).

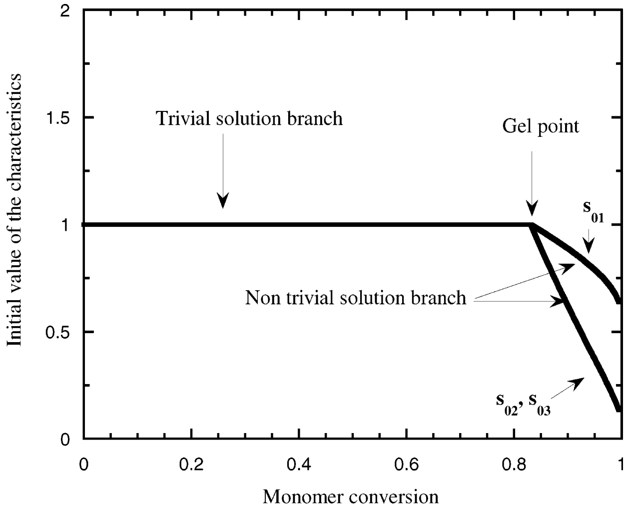

Figure 9. Physically meaningful solution branches for the system of characteristics.

are represented the initial values of the characteristics for the two physically meaningful solution branches of the problem, generated by collecting the starting values for each final conversion. In this representation, one can clearly identify the gel point, which is the bifurcation point between the trivial branch and the second branch with $s_{j_0} < 1$.

Prediction of average molecular weights

Prediction of average molecular weights can be split in two sub-problems. Before gelation, one must integrate the equations of the moments along the trivial solution for the characteristics. This is an initial value problem to be solved using, for instance, integrator RADAU5. If the goal is the prediction of number and weight-average molecular weights, moments up to the second order must be obtained. In this particular chemical system, one must integrate a system of $N_{eq} = N_A + N_P + N_P(N_P + 1)/2 + 1 = 37$ ordinary differential equations. Once the characteristics are known, there are $N_{A_P} = 4$ differential equations which need not be integrated again. Because of the symmetry of second-order moments, there are only $N_P(N_P + 1)/2 = 21$ which have to be calculated.

Writing explicitly the differential equations for moments (from the derivatives of eq 2) is a time-consuming and error-prone task (see ref 18 for a typical example). It is preferable to use a generic computer program, as we have done in several occasions,[17,19,20] where these equations are generated automatically. One must feed the program with the kinetic scheme (number and type of reactions and stoichiometric coefficients) and the initial conditions of the polymerization. This is a rather general program, independent of the chemical system, and for this reason the general model developed by this authors can be thought as a kind of interpreter of irreversible polymerization schemes.

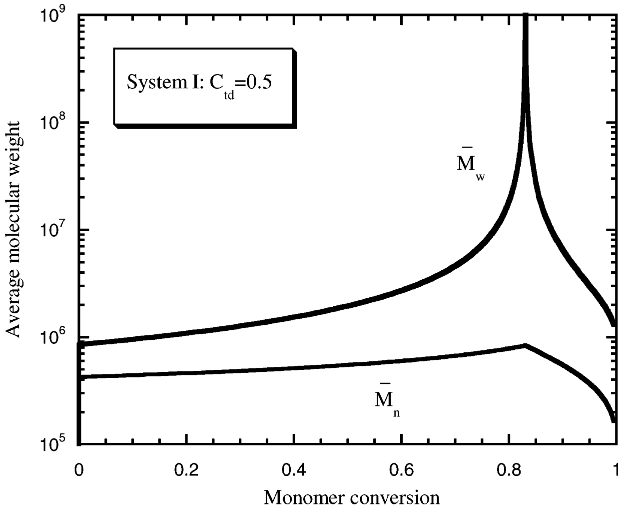

Figure 10. Average molecular weights before and after gelation for system I with $C_{td} = 0.5$.

The whole computation of average molecular weights before gelation is done with a single integration in which the gel point is identified by the divergence of the second-order moments. For the current chemical systems in analysis required CPU times are about 8 s.

After gelation, for each prescribed time in which it is wished to obtain the average properties of the polymer, a single particular problem must be solved (as there is for the moment no known working continuation procedure). First the computation of the correspondent non-trivial solution of the characteristics is carried out, and then, the integration of the moments along this solution. The first step is carried out as explained before with code ACDC. The solution for the characteristics thus obtained is fed to RADAU5 integrator, which performs the integration of the moments until the desired final time. In this way, we prevent the numerical “blow up” of the characteristics. Typically, in this chemical system, a single point in the postgel region needs 385 s of CPU time (and 15% of memory) to be obtained. This clearly demonstrates that the solution of the characteristics is the controlling step in terms of CPU time in the postgel region.

To investigate the influence of the kinetic parameters (or kinetic scheme) in the polymer average properties, based in the representative example presented in Table 5, a set of systems was generated by perturbation of some kinetic parameters (see Table 6). System I is the complete kinetic scheme in which the influence of the mode of termination was simulated by changing the ratio of termination $C_{td} = k_{td}/k_t$ (notice that $C_{tc} = k_{tc}/k_t = 1 - C_{td}$). In this system (unless $C_{td} = 0$), all mechanisms of branching are present. In Figure 10 are presented the predicted average molecular weights of the polymer before and after gelation for $C_{td} = 0.5$, the

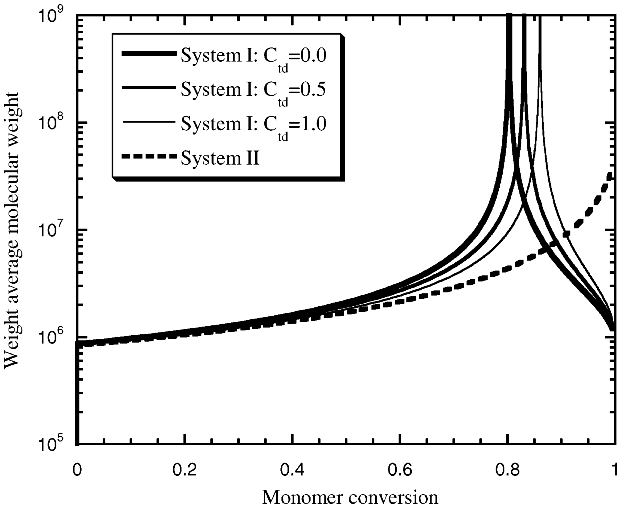

Figure 11. Weight-average molecular weight for system I (with different ratios of termination) and system II.

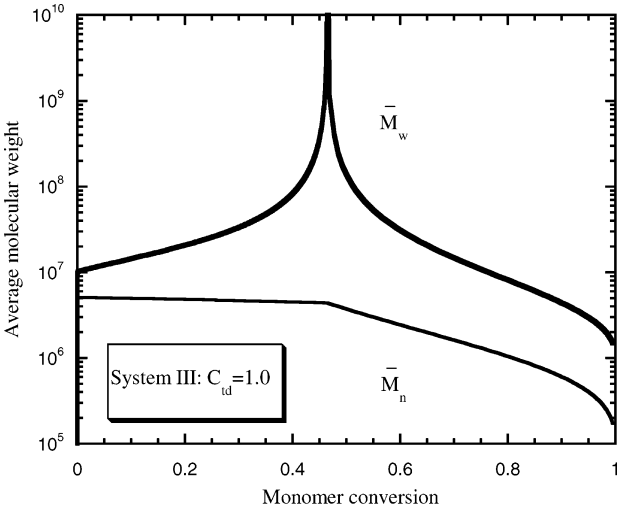

Figure 12. Average molecular weights before and after gelation for system III with $C_{td} = 1.0$.

computation of which obeys to the principles just explained. The contribution of termination by radical coupling to gelation prevails over termination by disproportionation despite the generation of terminal double bonds by this mechanism (Figure 11).

System II represents the usual accepted mechanism for vinyl acetate polymerization. The termination is by disproportionation ($C_{td} = 1$), but the terminal double bonds generated by this mechanism are inactive ($K_3 = 0$). With this combination of kinetic parameters, no gelation is predicted, a fact that agrees with several experimental observations (Figure 11).

In system III, transfer to monomer is absent. So, terminal double bonds from the monomer are also absent, but terminal double bonds from disproportionation can exist (unless $C_{td} = 0$). From the results shown in Figures 12 and 13, in comparison with system I, we conclude that transfer to monomer delays strongly the gelation (despite the terminal double bonds) because the growth of the chains is prevented. This shows that gelation is possible only with transfer to polymer and some sort of bimolecular termination reaction. Once again, the contribution for gelation of termination by coupling is dominant.

In system IV, transfer to polymer is absent. The gelation occurs due to the polymerization of terminal double bonds from the monomer and disproportionation (unless $C_{td} = 0$). In this system the mode of termination has a very small influence in the properties of the polymer. Gel conversions of 0.932, 0.934, and 0.937 were predicted for $C_{td} = 0.0$, $C_{td} = 0.5$, and $C_{td} = 1.0$, respectively. In Figure 14, the representative behavior of this system is shown.

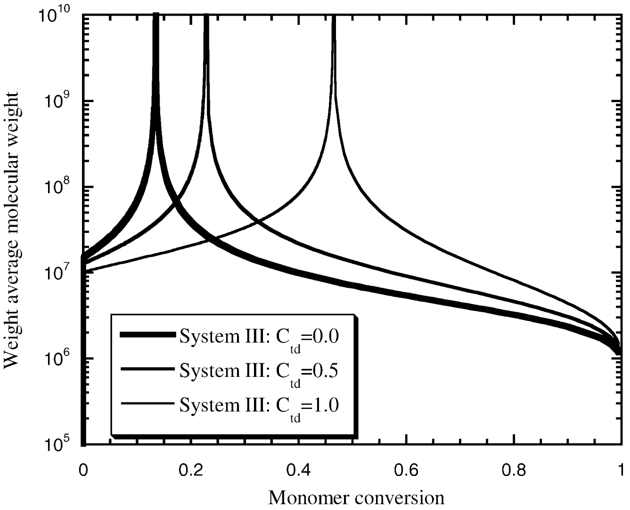

Figure 13. Weight-average molecular weight for system III with different ratios of termination.

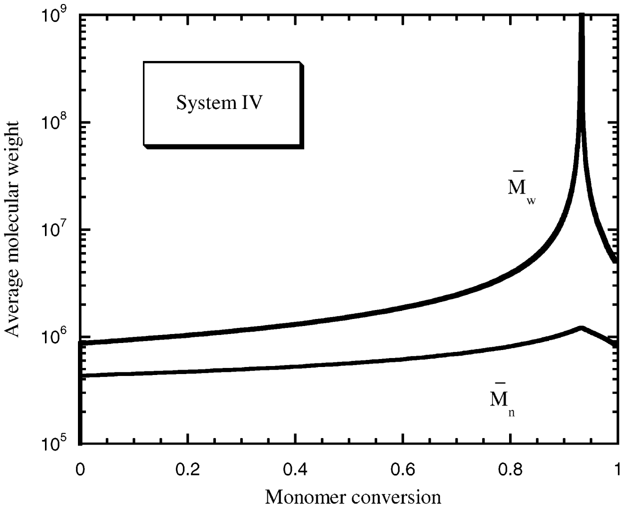

Figure 14. Average molecular weights before and after gelation for system IV.

In Figures 15 and 16 is presented the comparison between the different systems in terms of weight-average molecular weight and weight fraction of sol in order to make clear the influence of the different parameters on the properties of the polymer.

Conclusions

In the treatment of nonlinear free-radical polymerizations, several simplifications with nonuniversal applicability have been introduced in the past in order to obtain some mathematically tractable model. Among the simplifications that are present in recent proposed models for the study of terminal branching and chain transfer to polymer or related aspects the following set can be referred:

- Pseudo-steady-state hypothesis for the concentration of radicals.
- Negligible concentration of multifunctional radicals.

Table 6. Kinetic Parameters of the Systems Simulated in the Free Radical Polymerization with Terminal Double Bonds Branching and Transfer to Polymer

system	perturbed parameters (relative to the basic set)	sources of branching
system I	$0 \le C_{td} \le 1$	terminal double bonds from transfer to monomer terminal double bonds from disproportionation (unless $C_{td} = 0$) transfer to polymer
system II	$C_{td} = 1$ $K_3 = 0$	terminal double bonds from transfer to monomer transfer to polymer
system III	$C_M = 0$ $0 \le C_{td} \le 1$	terminal double bonds from disproportionation (unless $C_{td} = 0$) transfer to polymer
system IV	$C_P = 0$ $0 \le C_{td} \le 1$	terminal double bonds from transfer to monomer terminal double bonds from disproportionation (unless $C_{td} = 0$)

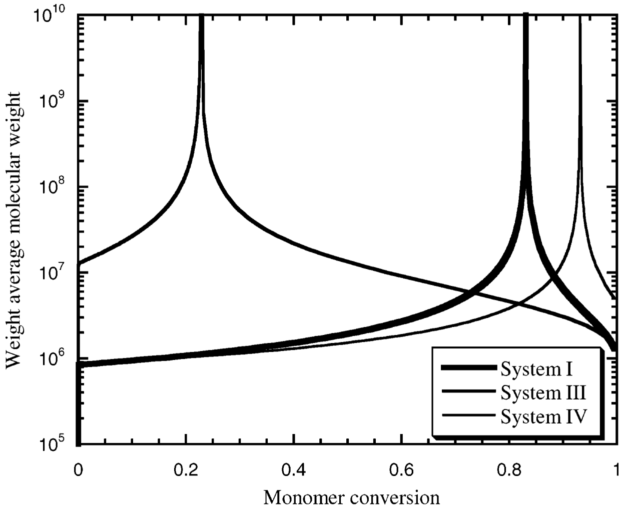

Figure 15. Weight-average molecular weight for systems I, III, and IV with $C_{td} = 0.5$.

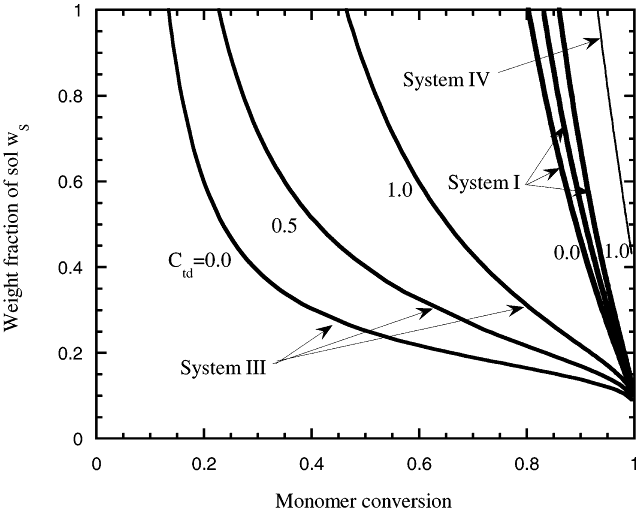

Figure 16. Weight fraction of sol for systems I, III, and IV.

- Negligible presence of more than one terminal double bond per molecule.
- The need for closure conditions for the moments equations.
- Kinetic schemes with separated analysis of the branching mechanisms.
- Transfer to polymer only over dead polymer.
- Some assumptions based on classical Flory's theory of branching.

Because of the very high computational effort, a straightforward use of Monte Carlo simulation of these systems has never been described in the literature, and therefore, some simplifying approximations had to be done to obtain practical results.

We have applied a rather general approach for irreversible nonlinear polymerizations to the study of terminal branching and chain transfer to polymer where all these assumptions were avoided. Complex chemical systems, before and after gelation, can be described without sacrificing mathematical exactness, and computations are very fast before gelation. This method should be regarded as a kind of interpreter of irreversible polymerization schemes, which makes possible their analysis in an automated way.

A way has been shown to circumvent the numerical difficulties in the integration of the characteristics, which is the main bottleneck of this method in the postgel predictions for nonlinear irreversible radical polymerizations.

Although in principle this approach should eventually be able to compute chain length distributions, the same computational bottleneck exists, and a serious improvement (with at least a gain of 1000 in speed) of the numerical methods for solving the stiff two-point boundary value problems is needed.

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