Modeling and Simulation of Free Radical Polymerization of Styrene under Semibatch Reactor Conditions

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Abstract: The first part of this approach is concerned with the elaboration of a radical polymerization model of styrene, based on a kinetic diagram that includes chemical and thermal initiation, propagation, termination by recombination and chain transfer to the monomer. Furthermore, volume contraction during polymerization is considered, as well as the gel and glass effects. The mathematical formalism that describes the model in terms of moments is explored in detail. The model was then used to predict the changes in monomer conversion and molecular weight after intermediate addition of initiator and monomer. The results of this operation are dependent on the conditions of the reaction mass, quantity, and moment of substance addition. Therefore, the simulations were performed at different times with respect to the gel effect; before, during and after this phenomenon, and also with respect to different temperatures and initiators. Increasing the initiator concentration before the gel effect leads to an earlier appearance of the phenomenon and to a decrease in molecular weight. The ratio $M_w/M_n$ reveals a polydispersity index smaller for the intermediate addition of initiator. No significant changes take place during or after the gel effect. If along with the initiator, unreacted monomer (used to dissolve the initiator) enters the reactor, a small dip in conversion is observed. The general conclusion of this paper reveals the intermediate addition of initiator as a method to control polymer properties and to prevent the “dead-end” polymerization of styrene.

Keywords: free radical polymerization, polystyrene, modeling and simulation, intermediate addition of initiator

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1 Introduction

The most common procedures for producing polystyrene are bulk and suspension polymerizations. These processes are usually initiated chemically, but at higher temperatures one should consider that thermal initiation could also occur.

The self-polymerization over 100 °C is a distinctive characteristic of styrene and it is believed to respect a third-order reaction with regard to monomer concentration. Since the free radicals resulting from the collision of monomer molecules are less active (they are stabilized by conjugation), the complete transformation of the monomer requires a longer time period.

The literature presents many experimental data and simulation attempts of the chemical initiation of styrene [1-3]. They reveal that processes initiated by a single initiator are dominated by the so-called “dead-end polymerization” phenomenon where, because of premature consumption of the initiator, some monomer might remain untransformed. To prevent this inconvenience, it was suggested to use two or more initiators, which decompose at different temperatures and also carry out the process in a step-increasing temperature regime.

Only a few known attempts use a mixture of initiators in nonisothermal polymerization. Kim [4] has reported that the initiation with two or more monofunctional initiators of considerably different thermal stabilities results in a reduction of the reaction time accompanied by an increase of conversion and molecular weight of the polymer. By using such initiating systems one may improve the performance of the polymerization reactor without major changes in process equipment.

In previous work [5] we have simulated the bulk polymerization of styrene and have proposed a model including chemical and thermal initiation, and also the gel and glass effects. The chemical initiation was realized with mixtures of two initiators of different decomposition temperatures: 1) \( \alpha - \alpha' \)-azobis(isobutyronitrile) (AIBN) and tert-butylperbenzoate (TBPB), and 2) benzoyl peroxide (BPO) and TBPB. The simulations were performed at different temperatures (70-120 °C) and initiator quantities, but under isothermal conditions. It was shown that in such conditions the dead-end polymerization is avoided and the molecular weight and reaction time may be controlled.

Another work [6] shows some results were obtained in styrene polymerization using a binary mixture of initiators and a temperature program consisting of a series of isothermal steps. The main purpose of these simulations was to obtain the lowest end-concentrations of initiators as possible, with maximum conversion of the monomer and a narrow polydispersity in a short reaction time.

This paper presents how an intermediate addition of an initiator and monomer can prevent dead-end polymerization, and also controls some properties of the polystyrene (molecular weight, polydispersity) and reaction time. We don’t know of any attempt in the literature dealing with the simulation of free radical polymerization of styrene under semi-batch operating conditions.
2 Kinetic Model for Styrene Polymerization

The kinetic diagram of the bulk polymerization of styrene contains the initiation step (chemical and thermal), propagation, termination by recombination, and chain transfer to monomer.

\[ I \xrightarrow{k_d} 2R^* \]

**Initiation**

\[ R^* + M \xrightarrow{k_i} P^*_1 \]
\[ 3M \xrightarrow{k_{term}} P^*_1 + P^*_2 \]

**Propagation**

\[ P^*_n + M \xrightarrow{k_p} P^*_{n+1} \]

**Chain transfer to monomer**

\[ P^*_n + M \xrightarrow{k_{tm}} D_n + P^*_1 \]

**Termination by recombination**

\[ P^*_n + P^*_m \xrightarrow{a \cdot k_{tc}} D_{n+m} \]

where \( I \) represents initiator; \( M \) - monomer; \( R^* \) - primary radical; \( P^*_n \) - macroradical with \( n \) monomer units; \( D_n \) - dead polymer; \( k_d, k_i, k_{term}, k_p, k_{tm}, k_{tc} \) - rate constants for initiator decomposition, initiation of polymerization, thermal initiation, propagation, chain transfer to monomer and termination by recombination, respectively; \( a = 1 \) for \( n \neq m \) and \( a = \frac{1}{2} \) for \( n = m \).

One observation must be made concerning the initiation step, that is, thermal initiation with three monomer molecules has a small probability of taking place.

Writing the conservation equations for the elements in the reaction mixture leads to an infinite system of differential and algebraic equations, depending on the type of reactor and operation conditions.

For a batch polymerization reactor, the balance equation for the conservation of a single element \( j \) having the concentration \( c_j \) has the following general form:

\[ \frac{1}{V} \frac{d(Vc_j)}{dt} = r_j \quad (1) \]

Where \( V \) is the volume of the reacting mixture; \( t \) is time; \( r_j \) is the consumption or generation rate of the element \( j \).

Applying the general design equation (1) for the elementary species of the reaction mixture, an infinite set of differential equations is obtained, representing the first form of the kinetic model of the considered system.

\[ \frac{1}{V} \frac{d(IV)}{dt} = -k_dI \quad (2) \]
\[ \frac{1}{V} \frac{d(MV)}{dt} = -k_iMR^* - 3k_{term}M^3 - k_pM \sum_{n=1}^{\infty} P^*_n - k_{tm}M \sum_{n=1}^{\infty} P^*_n \quad (3) \]
\[ \frac{1}{V} \frac{d(R^*V)}{dt} = 2fk_dI - k_iR^*M \quad (4) \]
\[ \frac{1}{V} \frac{d(P^*_1V)}{dt} = k_iR^*M + k_{term}M^3 - k_pMP^*_1 \]
\[-k_{tm}M P^*_1 + k_{tm} M \sum_{n=1}^{\infty} P^*_n - k_{tc} P^*_1 \sum_{n=1}^{\infty} P^*_n\]  
(5)

\[
\frac{1}{V} \frac{d(P^*_2 V)}{dt} = k_{term} M^3 - k_p M P^*_2 + k_p M P^*_1 \\
- k_{tm} M P^*_2 - k_{tc} P^*_2 \sum_{n=1}^{\infty} P^*_n\]  
(6)

\[
\frac{1}{V} \frac{d(P^*_n V)}{dt} = k_p M (P^*_{n-1} - P^*_n) - k_{tm} MP^*_n - k_{tc} P^*_n \sum_{n=1}^{\infty} P^*_n\]  
(7)

\[
\frac{1}{V} \frac{d(D_1 V)}{dt} = k_{tm} M P^*_1\]  
(8)

\[
\frac{1}{V} \frac{d(D_2 V)}{dt} = k_{tm} M P^*_2 + \frac{1}{2} k_{tc} P^*_1 P^*_1\]  
(9)

\[
\frac{1}{V} \frac{d(D_3 V)}{dt} = k_{tm} M P^*_3 + k_{tc} P^*_1 P^*_2\]  
(10)

\[
\frac{1}{V} \frac{d(D_n V)}{dt} = k_{tm} P^*_n M + \frac{1}{2} k_{tc} \sum_{m=1}^{n-1} P^*_m P^*_{n-m}\]  
(11)

In the above equations \(f\) is the efficiency of the initiator. The monomer conversion and volume contraction are defined as follows:

\[x = \frac{M_0 V_0 - MV}{M_0 V_0}\]  
(12)

\[V = V_0 (1 + \varepsilon x)\]  
(13)

\(M_0\) and \(V_0\) being the monomer concentration and the volume of the system for zero conversion respectively, and \(\varepsilon\) is an expansion factor of the volume, which is dependent on monomer (\(d_m\)) and polymer (\(d_p\)) densities:

\[\varepsilon = \frac{d_m - d_p}{d_p}\]  
(14)

Based on the definitions (12) and (13), the following relation between \(M\) and \(x\) is obtained:

\[M = M_0 \frac{1 - x}{1 + \varepsilon x}\]  
(15)

Using the relations (1) and (13), the consumption or generation rate expression given by equation (1) becomes:

\[\frac{dc_j}{dt} = r_j - \frac{\varepsilon}{1 + \varepsilon} \frac{dx}{c_j dt}\]  
(16)

From equations (3) and (16) the variation of monomer concentration with respect to time is obtained:

\[\frac{dM}{dt} = -k_i M R^* - k_{term} M^3 - k_p M \lambda_0 - k_{tm} M \lambda_0 - \frac{\varepsilon}{1 + \varepsilon} M \frac{dx}{dt}\]  
(17)
Where \( \lambda_0 \) is the 0th distribution moment of concentration of the increasing polymer chain lengths.

Equations (17) and (15) give:

\[
\frac{dx}{dt} = \left( k_i R^* + 3k_{term} M^2 + k_p \lambda_0 + k_{tm} \lambda_0 \right)(1 - x)
\] (18)

Equation (18) will be kept for the kinetic model of styrene polymerization.

A second equation of the kinetic model is derived from (2), (16) and (18):

\[
\frac{dI}{dt} = -k_d I - \frac{\varepsilon I}{1 + \varepsilon x}(k_i R^* + k_{term} M^2 + k_p \lambda_0 + k_{tm} \lambda_0)(1 - x)
\] (19)

Whereas for the radical concentrations \( R^* \) we use equations (4), (16) and (18) and obtain:

\[
\frac{dR^*}{dt} = 2f k_d I - k_i R^* M - \frac{\varepsilon}{1 + \varepsilon x} R^* (k_i R^* + 3k_{term} M^2 + \varepsilon k_p \lambda_0 + k_{tm} \lambda_0)(1 - x)
\] (20)

In the system (2)-(11), the equations that show how the increasing polymer chains \( P_n^* \) are obtained (equations 5, 6, 7) will be written according to equation (16) as follows:

\[
\frac{dP_1^*}{dt} = k_i R^* M + k_{term} M^3 - k_p M P_1^* - k_{tm} M P_1^* + k_{tm} M \lambda_0 - k_{tc} P_1^* \lambda_0 - \frac{\varepsilon}{1 + \varepsilon x} P_1^* \frac{dx}{dt}
\] (21)

\[
\frac{dP_2^*}{dt} = k_{term} M^3 + k_p M P_1^* - k_p M P_2^* - k_{tm} M P_2^* - k_{tc} P_2^* \lambda_0 - \frac{\varepsilon}{1 + \varepsilon x} P_2^* \frac{dx}{dt}
\] (22)

\[
\frac{dP_n^*}{dt} = k_p M P_{n-1}^* - k_p M P_n^* - k_{tm} M P_n^* - k_{tc} P_n^* \lambda_0 - \frac{\varepsilon}{1 + \varepsilon x} P_n^* \frac{dx}{dt}
\] (23)

The equations (21)-(23) representing an infinite sequence are replaced by a finite number of equations that involve the distribution moments of concentrations of the increasing polymers’ chain lengths \( \lambda_k \) (\( k = 0, 1, 2 \)):

\[
\frac{d\lambda_0}{dt} = \frac{dP_1^*}{dt} + \frac{dP_2^*}{dt} + \ldots + \frac{dP_n^*}{dt} + \ldots
\] (24)

\[
\frac{d\lambda_0}{dt} = k_i R^* M + 2k_{term} M^3 - k_{tc} \lambda_0^2 - \frac{\varepsilon \lambda_0}{1 + \varepsilon x} \frac{dx}{dt}
\] (25)

\[
\frac{d\lambda_0}{dt} = k_i R^* M + 2k_{term} M^3 - k_{tc} \lambda_0^2 - \frac{\varepsilon \lambda_0}{1 + \varepsilon x} (k_i R^* + 3k_{term} M^2 + k_p \lambda_0 + k_{tm} \lambda_0)(1 - x)
\] (26)

For the first degree moment (\( \lambda_1 \)), summing up equations (21)-(23) will follow their multiplication by \( n \) (\( n=1, 2, 3, \ldots \)):
\[ \frac{d\lambda_1}{dt} = \frac{dP_1^*}{dt} + 2 \frac{dP_2^*}{dt} + 3 \frac{dP_3^*}{dt} + \ldots + n \frac{dP_n^*}{dt} + \ldots \] (27)
\[ \frac{d\lambda_1}{dt} = k_iR^*M + 3k_{iterm}M^3 + k_pM\lambda_0 - k_{tc}\lambda_0\lambda_1 \]
\[ -\lambda_1 \varepsilon \frac{1-x}{1+\varepsilon x} (k_iR^* + 3k_{iterm}M^2 + k_p\lambda_0 + k_{tm}\lambda_0) - k_{tm}M(\lambda_1 - \lambda_0) \] (28)

Similarly, for the moment \( \lambda_2 \), the equations (21)-(23) are each multiplied by \( n^2 \) and then all summed up:
\[ \frac{d\lambda_2}{dt} = \frac{dP_1^*}{dt} + 4 \frac{dP_2^*}{dt} + 9 \frac{dP_3^*}{dt} + \ldots + n^2 \frac{dP_n^*}{dt} + \ldots \] (29)
\[ \frac{d\lambda_2}{dt} = k_iR^*M + 5k_{iterm}M^3 + k_pM(2\lambda_1 + \lambda_0) - k_{tc}\lambda_0\lambda_2 \]
\[ -\lambda_2 \varepsilon \frac{1-x}{1+\varepsilon x} (k_iR^* + 3k_{iterm}M^2 + k_p\lambda_0 + k_{tm}\lambda_0) - k_{tm}M(\lambda_2 - \lambda_0) \] (30)

In the system (2)-(11), the equation shows how the inactive polymer chains \( D_n \) are obtained and are written according to equation (16) in the following way:
\[ \frac{dD_1}{dt} = k_{tm}MP_1^* - \frac{\varepsilon D_1}{1+\varepsilon x} \frac{dx}{dt} \] (31)
\[ \frac{dD_2}{dt} = k_{tm}MP_2^* + \frac{1}{2}k_{tc}P_1^*P_1^* - \frac{\varepsilon D_2}{1+\varepsilon x} \frac{dx}{dt} \] (32)
\[ \frac{dD_3}{dt} = k_{tm}MP_3^* + k_{tc}P_1^*P_2^* - \frac{\varepsilon D_3}{1+\varepsilon x} \frac{dx}{dt} \] (33)
\[ \frac{dD_n}{dt} = k_{tm}MP_n^* + \frac{1}{2}k_{tc}\sum_{m=1}^{n-1} P_m^*P_{n-m}^* - \frac{\varepsilon D_n}{1+\varepsilon x} \frac{dx}{dt} \] (34)

For the inactive species \( D_n \), the distribution moments \( \mu_k \) (\( k = 0, 1, 2 \)) are introduced in the model. The equations are obtained identically with those of the \( \lambda_k \) moments.
\[ \frac{d\mu_0}{dt} = \frac{dD_1}{dt} + \frac{dD_2}{dt} + \ldots + \frac{dD_n}{dt} \] (35)
\[ \frac{d\mu_1}{dt} = \frac{dD_1}{dt} + 2 \frac{dD_2}{dt} + \ldots + n \frac{dD_n}{dt} \] (36)
\[ \frac{d\mu_2}{dt} = \frac{dD_1}{dt} + 2^2 \frac{dD_2}{dt} + \ldots + n^2 \frac{dD_n}{dt} \] (37)
\[ \frac{d\mu_0}{dt} = \frac{1}{2}k_{tc}\lambda_0^2 - \mu_0 \varepsilon \frac{1-x}{1+\varepsilon x} (k_iR^* + 3k_{iterm}M^2 + k_p\lambda_0 + k_{tm}\lambda_0) \]
\[ + k_{tm}M\lambda_0 \] (38)
\[ \frac{d\mu_1}{dt} = k_{tc}\lambda_0\lambda_1 - \mu_1 \varepsilon \frac{1-x}{1+\varepsilon x} (k_iR^* + 3k_{iterm}M^2 + k_p\lambda_0 + k_{tm}\lambda_0) \]
\[ + k_{tm}M\lambda_1 \] (39)
\[ \frac{d\mu_2}{dt} = k_{tc}\lambda_0\lambda_2 - \mu_2 \varepsilon \frac{1-x}{1+\varepsilon x} (k_iR^* + 3k_{iterm}M^2 + k_p\lambda_0 + k_{tm}\lambda_0) \]
\[ + k_{tm}M\lambda_2 + k_{tc}\lambda_1^2 \] (40)
The final structure of the model written as moments is given by the equations 18, 19, 20, 26, 28, 30, 38, 39, 40.

The kinetic model may be simplified, if the polymerization allows it, by applying a hypothesis such as the long chain hypothesis (LCH) and the quasi-state state approximation (QSSA). LCH implies that the monomer is consumed in the propagation phase only, its consumption in the initiation reaction being neglected. Under these circumstances, equation (18) becomes:

\[
\frac{dx}{dt} = \left(3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right)(1-x) \tag{41}
\]

The QSSA assumes that the effective rate of the increasing radical chain formation is close to zero.

\[
\frac{1}{V} \frac{d(VR^*)}{dt} = 0 \Rightarrow k_iR^*M = 2f_kdI \tag{42}
\]

After the above approximations are applied, we obtain the final equations of the mathematical model:

\[
\frac{dI}{dt} = -k_dI - I\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right] \tag{43}
\]

\[
\frac{dx}{dt} = \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right](1-x) \tag{44}
\]

\[
\frac{d\lambda_0}{dt} = 2f_kdI + 2k_{iterm}M_0^3 \left(\frac{1-x}{1+\varepsilon x}\right)^3 - k_{tc}\lambda_0^2
\]

\[
-\lambda_0\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right] \tag{45}
\]

\[
\frac{d\lambda_1}{dt} = 2f_kdI + 3k_{iterm}M_0^3 \left(\frac{1-x}{1+\varepsilon x}\right)^3 + kpM_0 \frac{1-x}{1+\varepsilon x}\lambda_0 - k_{tc}\lambda_0\lambda_1
\]

\[
-\lambda_1\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right]
\]

\[
-k_{tm}M_0 \frac{1-x}{1+\varepsilon x}(\lambda_1 - \lambda_0) \tag{46}
\]

\[
\frac{d\lambda_2}{dt} = 2f_kdI + 5k_{iterm}M_0^3 \left(\frac{1-x}{1+\varepsilon x}\right)^3 + kpM_0 \frac{1-x}{1+\varepsilon x}(2\lambda_1 + \lambda_0) - k_{tc}\lambda_0\lambda_2
\]

\[
-\lambda_2\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right]
\]

\[
-k_{tm}M_0 \frac{1-x}{1+\varepsilon x}(\lambda_2 - \lambda_0) \tag{47}
\]

\[
\frac{d\mu_0}{dt} = \frac{1}{2}k_{tc}\lambda_0^2 - \mu_0\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right]
\]

\[
+ k_{tm}M_0 \frac{1-x}{1+\varepsilon x}\lambda_0 \tag{48}
\]

\[
\frac{d\mu_1}{dt} = k_{tc}\lambda_0\lambda_1 - \mu_1\varepsilon \frac{1-x}{1+\varepsilon x} \left[3k_{iterm}M_0^2 \left(\frac{1-x}{1+\varepsilon x}\right)^2 + k_p\lambda_0 + k_{tm}\lambda_0\right]
\]
\[ + k_{tm} M_0 \frac{1-x}{1+\varepsilon x} \lambda_1 \]

\[ \frac{d\mu_2}{dt} = k_{tc} \lambda_0 \lambda_2 + k_{tc} \lambda_1^2 - \mu_2 \varepsilon \frac{1-x}{1+\varepsilon x} \left[ 3k_{iterm} M_0^2 \left( \frac{1-x}{1+\varepsilon x} \right)^2 + k_p \lambda_0 + k_{tm} \lambda_0 \right] \]

\[ + k_{tm} M_0 \frac{1-x}{1+\varepsilon x} \lambda_2 \] (49)

The model can be used for a large temperature range. Below 100 °C, consideration is given only for the chemical initiation (initiator decomposition), so \( k_{iterm} = 0 \), but beyond this temperature both the chemical and thermal initiations should be taken into account.

During polymerization, the \( k_{tc} \), \( k_p \) and \( k_{tm} \) constants decrease because of diffusion constraints (gel and glass effects, respectively). For the first two constants, Chiu et al. [7] have proposed the following models:

\[ \frac{1}{k_{tc}} = \frac{1}{k_{tc0}} + \theta_{tc} \exp \left[ \frac{\lambda_0}{2.303(1-x)} \right] \]

\[ \frac{1}{k_p} = \frac{1}{k_{p0}} + \theta_p \exp \left[ \frac{\lambda_0}{2.303(1-x)} \right] \] (51)

\[ \theta_{tc} = \frac{\theta_{tc0}}{T_0} \exp \left( \frac{E_{\theta_{tc}}}{RT} \right) \]

\[ \theta_p = \theta_{p0} \exp \left( \frac{E_{\theta_p}}{RT} \right) \] (52)

\[ A = C_1 - C_2 (T - T_{gp})^2 \] (53)

\[ \lambda_0 = 1 + \theta_{tc} \exp \left( \frac{E_{\theta_{tc}}}{RT} \right) \]

\[ \lambda_0 = 1 + \theta_p \exp \left( \frac{E_{\theta_p}}{RT} \right) \] (54)

Where: \( A, B, C_1, C_2 \) are terms in diffusion equations for propagation and termination rate constants; \( k_{p0}, k_{tc0} \) are rate constants for propagation and termination reactions in the absence of the glass and gel effects; \( E_{\theta_{tc}}, E_{\theta_p} \) are activation energies for \( \theta_{tc} \) and \( \theta_p \); \( T \) is the polymerization temperature; \( T_{gp} \) is the glass transition temperature of the polymer; \( \theta_{tc}, \theta_p \) are migration times; \( \theta_{tc0}, \theta_{p0} \) are the pre-exponential factors for \( \theta_{tc} \) and \( \theta_p \).

The rate constant for chain transfer to monomer was proposed to be similar to the decrease in the propagation rate constant [8] because both reactions involve the same diffusion mechanism where the monomer molecules migrate toward the growing macro-radicals.

\[ k_{tm} = k_{tm0} \frac{k_p}{k_{p0}} \] (55)

Where \( k_{tm0} \) is the rate constant for chain transfer to monomer in the absence of the glass effect.

At high temperatures (\( > T_{gp} \)), the glass effect is ignored. The cage effect, implying the variation of initiator concentration, was also neglected.
$k_d^0(TBPB) = 8.439 \times 10^{13} s^{-1}$; $k_d^0(BPO) = 1.2 \times 10^{13} s^{-1}$

$k_{p0}^0 = 1.051 \times 10^4 m^3/(mol\cdot s)$; $k_{tm0}^0 = 2.31 \times 10^3 m^3/(mol\cdot s)$

$k_{tc0}^0 = 1.26 \times 10^6 m^3/(mol\cdot s)$; $k_{iterm}^0 = 2.19 \times 10 (m^3)^2/(mol^2\cdot s)$

$E_{iterm} = 1.56 \times 10^5 J/mol$; $E_d(TBPB) = 1.34 \times 10^5 J/mol$

$E_d(BPO) = 1.2 \times 10^5 J/mol$; $E_p = 2.958 \times 10^4 J/mol$

$E_{tm} = 5.275 \times 10^4 J/mol$; $E_{tc} = 7.04 \times 10^3 J/mol$

$f(TBPB) = 0.637$; $f(POB) = 0.6$

$C_1 = 0.091678$; $C_2 = 1.142 \times 10^{-5}$

$B = 0.02$; $T_{gp} = 373.16$ K; $\theta_p^0 = 7.4053 \times 10^{-3}$ s

$E_{dp} = 4.634 \times 10^4 J/mol$; $\theta_{tc}^0 = 0.53598 \times 10^{-8} (mol\cdot s)/m^3$

$E_{d_{tc}} = 9.5722 \times 10^4 J/mol$; $d_m = 924 - 0.918 \times T [\degree C] kg/m^3$

$d_p = 1084.8 - 0.685 \times T [\degree C] kg/m^3$

$k_{p0} = k_{p0}^0 \exp (-E_p/(RT))$; $k_{tm0} = k_{tm0}^0 \exp (-E_{tm}/(RT))$;

$k_{tc0} = k_{tc0}^0 \exp (-E_{tc}/(RT))$; $k_{iterm} = k_{iterm}^0 \exp (-E_{iterm}/(RT))$

| Table 1 Numerical Values of the Parameters for Styrene Polymerization |
|---------------------------------------------------------------|

### 3 Results and Discussions

Initially, the model was tested for batch operating conditions performing simulations at different temperatures and initiator concentrations [8]. The simulation results were in very good agreement with the experimental data.

Semi-batch operations are quite a common practice in the polymer manufacturing industry since it is considered a method for controlling the molecular weight and polydispersity of the polymer.

The model (43) – (56) was used to predict the changes for monomer conversion and molecular weight after the intermediate addition of initiator and monomer. The results of this operation depend on the conditions of the reaction mass, amount, and moment of substance addition. Therefore, the operations were simulated at different times with respect to the gel effect (before, during, and after this phenomenon) for different temperatures and initiators.

For solving stiff differential equations of the model under different semi-batch conditions, the Matlab software program was used. The associated constants are given in Table 1[4, 8].

In Table 1, $k_d^0$, $k_{iterm0}^0$, $k_{p0}^0$, $k_{tc0}^0$, $k_{tm0}^0$ are frequency factors and $E_d$, $E_{iterm}$, $E_p$, $E_{tc}$, $E_{tm}$ are activation energies.

For an instantaneous addition of BPO from 25 mol/m$^3$ to 50 mol/m$^3$ at $t = 200$ min (before the gel effect) and $T = 80 \degree C$, Figure 1 shows the variation in time of monomer...
conversion in batch (curves 1 and 2, with $I_01 = 25 \text{ mol/m}^3$ and $I_02 = 50 \text{ mol/m}^3$) and semi-batch (curve 3 – initiator adding) conditions. In the last case, the gel effect occurs earlier as compared to the reference curve of $I_01 = 25 \text{ mol/m}^3$ (starting point of the simulation).

![Conversion histories for styrene polymerization with BPO at T = 80°C, $I_0 = 25 \text{ mol/m}^3$ (1), $I_0 = 50 \text{ mol/m}^3$ (2) and increasing BPO from 25 to 50 mol/m$^3$ at t = 200 min (before the gel effect – curve 3).](image)

Increasing the initiator concentration results in a decrease of numeric ($\bar{M}_n$) and gravi-metric ($\bar{M}_w$) molecular weights as can be seen in Figures 2 and 3 (curve 3 compared to curve 1).

The ratio $\bar{M}_w/\bar{M}_n$ reveals a polydispersity index (Q) smaller for the intermediate addition of initiator (Figure 4).

The addition of a supplementary amount of initiator during the gel effect leads to a decrease in the molecular weight and polydispersity by the end of the process. The monomer conversion does not change along with this operation. Figures 5 – 8 were obtained with the following conditions: $T = 80^\circ C$, $I_0 = 25 \text{ mol/m}^3$ (curve 1), $I_0 = 50 \text{ mol/m}^3$ (curve 2) and with an increasing BPO concentration from $I_0 = 25 \text{ mol/m}^3$ to $I_0 = 50 \text{ mol/m}^3$ (curve 3) at $t = 547 \text{ min}$ (during the gel effect).

The value $t = 547 \text{ min}$ corresponds to a sudden increase in both the monomer conversion and molecular weight. If the semi-batch operation is performed after the gel effect, no significant changes are observed.

The following simulations were performed with regard to the instantaneous addition of supplementary amounts of BPO at various reaction times at $T = 120^\circ C$, with focus on the analysis of monomer conversion, molecular weight and polydispersity. As in the previous case ($T = 80^\circ C$), significant changes of the examined values occur if the semi-batch operation is carried out before or during the gel effect. Figures 9-13 are examples
Fig. 2 Numeric average molecular weight histories for styrene polymerization with BPO at T = 80 °C and \( I_0 = 25 \text{ mol/m}^3 \)(1), \( I_0 = 50 \text{ mol/m}^3 \)(2), and BPO increasing from 25 to 50 mol/m\(^3\) at t = 200 min (before the gel effect – curve 3).

Fig. 3 Gravimetric average molecular weight histories for styrene polymerization with BPO at T = 80 °C, and \( I_0 = 25 \text{ mol/m}^3 \)(1), \( I_0 = 50 \text{ mol/m}^3 \)(2), and BPO increasing from 25 to 50 mol/m\(^3\) at t = 200 min (before the gel effect – curve 3).

of these situations, whereby starting with an initial polymerization at T = 120 °C and \( I_0 = 25 \text{ mol/m}^3 \), further BPO addition of 25 mol/m\(^3\) at t = 20 min (before the gel effect) produces an increase in conversion from 0.6 to 0.9 (Figure 9).

Curve (1) from figure 9 shows the “dead-end” polymerization in which some monomer
remains unconsumed at the end of the process. As a consequence of the temperature being high, the initiator decomposed quickly (Figure 10).

The semi-batch operation fixes this shortcoming with a greater conversion and a shorter reaction time compared with the $I_0 = 50 \text{ mol/m}^3$ case (Figure 9, curve 3).

Numeric and gravimetric average molecular weights are presented in Figures 11 and 12. A special situation is presented in Figure 12, namely the lower molecular weight...
Fig. 6 Numeric average molecular weight histories for styrene polymerization with BPO at $T = 80^\circ C$, $I_0 = 25 \text{ mol/m}^3$ (1), $I_0 = 50 \text{ mol/m}^3$ (2) and increasing BPO from 25 to 50 mol/m$^3$ at $t = 547 \text{ min}$ (during the gel effect - curve 3).

corresponding to the concentration $I_0 = 25 \text{ mol/m}^3$ (curve 1 from Figure 12) compared to $I_0 = 50 \text{ mol/m}^3$ (curve 2 in Figure 12) and correlated with the rapid initiator consumption (Figure 10) at a high temperature.

In the above presented case, adding a further 25 mol/m$^3$ of BPO a short time after
starting the reaction causes an appreciable increase in conversion (curve 3 from Figure 9), whilst still maintaining low values for polydispersity (Figure 13). If we had used 50 mol/m$^3$ BPO from the start, the polydispersity at the end of the reaction would have reached greater values, ($Q \approx 9$) (curve 2 in Figure 9), in comparison to the situation
Fig. 10 Variation in time of monomer conversion at $T = 120^\circ C$ and $I_0 = 25 \text{ mol/m}^3$ (1) and BPO concentration (2).

Fig. 11 Numeric average molecular weight histories for styrene polymerization with BPO at $T = 120^\circ C$, $I_0 = 25 \text{ mol/m}^3$ (1), $I_0 = 50 \text{ mol/m}^3$ (2) and increasing BPO from 25 to 50 mol/m$^3$ at $t = 20 \text{ min}$ (before the gel effect – curve 3).

of adding the same initiator quantity progressively, and thus leading to a much lower polydispersity ($Q \approx 2.5$) (curve 3 from Figure 13).

By comparison of the plots 1 and 9, 2 and 11, 3 and 12, 4 and 13, respectively,
we have emphasized the influence of temperature on semi-batch polymerization initiated with BPO. A relevant conversion change takes place at $120^\circ C$ (Figure 9) rather than at the lower temperature $T = 80^\circ C$ (Figure 1) due to the fast depletion of the initiator in
the first case. Concerning the molecular weight and the polydispersity, significant changes are observed at lower temperatures (Figures 3 and 4 compared to Figures 12 and 13).

TBPB is a much slower initiator than BPO. At 100 °C, the half-life of TBPB is 12.9 hrs, while that of BPO is 1 hr. As in the case of BPO initiation, the relevant changes occur when adding the initiator (TBPB) before the gel effect: the molecular weights and the polydispersity decrease and the gel effect takes place earlier. Examples are shown in Figures 14-17.

Fig. 14 Conversion histories for styrene polymerization with TBPB at T = 120 °C, I₀ = 25 mol/m³ (1), I₀ = 50 mol/m³ (2) and increasing TBPB from 25 to 50 mol/m³ at t = 50 min (before the gel effect - curve 3).

Usually, along with the initiator, some amount of unreacted monomer (used to dissolve the initiator) also enters the reactor thus lowering the overall conversion (based on total monomer added). Figures 18-21 consider the situation where the addition of initiator and monomer for polymerization initiated with TBPB at 120 °C. The simulation was performed for a semi-batch operation at t = 50 min (before the gel effect) with the following supplementary amounts: 25 mol/m³ initiator (I₀) (yellow curve noted 1), 25 mol/m³ initiator dissolved in 100 mol/m³ monomer (M₀) (curve 2, plotted with *) and 25 mol/m³ initiator dissolved in 1000 mol/m³ monomer (red curve 3). Curve 3 illustrates the sudden dip in monomer conversion at the moment of intermediate addition of monomer. The difference between curves 1 and 2 corresponding to the addition of the initiator with and without monomer was not significant.

In the range of the gel effect, the polymerization rate begins to increase to a much higher level, resulting in a greater slope. An increase in the conversion rate usually leads to a temperature rise, which results in a yet higher conversion rate, which yet again causes higher temperatures. Thus, the magnitude of the conversion versus time slope during the gel effect depends on the effectiveness of heat transfer. As faster kinetics
Fig. 15 Numeric average molecular weight histories for styrene polymerization with TBPB at $T = 120\, ^\circ\, \text{C}$, $I_0 = 25\, \text{mol/m}^3$ (1), $I_0 = 50\, \text{mol/m}^3$ (2) and increasing TBPB from 25 to 50 mol/m$^3$ at $t = 50\, \text{min}$ (before the gel effect – curve 3).

Fig. 16 Gravimetric average molecular weight histories for styrene polymerization with TBPB at $T = 120\, ^\circ\, \text{C}$, $I_0 = 25\, \text{mol/m}^3$ (1), $I_0 = 50\, \text{mol/m}^3$ (2) and increasing TBPB from 25 to 50 mol/m$^3$ at $t = 50\, \text{min}$ (before the gel effect – curve 3).

allows less time for sufficient heat transfer, the free radical polymerization systems are not isothermal. This problem is even worse for faster polymerization systems (such as methyl methacrylate as opposed to styrene) or for any system at higher temperatures
Fig. 17 Polydispersity histories for styrene polymerization with TBPB at $T = 120 \, ^\circ\text{C}$, $I_0 = 25 \, \text{mol/m}^3$ (1), $I_0 = 50 \, \text{mol/m}^3$ (2) and increasing TBPB from 25 to 50 mol/m$^3$ at $t = 50 \, \text{min}$ (before the gel effect – curve 3).

Therefore, our simulations at 120 $^\circ\text{C}$ for styrene polymerization approximate an isothermal situation. A rigorous attempt will consider the changes of temperature during the gel and glass effects.

Fig. 18 Conversion histories for styrene polymerization with TBPB at $T = 120 \, ^\circ\text{C}$, $I_0 = 25 \, \text{mol/m}^3$, $I_{ad} = 25 \, \text{mol/m}^3(1)$, $I_{ad} = 25 \, \text{mol/m}^3$ and $M_{ad} = 100 \, \text{mol/m}^3(2)$, $I_{ad} = 25 \, \text{mol/m}^3$ and $M_{ad} = 1000 \, \text{mol/m}^3$ (3) at $t = 50 \, \text{min}$ (before the gel effect).

To validate the mathematical model, experiments are in progress. Preliminary tests
Fig. 19 Numeric average molecular weight histories for styrene polymerization with TBPB at $T = 120\, ^\circ C$, $I_0 = 25\, \text{mol/m}^3, I_{ad} = 25\, \text{mol/m}^3$ (1), $I_{ad} = 25\, \text{mol/m}^3$ and $M_{ad} = 100\, \text{mol/m}^3$ (2), $I_{ad} = 25\, \text{mol/m}^3$ and $M_{ad} = 1000\, \text{mol/m}^3$ (3) at $t = 50\, \text{min}$ (before the gel effect).

Fig. 20 Gravimetric average molecular weight histories for styrene polymerization with TBPB at $T = 120\, ^\circ C$, $I_0 = 25\, \text{mol/m}^3, I_{ad} = 25\, \text{mol/m}^3$ (1), $I_{ad} = 25\, \text{mol/m}^3$ and $M_{ad} = 100\, \text{mol/m}^3$ (2), $I_{ad} = 25\, \text{mol/m}^3$ and $M_{ad} = 1000\, \text{mol/m}^3$ (3) at $t = 50\, \text{min}$ (before the gel effect).
Fig. 21 Polydispersity histories for styrene polymerization with TBPB at $T = 120^\circ$C, $I_0 = 25$ mol/m$^3$, $I_{ad} = 25$ mol/m$^3$ (1), $I_{ad} = 25$ mol/m$^3$ and $M_{ad} = 100$ mol/m$^3$ (2), $I_{ad} = 25$ mol/m$^3$ and $M_{ad} = 1000$ mol/m$^3$ (3) at $t = 50$ min (before the gel effect).

show a satisfactory concordance between simulation and experimental data, but an improvement of this concordance should be obtained by adjusting the parameters of gel and glass effects models.

4 Conclusions

This approach had two goals, to elaborate on the kinetic model for free radical polymerization of styrene and to use it under semi-batch reaction conditions. The model is complete including chemical and thermal initiation, volume variation, along with the gel and glass effects.

The results of the semi-batch operation are a function of reaction temperature, type and amount of initiator and the moment of intermediate addition (before, during or after the gel effect).

Adding a supplementary amount of initiator before the onset of the gel effect leads to an earlier appearance of this phenomenon (the reaction time becomes shorter) and a decrease in molecular weight and polydispersity of the polymer. These changes of product quality and of reaction characteristics are less significant if the semi-batch operation takes place during or after the gel effect. For instance, the monomer conversion does not change.

Both the nature of the initiator and the temperature had an appreciable influence on the process carried out under semi-batch conditions. Important changes for monomer conversion at high temperatures and for molecular weight and polydispersity at low temperatures, have taken place. Moreover, using a fast initiator (BPO comparing to TBPB) determines greater differences between semi-batch and batch operations. For example,
adding 25 mol/m$^3$ BPO at an initial amount of 25 mol/m$^3$, at 120 °C and t = 20 min (before the gel effect) results in a 90 % conversion compared to 60 % in batch polymerization.

An addition of a supplementary amount of monomer during the polymerization results in a decrease in conversion at the moment of operation, but after that, the trajectory of conversion or molecular weight is the same as in the batch polymerization.

Intermediate addition of initiator (preferably before the gel effect) is a way of controlling polymer properties (molecular weight, polydispersity), reaction characteristics (conversion, time of reaction, onset of the gel effect) and, also, avoiding the dead-end polymerization of styrene.

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