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Transition into the gel regime for crosslinking radical polymerisation in a continuously stirred tank reactor

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Abstract

Crosslinking radical polymerisation in a continuously stirred tank reactor has been studied by means of a four-dimensional population balance model accounting for chain length, free pending double bonds, crosslinks, and multiradicals as dimensions. The model covers both pre-gel and gel regimes in a straightforward manner. Approximations on radial basis functions have been employed to reduce the size of the system with minimal information loss. The comparison with Monte Carlo simulations shows interesting and unexpected features.

Keywords: Gel; CSTR; Population balance equation; Multiradicals, Crosslinking

Introduction

Copolymerization of vinyl monomer with a small amount of divinyl monomer causes cross-linking among different chains and produces branched polymers. Successive intermolecular crosslinking rapidly increases the branched polymer molecular weight and yields gelation, that is, the formation of an insoluble network [1].

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Modelling of crosslinking polymerisation in a deterministic way has always been associated with multidimensional models. One of the first detailed crosslinking models proposed by Zhu and Hamielec [2], already accounted for two dimensions: chainlength and radical centres. More recently, Hernández-Ortiz et al. considered detailed models in three [3, 4, 5, 6] and five [7] dimensions. Lazzari et al. [8, 9] focused on the issue of multiradicals importance employing models of three parametric dimensions. With no exceptions, the level of exactitude intended by multidimensional description was reduced in the above-mentioned studies as a consequence of further treatment by the moment approach: only average quantities are recovered but not the original multidimensional distributions that the models are based on.

Regarding stochastic methods, very detailed Monte Carlo (MC) studies were performed by Hamzehlou et al. [10, 11], and a percolation model was considered by Lattuada et al. [12]. Despite of a significant industrial interest, few studies consider the topic of the deterministic modelling of the system with regard to the continuously stirred tank reactor (CSTR); while stochastic Monte Carlo results are in a better development, for instance those achieved by Tobita [13, 14, 15].

In our previous work[16] we discovered that neglecting multiradicals by distinguishing only 'dead' and 'living' polymer chains might lead to serious modelling errors when considering crosslinking polymerisation in the close-to-gel regime in a batch reactor. Even though multiradicals seem to be important, available deterministic modelling studies concerning the CSTR have not devoted any attention to the issue.

Among the mono-radical models in CSTR, studies performed using the numerical fractionation approach [17, 18] were capable to describe certain average quantities of the crosslinking polymerisation system on both sides of the gel point. Yet, the spectrum of the data generated is rather limited. On the other hand, the novel simulation approach that has appeared recently[19] allows to consider deterministic population balance models (PBMs) of high dimensionality. For instance, a two-dimensional PBM has been considered to study a copolymerisation process with substitution and shielding effects [19]; a three-

dimensional PBM has been employed in Ref. [20] to study the chain coupling reaction during degradation of high density polyethylene; a four-dimensional PBM has been considered to describe crosslinking copolymerisation in a batch reactor in Ref. [21].

In the current work, the polymerisation system is studied by means of a four-dimensional population balance model accounting for chain length, free pending double bonds, crosslinks, and multiradicals as dimensions. Since a purely distributional population balance equation does not account for gel even when an analytical solution is known [22], additional scalar quantities were added to encode some gel properties into the population balance model. In view of the large size of the problem the solution technique includes an approximation on radial basis functions, which permits to save computation resources considerably, and therefore employ a more realistic model. The population balance equation is designed to be valid in both pre-gel and gel regimes, it also capable of capturing the state of the polymerisation system exactly at the gel point, where the numerical solution develops a shock.

As results we present various distributional data: chain length, free pending double bonds (FPDBs), crosslinks, radical sites, and their dependants on residence time; bi-, tri-, and quad-variate distributions, data on FPDB and crosslink densities. Non-trivial patterns in the time evolution of average quantities that have been partly observed in prior studies [17, 18, 23, 24] (e.g. crosslink and FPDB densities, molecular weight, etc.) are naturally obtained by computing marginals of the four-dimensional distribution possessing a particular multimodal structure. The influence of the two termination mechanisms on the topological properties: recombination and disproportionation, was studied in detail. Some of the results were also examined with respect to multiradical limitations and the sensitivity to divinyl content in the reactor feed.

Figure 1: Monomer units as appearing in the topology are labelled according to chemical context; v: monovinyl, d: divinyl, r: radical site. The figure illustrates a possible polymerisation scenario. (*Left:*) mono-vinyl and divinyl monomers present initially; (*centre:*) an intermediate branched topology formed after a few reaction steps; (*right:*) a polymer network. An example of possible reaction channels is indicated by numbers: 1) divinyl propagation; 2) vinyl propagation, 3) crosslinking 4) termination by recombination.

1. The mathematical model

1.1. Reaction mechanisms

As usual, we ignore spatial configurations and focus exclusively on molecular topologies arising from the copolymerisation process. Any two arbitrary topologies are treated as equivalent if all four properties: chain length x , FPDB y , crosslinks c , radicals z , coincide. This allows talking about a concentration of molecules (x, y, c, z) and, eventually, about a set of concentrations of all possible configurations for these four properties: a four-dimensional distribution $R_{x,y,c,z}$. In our previous paper we considered the analogous polymerisation system in a batch reactor [21]. In the current paper, we study the polymerisation in a CSTR

including the following reaction mechanisms:

Since several radicals are permitted to reside on a polymer molecule, the termination reactions do not immediately imply a full stop of growth of the molecule. The reaction mechanisms are illustrated in Figure 1.

1.2. System state and deterministic balance equations

The reaction mechanisms (1) are equivalent to the full four-dimensional PBE, with the right hand side,

$$\begin{aligned}
\mathcal{L}_{full}(R_{x,y,c,z}) = & k_{p1}m_1c_i\delta_{x-1,y,c,z-1} + k_{p2}m_2c_i\delta_{x-1,y-1,c,z-1} + \\
& k_{p1}m_1z(R_{x-1,y,c,z} - R_{x,y,c,z}) + \\
& k_{p2}m_2z(R_{x-1,y-1,c,z} - R_{x,y,c,z}) + k_{td}c_{rd}((z+1)R_{x,y,c,z+1} - zR_{x,y,c,z}) + \\
& k_{tc} \left(\sum_{(x',y',c',z')=(1,0,0,0)}^{(x-1,y,c,z)} z'(z-z')R_{x',y',c',z'}R_{x-x',y-y',c-c',z-z'+2} - 2c_{rd}zR_{x,y,c,z} \right) + \\
& k_c \left(\sum_{(x',y',c',z')=(1,0,0,0)}^{(x-1,y,c,z)} z'(y-y')R_{x',y',c',z'}R_{x-x',y-y'+1,c-c'-1,z-z'} - (c_{rd}y - c_{db}z)R_{x,y,c,z} \right),
\end{aligned} \tag{2}$$

where

$$\delta_{x,y,c,z} = \begin{cases} 1, & x = y = c = z = 0; \\ 0, & \text{otherwise.} \end{cases} \tag{3}$$

Except of distribution $R_{x,y,c,z}$ a few scalar quantities is also necessary to fully define the state of the system: c_{rd} is the total number of radicals, c_{db} is the total number of FPDB, m_1 denotes the concentration of monomer, m_2 denotes the concentration of divinyl, c_{i2} is concentration of initiator, and c_i concentration of initiator radical. The PBE is brought to a reduced form by dropping one of the two dimensions, the number of crosslinks c or chain length x , and denoting the state of the system employing the three-dimensional marginals instead: $f(x, y, z) = \sum_c R_{x,y,c,z}$ or $g(y, z, c) = \sum_x R_{x,y,c,z}$. Therefore the state of the system utilising the three-dimensional marginals and the scalar quantities reads as

$$S = (f(x, y, z), g(x, y, z), m_1, m_2, c_{rd}, c_{db}, c_{i2}, c_i)^T,$$

and the full model is defined with an aid of the operator

$$F_r \begin{pmatrix} f \\ g \\ m_1 \\ m_2 \\ c_{db} \\ c_{rd} \\ c_{cl} \\ c_{i2} \\ c_i \end{pmatrix} = \begin{pmatrix} \mathcal{L}^x(f) \\ \mathcal{L}^c(g) \\ -k_{p1}m_1(c_{rd} + c_i) \\ -k_{p2}m_2(c_{rd} + c_i) \\ k_{p2}m_2(c_{rd} + c_i) - k_c c_{db}(c_{rd} + c_i) \\ -k_{td}c_{rd}^2 + (k_{p1}m_1 + k_{p2}m_2)c_i \\ k_c c_{db}c_{rd} \\ -k_d c_{i2} \\ -k_{p1}m_1c_i - k_{p2}m_2c_i + 2k_d c_{i2} \end{pmatrix} \quad (4)$$

where

$$\begin{aligned} \mathcal{L}^x(f(x, y, z)) = & k_{p1}m_1c_i\delta(x-1, y, z-1) + k_{p2}m_2c_i\delta(x-1, y-1, z-1) + \\ & k_{p1}z m_1 \left(f(x-1, y, z) - f(x, y, z) \right) + \\ & k_{p2}z m_2 \left(f(x-1, y-1, z) - f(x, y, z) \right) + \\ & k_{td}c_{rd} \left((z+1)f(x, y, z+1) - zf(x, y, z) \right) + \\ & k_{tc} \left(T_{0,0,-2}(zf(x, y, z) * zf(x, y, z)) - 2zc_{rd}f(x, y, z) \right) + \\ & k_c \left(T_{0,-1,0}(zf(x, y, z) * yf(x, y, z)) - (yc_{rd} + zc_{db})f(x, y, z) \right). \end{aligned} \quad (5)$$

$$\begin{aligned}
\mathcal{L}^c(g(y, c, z)) = & k_{p1} m_1 c_i \delta(y, c, z - 1) + k_{p2} m_2 c_i \delta(y - 1, c, z - 1) + \\
& k_{p2} z m_2 (g(y - 1, c, z) - g(y, c, z)) + \\
& k_{td} c_{rd} ((z + 1)g(y, c, z + 1) - zg(y, c, z)) + \\
& k_{tc} (T_{0,0,-2} (zg(y, c, z) * zg(y, c, z)) - 2z c_{rd} g(y, c, z)) + \\
& k_c (T_{0,-1,+1} (zg(y, c, z) * yg(y, c, z)) - (y c_{rd} + z c_{db})g(y, c, z)).
\end{aligned} \tag{6}$$

Here $f(x, y, z) * g(x, y, z)$ denotes the convolution, and the distributional translation is denoted as

$$T_{s_1, s_2, s_3} (f(x, y, z)) = f(x - s_1, y - s_2, z - s_3).$$

The definition of the coefficients employed in equations (5)(6)(4) is given in Table 3.

General speaking, the state S is treated as time dependent $S(t)$, $t \in [0, t_{end}]$, and the operator (4) is used to construct the population balance equation,

$$\dot{S}(t) = F(S(t)) + \frac{1}{\tau}(S_0 - S), \quad t \in [0, t_{end}], \quad S(0) = \bar{0}, \tag{7}$$

where $S_0 = (0, 0, m_{1|feed}, m_{2|feed}, 0, 0, 0, c_{i2|feed}, 0)^T$ denotes tractors feed and τ is a residence time. The dynamics of the differential equation (7) leads to a steady state, which is the main information we are interested in. Therefore, the equation (7) will be replaced by an algebraic one in most of the study cases,

$$F(S) + \frac{1}{\tau}(S_0 - S) = \bar{0}. \tag{8}$$

1.3. Mathematical description of gel

As discussed in by Wattis [16], a single distribution, even when it is defined on $[0, \infty)$, simply provides too little information to keep track of gel. Therefore, the gel is defined as the material that does not fit into the distribution predicted by PBE and thus, separate scalar variables are introduced to store information on basic gel properties. The total number of crosslinks c_{cl} , FPDBs c_{db} , and radicals c_{rd} in gel are accounted for as an additional scalar quantities in (4).

Consequently, the following equalities balance both sol and gel polymer,

$$\begin{aligned}
c_m &= c_{m|sol} + c_{m|gel}, c_{m|sol} = \sum_{x,y,z} x f(x, y, z) \\
c_{db} &= c_{db|sol} + c_{db|gel}, c_{db|sol} = \sum_{x,y,z} y f(x, y, z) = \sum_{y,z,c} y g(y, z, c) \\
c_{rd} &= c_{rd|sol} + c_{rd|gel}, c_{rd|sol} = \sum_{x,y,z} z f(x, y, z) = \sum_{y,z,c} z g(y, z, c) \\
c_{cl} &= c_{cl|sol} + c_{cl|gel}, c_{cl|sol} = \sum_{y,z,c} c g(y, z, c)
\end{aligned} \tag{9}$$

An important feature of the model expressed by (8) is that the total mass conservation is naturally satisfied in both pre-gel and gel regions,

$$\begin{aligned}
c_{db} + c_{cl} + m_2 &= \text{const}; \\
m_1 + c_m - c_{db} - c_{cl} &= \text{const}.
\end{aligned} \tag{10}$$

Equations (9) and (10) can be used to obtain the weight fractions of FPDB, crosslinks, and radicals in gel,

$$\begin{aligned}
\omega_{db} &= \frac{c_{db} - c_{db|sol}}{c_{db}}, \\
\omega_{rd} &= \frac{c_{rd} - c_{rd|sol}}{c_{rd}}, \\
\omega_{cl} &= \frac{c_{cl} - c_{cl|sol}}{c_{rd}},
\end{aligned} \tag{11}$$

the weight fraction of monomers in the gel reads,

$$\omega_m = \frac{c_{m1|feed} - c_{m1} - c_{db} - c_{cl} - c_{m|sol}}{c_{m1|feed} - c_{m1} - c_{db} - c_{cl}}. \tag{12}$$

Crosslinks contained in the gel $c_{cl|gel}$ can be distinguished according to their origin: being created in sol and consequently transferred to gel $c_{cl|t-gel}$ or created in the gel itself $c_{cl|o-gel}$.

$$\begin{aligned}
c_{cl|t-gel} &= k_c \int_0^{t_{end}} (c_{db|sol} c_{rd|gel} + c_{db|gel} c_{rd|sol}) dt \\
c_{cl|o-gel} &= k_c \int_0^{t_{end}} c_{db|gel} c_{rd|gel} dt
\end{aligned} \tag{13}$$

Having information on marginals $f(x, y, z)$ and $g(y, c, z)$ at hand, it is possible to reconstruct, with a certain degree of proximity, the marginal connecting x, y, c by making an assumption on the conditional independence of chain length x and crosslinks c under condition FPDB y [21],

$$P(x \wedge y \wedge c) = \sum_{z=0}^{\infty} \frac{f(x, y, z)g(y, c, z)}{\sum_{x=0}^{\infty} f(x, y, z)}.$$

1.4. Approximation scheme

By applying an approximation on Gaussian basis functions[25, 26], we search for an approximation to the distributional part of the state S , $f(x, y, z)$, $g(y, c, z)$ as a linear combination of pre-defined basis functions $\phi_{i,z}(x, y)$, $i = 1, \dots, N$, $z = 0, \dots, z_{max}$ and coefficients $\alpha_{i,z}$ that have to be determined,

$$f(x, y, z) \approx \sum_{i=1}^N \alpha_{i,z}^f \phi_i(x, y) \quad (14)$$

$$g(y, c, z) \approx \sum_{i=1}^N \alpha_{i,z}^g \phi_i(y, c)$$

$$\phi_i(x, y) = e^{-\frac{(x-x_i)^2}{\sigma_{x,i}} - \frac{(y-y_i)^2}{\sigma_{y,i}}},$$

$$\phi_i(y, c) = e^{-\frac{(y-y_i)^2}{\sigma_{y,i}} - \frac{(c-c_i)^2}{\sigma_{c,i}}}; \quad (15)$$

$$\sigma_{x,i}, \sigma_{y,i}, \sigma_{c,i} > 0, \quad i = 1, \dots, N,$$

where the dimensions of the distributions $f(x, y, z)$, $g(y, c, z)$ are limited by a maximum chain length, maximum number of FPDBs y_{max} , maximum number of crosslinks c_{max} , and maximum number of radical sites z_{max} .

As a result of implementation of the equation (14), the unknown distributions are substituted by sets of coefficients, the population balance - by a new population balance defining coefficient evolution. An algorithm for designing the coefficient population balance for crosslinking reaction mechanisms is discussed in details in [21].

1.5. The model in relation to Monte Carlo approach

Monte Carlo (MC) simulations provide an alternative to the deterministic solution of the polymerisation problem at hand. In practice, the MC data are

Figure 2: Sets of reaction rates that induce an invariant Monte Carlo solution

highly scattered, which reduces its usability for process optimisation and parameter estimation routines. However, certain detailed topology related properties, for instance the distance between branch points[11], can be only recovered using the MC method. For instance, the MC method introduced by Tobita [27, 13, 28] and later extended to crosslinking polymerisation in a CSTR in Ref. [16], enables observing the structure of each polymer molecule directly. Instead of reaction rates and initial concentrations as required by the PBE model (8) that produces distributions, the input information for the MC method is based on probabilistic information. The probabilistic parameters required by the MC simulations are derived by solving the low-molecular part of the PBE balance model (4). Therefore, a straightforward relation between the set of the kinetic parameters of the deterministic model and the MC parameters exists. However, in the present case of crosslinking polymerisation in a CSTR the relation is not one-to-one. As illustrated in Figure 2, multiple sets of kinetic coefficients correspond to a unique MC parameter set and hence to a single MC solution. This allows changes in the values of, for instance, the propagation rate coefficient k_p , while the MC parameters remain invariant, if these changes are accompanied by specific changes in other kinetic rate parameters. In this section we try to answer the question: do different kinetic parameter sets that lead to a single MC solution also lead to a single deterministic solution? The input parameters for the MC simulations are conversion for both monomers χ_1 , χ_2 , average primary polymer length $\bar{n}$, instantaneous and additional ρ_a crosslinking density. The fraction of divinyl monomers incorporated f_a , can be expressed in terms of the

rate coefficients and reactor feed concentrations as follows,

$$\begin{aligned}
\chi_1 &= 1 - \frac{m_1}{m_{1|feed}} \\
\chi_2 &= 1 - \frac{m_2}{m_{2|feed}} \\
\bar{n} &= \frac{k_{p1}m_1 + k_{p2}m_2}{k_{td}c_{rd}} \\
\rho_i &= \frac{k_c c_{db}}{k_{p1}m_1 + k_{p2}m_2 + k_c c_{db}} \\
\rho_a &= \frac{k_{p2}m_2(1 - \exp(-k_c(c_{rd} + c_i)\tau))}{k_{p1}m_1 + k_{p2}m_2 + k_c c_{db}} \\
f_a &= \frac{k_{p2}m_2}{k_{p1}m_1 + k_{p2}m_2 + k_c c_{db}}
\end{aligned} \tag{16}$$

where m_1, m_2, c_{db}, c_{rd} solve the low-molecular part of the population balance (8),

$$\begin{cases}
-k_{p1}m_1(c_{rd} + c_i) + \frac{m_{1|feed} - m_1}{\tau} = 0, \\
-k_{p2}m_2(c_{rd} + c_i) + \frac{m_{2|feed} - m_2}{\tau} = 0, \\
k_{p2}m_2(c_{rd} + c_i) - k_c c_{db} c_{rd} - \frac{c_{db}}{\tau} = 0, \\
-k_{td}c_{rd}^2 + (k_{p1}m_1 + k_{p2}m_2)c_i - \frac{c_{rd}}{\tau} = 0, \\
-(k_{p1}m_1 + k_{p2}m_2)c_i + 2k_d c_{i2} - \frac{c_i}{\tau} = 0, \\
c_{i2} = \frac{c_{i|feed}}{(1 + k_d\tau)}.
\end{cases} \tag{17}$$

Let's fix $m_{1|feed}, m_{2|feed}$ and consider a family of kinetic parameters of the deterministic model for each scaling factor ξ . Without loss of generality we consider $k_{p1} = \xi k_{p1}^0$. The rest of the parameters are recovered so the MC parameters are kept invariant by satisfying the conditions,

$$\begin{aligned}
\frac{\partial \chi_1}{\partial \xi} &= 0, \quad \frac{\partial \chi_2}{\partial \xi} = 0, \\
\frac{\partial \rho_a}{\partial \xi} &= 0, \quad \frac{\partial \rho_i}{\partial \xi} = 0, \\
\frac{\partial \bar{n}}{\partial \xi} &= 0, \quad \frac{\partial f_a}{\partial \xi} = 0.
\end{aligned} \tag{18}$$

Figure 3: Concentration profiles for the total number of free pending double bonds (*left*), crosslinks (*centre*), radicals (*right*) as obtained from the kinetic model for a continuous stirred-tank reactor with residence time $\tau = 1000$ s, conditions under which gel formation is expected.

Solving the system (18) analytically leads to the following family of deterministic parameters that yield an invariant MC result:

$$\begin{aligned} k_{p1} &= \xi k_{p1}^0, \quad k_{p2} = \xi k_{p2}^0, \quad k_c = \xi k_c^0 \\ k_{td} &= \frac{\alpha(\xi)c_i(\xi) - c_{rd}(\xi)}{c_{rd}^2(\xi)\tau}, \quad c_{i|feed} = \frac{\alpha(\xi)(c_i(\xi) + 1)}{2k_d\tau(1 + k_d\tau)}, \end{aligned} \quad (19)$$

where $k_{p1}^0, k_{p2}^0, k_c^0$ are constants, $c_{rd}(\xi), c_i(\xi), \alpha(\xi)$ are functions of ξ ,

$$\begin{aligned} c_{rd}(\xi) &= \frac{\chi_1 m_{1|feed} + \chi_2 m_{2|feed}}{\alpha(\xi)} - c_i(\xi), \\ c_i(\xi) &= (\chi_1 m_{1|feed} + \chi_2 m_{2|feed}) \left(\frac{1}{\bar{n}(\alpha(\xi) + 1)} + \frac{1}{\alpha(\xi)(\alpha(\xi) + 1)} \right), \\ \alpha(\xi) &= \xi \tau (k_{p1}^0 (1 - \chi_1) m_{1|feed} + k_{p2}^0 (1 - \chi_2) m_{2|feed}). \end{aligned} \quad (20)$$

As will be shown in the next section by numerical results obtained for various values of ξ , the sets of parameters that are associated with an invariant MC solution do not lead to invariant deterministic solutions.

2. Simulation results and discussion

2.1. Low molecular species and gel fraction

In this paragraph we present the results of our new, in the context of CSTR, model as was presented earlier in the paper. The kinetic parameters used have been listed in Table 1. Part of the results is compared to Monte Carlo simulations, carried out in the manner described above. The mathematical model for the CSTR accounts for feed and outflow as in equations (7). Although we are

Figure 4: Evolution of the second FPDB moment as CSTR establishes an equilibrium mode. The results obtained for various values of residence time τ can be separated in two groups pre-gel regime, $\tau \leq 300$ and active gelation, $\tau > 300$.

Rate constants:	value	description	Units
k_d	$3.4 \cdot 10^{-5}$	initiator dissociation rate	s^{-1}
k_{p1}	462	monovinyl propagation rate	$m^3 \text{ kmole}^{-1} s^{-1}$
k_{p2}	689	divinyl propagation rate	$m^3 \text{ kmole}^{-1} s^{-1}$
k_c	232	crosslinking rate	$m^3 \text{ kmole}^{-1} s^{-1}$
k_{td}	$1.054 \cdot 10^7 k_{li}(\chi)$	disproportionation termination rate	$m^3 \text{ kmole}^{-1} s^{-1}$
k_{tc}	$1.0127 \cdot 10^7 k_{li}(\chi)$	termination by recombination rate	$m^3 \text{ kmole}^{-1} s^{-1}$
$k_{li}(\chi)$	$e^{-(3.27\chi - 9.67\chi^2 + 56\chi^3)}$	conversion dependent termination factor	
$m_{1 feed}$	9.2553	initial concentration of vinyl	kmole m^{-3}
$m_{2 feed}$	0.0530	initial concentration of divinyl	kmole m^{-3}
$c_{i2 feed}$	0.01712	initial concentration of initiator	kmole m^{-3}

Table 1: Conversion dependant reaction rates, as suggested in the experimental work one by Li and Hamielec [29]

mainly interested in the steady-state behaviour of the CSTR, it is interesting to show the results of a few dynamic simulations. For a given set of kinetic parameters (Table 1) we show the time profiles for total number of FPDB, crosslinks and radicals, Figure 3. Dynamic results for the second moment of FPDB distribution in the sol part of polymer is illustrated in Figure 4 for various residence times passing through the gel point. Below $\tau = 300$ one observes that steady-state is reached in a smoothly increasing way. Above the gel point, $\tau = 377$, a clear peak is seen before the steady-state is established. In the remainder of this text we will ignore the transition period and focus on the results obtained under steady state condition. Also for these steady-state simulations we have varied the residence time as the key variable to examine the behaviour of the system around the gel point. The results of the simulations, the topological properties, will mostly be presented as a function of conversion of monomers χ , that obviously is changing with residence time.

As shown above, the polymerisation in a CSTR tends to feature gelation if residence time or conversion χ exceeds a particular value, the gel point. The gel fractions of monomer units, FPDBs, crosslinks, and radicals are depicted in Figure 5. It can be observed that the gel fraction of FPDBs practically coincides with the gel fraction of the total monomer material: although the absolute concentration of vinyl and free pending double bonds is very different, their relative fraction in gel is equal. In the other words, the process of transferring a sol molecule to gel has no preference towards more (or less) saturated with FPDB molecules. While similar statement about crosslinks, for instance, is not true: molecules with high number of crosslinks are more likely to be transferred to the gel.

2.2. Chain length and FPDB distributions

The evolution of the first three moments of the FPDB distribution are presented in Figure 6. All three moments converge even for a small number of radical sites assumed in the model. The FPDB distribution of the sol polymer at the gel point, presented together with its radical components at a logarithm

Figure 5: Weight fraction of FPDB, crosslinks, radicals, and total monomer material in gel as a function of conversion in the CSTR.

Figure 6: Evolution of 0th, 1st and 2nd moments of FPDB distribution as conversion passes through the gelation point. The maximum number of radicals used is indicated.

Figure 7: Double weighted FPDB distribution along with the distributions per class of polymer molecules with given numbers of radicals as obtained at the gelation point for a CSTR. Although as number of radicals, z increases the distributions become narrower and more shifted towards larger numbers of FPDB, the influence on the overall distribution indicated by the dashed line is minor. The overall distribution obtains its major contribution from molecules without radical sites, $z = 0$.

scale in Figure 8, does not feature an algebraic asymptotic decay. In the intermediate range of FPDBs the distribution follows a slope of -2.9 , but eventually decays exponentially, so all moments are finite.

As a way to mimic the experimental measurements, it is common to employ the gel permeation chromatography (GPC) representations for depicting chain length distributions. Throughout the text, we refer to GPC representation as to a weighted with a square of the coordinate and normalised form of an arbitrary distribution.

For instance the GPC plots for the FPDB distribution and its radical components are shown in Figure 7. The distribution corresponding to populations of polymer molecules with a large number of radicals are considerably shifted to the range with large number of FPDBs and hence contribute to the tail of the overall distribution. However, the major contribution to the overall FPDB distribution originates from polymer without radicals, $z = 0$.

Sol molecules at the gel point turn out to be distributed according to the

Figure 8: FPDB and chain length distributions of sol polymer at the gel point in a CSTR for each radical class.

Figure 9: Double weighted chain length distribution (*dashed line*), plotted along with the chain length distribution for each radical class of sol polymer. The results are obtained for a CSTR operating at the gel point.

Figure 10: Distribution of the sol polymer with respect to chain length and FPDB as obtained at the gel point in the CSTR for three values of divinyl content at feed: a nominal value of 0.01%, a factor 8 larger and a factor 8 smaller.

chain length in a comparable manner as according to FPDBs; a comparison of the two distributions is given in Figure 8. It can be seen that FPDB and chain length distributions are especially very similar at the tail. When viewed at the logarithmic scale, the FPDB distribution decays gradually almost from the beginning, whereas the chain length distribution has a flat plateau with almost constant values for chains shorter than 10^3 . The GPC representation of the chain length distribution is shown in Figure 9. It appears that chain length and FPDBs are closely correlated: as shown in Figure 10, the two dimensional distribution connecting these two properties emerges as a particularly narrow structure. Note that for every chain length the number of FPDBs varies over a very short range, but conversely, one observes that for a wide range of short molecules the number of FPDBs is close to 0. When the chain length property is viewed as a function of residence time, concentrations of big molecules are considerably larger in the region of the gel point. Number and weight averages of the chain length exhibit maxima at the gel point as depicted in Figure 11. Although theoretically $\tau = 0$ should yield zero chain length, a considerable large average chain length is already observed for very small $\tau > 0$. Further increase of residence time, $0 < \tau < \tau_{gel}$, causes a less rapid increase in chain length; after crossing the gel point the average chain length decreases gradually.

Results from a parametric study of the two-dimensional distribution chain length-FPDB for various values of the residence time reveal that only the tail of the distribution is more pronounced at the gel point, which enhances the number- and the weight-, averages for these properties.

2.3. Sensitivity to divinyl concentration at reactor feed

The inflow concentration of divinyl monomer has a pronounced influence on the FPDB distribution. Figure 13 illustrates how the scaling of divinyl content by various factors between 0.25 and 64 affects the GPC representations of the FPDB distribution obtained at the gel-point. The same distributions plotted at double logarithmic axes demonstrate an intermediate algebraic decay with various slopes for each divinyl content as depicted in Figure 15. The effect of the

Figure 11: Evolution of chain length averages obtained for a CSTR at varying residence time.

initial divinyl fraction on the double weighted chain length distribution may be followed in Figure 14. As shown in Figure 10, the two dimensional distribution of chain length/FPDB is translated to shorter chain length and larger FPDBs when divinyl fraction in the reactor feed is increased or vice versa. The bended shape of the two-dimensional distribution implies a non constant FPDB density as a function of chain length. Indeed, the FPDB density increases up to its maximum for short chains and remains constant for long chains. The effect is visible in Figure 16, that also demonstrates the dependence on initial divinyl fraction.

The minimum residence time required for gel formation clearly depends on the initial ratio of divinyl over total amount of monomers. As depicted in Figure 12, one observes that the minimum gelation residence time as a function of divinyl fraction exhibits an algebraic dependence.

2.4. Evolution of multiradicals

As in the batch case [21] we investigated the effect of setting a maximum to the number of radical sites per molecule at the gel point. Again, the higher this maximum, the more extended the overall FPDB and chain length distributions become. Hence, accounting for multiradicals improves the prediction of the tail

Figure 12: Minimal residence times sufficient to switch CSTR into the gel mode as a function of divinyl fraction in reactor feed exhibits algebraic behaviour. Similar phenomena was also observed for crosslinking in batch reactors in Ref. [21].

Figure 13: The GPC representation of FPDB distributions obtained at the gel point for various values of divinyl content in the reactor feed.

Figure 14: Sensitivity of the double weighted chain length distribution to divinyl content in the reactor feed. The simulations are obtained for a CSTR operating at the gel point. Along with the nominal value of 0.01% of divinyl two distributions, one corresponding to eight times larger and another to eight times smaller divinyl concentration are shown.

Figure 15: FPDB distributions obtained at the gel point for various values of divinyl content in the range 0.125 – 32% are depicted by colour solid lines. The vertical colour scale represents gelation time that is associated for each initial divinyl content.

Figure 16: Densities of FPDB as a function of chain length as obtained from CSTR simulations for three values of the divinyl content: a nominal value of 0.01%, a factor 8 larger and a factor 8 smaller.

Figure 17: Concentration of molecules with various amount of radicals versus conversion as the reaction passes the gel point. The first 32 classes of multiradicals are depicted.

Figure 18: Concentration of molecules with various amount of radicals versus conversion as the reaction passes the gel point. The results are obtained for a CSTR assuming absence of termination by recombination. The first 32 classes of multiradicals are shown.

and thus the properties associated with the tail (e.g. rheological ones). The concentration of molecules with a high number of radicals is increasing rapidly near the gelation point and gradually decreases beyond the gel point. This can be explained by the fact that sol molecules with a high number of radicals are more likely to be transferred to the gel if such is present. As depicted in Figure 17, molecules with a large number of radical sites are present in the system only temporally in the region around the gel point. The termination mechanism has a remarkable effect on the multiradical concentration: the absolute concentrations of multiradicals at the gel point are much higher if only termination by disproportionation is present, as opposed to the case where also recombination termination is active. The effect can be seen in Figures 18 and 17. The classes of molecules with a large number of multiradicals predominately consist of molecules with large number of vinyl and di-vinyl monomers, FPDBs, and crosslinks. This effect is visible in Figure 19, where the level lines of the trivariate distribution $f(x, y, z)$ are shown at the gel point.

Figure 19: Level lines of the trivariate distribution $f(x, y, z, t)$ depicting sol polymer at the gel point in CSTR with respect to three dimensions: chain length x , FPDB y , radicals z . The colour indicates the relative frequency.

2.5. Formation of crosslinks

The density of FPDB is calculated as the ratio,

$$d_{db}(x) = \frac{\sum_{(y,z)=0}^{\infty} y f(x, y, z)}{\sum_{(y,z)=0}^{\infty} x f(x, y, z)}. \quad (21)$$

As shown in Figure 20 the ratio (21) is not constant; it varies in chain length and residence time. The FPDB density of the sol polymer is typically lower for smaller molecules, while it reaching peak values at the gel point.

Once a divinyl monomer has been incorporated into a growing chain, it constitutes a potential place for a crosslink to form. The crosslinking reaction that converts FPDBs into crosslinks does not progresses equally fast for all molecules. Indeed, as depicted in Figure 21, large molecules exhibit a higher conversion of their FPDB. The conversion of FPDBs decreases for smaller molecules and is close to zero for molecules with low number of FPDBs. The effect can be understood by analysing the two dimensional distribution crosslinks-FPDB, as shown in Figure 22. The distribution has a remarkable bended shape: for every number of FPDBs the number of crosslinks varies in a very narrow range, while the

Figure 20: FPDB density as a function of chain length at varying x as obtained for various values of residence time: in pre-gel regime (a) and gel regime (b).

Figure 21: Conversion of FPDBs into crosslinks as a function of FPDB number obtained at various levels of conversion.

Figure 22: Distribution of sol polymer with respect to two dimensions, crosslinks and FPDB. Results obtained for a CSTR operating at the gel point. The colours denote the logarithm of relative frequency.

converse is not true. Similar pattern may be observed in the two-dimensional distribution chain length-crosslinks, as depicted in Figure 23. Regarding the crosslink formation we infer another interesting property from the modelling results. The crosslink density, being a characteristic that is dependent on chain length, is not identical in sol and gel parts of the polymer.

2.6. Contribution of termination mechanisms

The results discussed above are obtained for a polymerisation model (8) that accounts for two termination mechanism: termination by disproportionation and termination by recombination. It is interesting to follow the impact of the recombination reaction mechanism by suppressing it and comparing the results with the original ones. There are a few fundamental differences that emerge for a zero recombination rate. As can be observed by comparing Figures 18 and 17, the distribution of radicals is strongly affected - the concentration of all multiradical polymer molecules increases considerably at the gel point.

Quite remarkably, a comparable effect on the impact of multiradicals, but now due to absence or presence of RTD is observed when comparing Figure 17

Figure 23: Distribution of sol polymer with respect to two dimensions, chain length and crosslinks. Results obtained for a CSTR operating at the gel point. Colours denote the logarithm of relative frequency.

for the CSTR and the similar plot for a batch reactor in our previous publication [21]. These plots have both been constructed for the case with recombination termination. We see that going from a batch reactor (no RTD) to a CSTR (a broad RTD) causes a similar attenuation of the multiradical effect as going, in a CSTR, from absence to presence of recombination. Thus, we see how the RTD influences the multiradical effect.

The increase of multiradical concentrations is strong enough to have significant impact on the other topological properties. For instance, the FPDB distribution features a much slower decay at the tail, as can be seen in Figure 24. It is also important to note, even when the absolute concentration of multiradicals is low, still the tails of FPDB or chain length distributions are still defined by multiradical classes, and have very little dependence on the class with one or less radicals. A good demonstration of this fact is Figure 19; it shows that large molecules are predominately multiradical. The slow decay at the tail of FPDB distribution induces higher values of the polydispersity. This fact is depicted in Figure 25, where the polydispersity is plotted as a function of the residence time for both cases: with and without recombination reaction.

Figure 24: FPDB distribution depicted at a logarithmic scale (dashed line) as obtained from simulations at the gel point for a CSTR in absence of recombination termination. Number of radical classes distributions corresponding to different number of radical sites, $z = 0, \dots, 32$, are shown by solid lines.

Figure 25: Polydispersity of the FPDB distribution as a function of conversion; obtained from a CSTR model with two termination mechanisms: recombination and disproportionation (*solid line*) and CSTR model with termination by disproportionation only (*dashed line*).

2.7. Four-dimensional distribution as full representation for crosslinking polymerisation

Even though the one- and two-dimensional distributions presented above represent important bits of information on topologies of the polymer, we still adhere to the three dimensional distribution $\sum_z R_{x,y,c,z}$ as the most complete representation - it ties pairwise independent properties of chain length, FPDBs, and crosslinks into a single relation. The distribution at the gel point is depicted in Figure 29. Three distinctive modes may be observed in the distribution: small molecules ($x < 10^2$) that do not possess FPDBs nor crosslinks; intermediate sized molecules ($10^2 < x < 10^4, y > 1$) that have more than one FPDB and can be crosslinked or linear; large molecules ($x > 10^5, y \gg 1, c \gg 1$) that are highly crosslinked and possess a large number of FPDBs. The properties x, y, c are strongly interdependent in large molecules. It is sufficient to fix one of them in order for the other two to become distributed in an extremely narrow range. The larger the molecule, the smaller is the deviation of the logarithm of the deviation. In contrast, linear molecules or those without FPDB, $y = 0$, deviate much more in the other two properties. The latter effects become even more apparent, when the two-dimensional marginals are plotted for classes of molecules with a fixed number of crosslinks or FPDBs, as shown in Figures 26a,b. The fraction of the three-dimensional distribution associated to the large molecules that is situated along a straight line, suggests that a simple relation exists between the logarithms of the main properties: chain length, FPDBs and crosslinks, $\log x \propto \log y \propto \log z$. For instance, the proportion implies a constant FPDB and crosslink densities for the large molecules, a phenomenon that is also observed in Figures 16,20. This proportionality of the main properties may also imply that self-similar structures develop in large polymer molecules at the gel point, i.e their topologies are built according to fractal principles.

2.8. Comparison to Monte Carlo generated data

The MC method, discussed in the previous section, produces identical results for sets of kinetic parameters of the deterministic model according to a

Figure 26: Chain length-FPDB distribution for classes of molecules with a fixed number of crosslinks (a). Chain length-crosslink distribution for classes of molecules with a fixed number of FPDBs. The transparent surfaces depict the complete distributions, i.e. overall distributions without crosslinks/FPDB restrictions.

Figure 27: FPDB distribution as obtained for various ratios $\xi = 2^{-5}, -4, \dots, 2$, from simulations with 64 radical classes. Scattered Monte Carlo generated data are present for comparison and show only agreement for one particular set of kinetic parameters, corresponding to $\xi = 0.5$

Rate constants:	value	description	Units
k_d	0.05	initiator dissociation rate	s^{-1}
k_{p1}	10 000	monovinyl propagation rate	$m^3 kmole^{-1} s^{-1}$
k_{p2}	5 000	divinyl propagation rate	$m^3 kmole^{-1} s^{-1}$
k_c	500	crosslinking rate	$m^3 kmole^{-1} s^{-1}$
k_{td}	$1.74 \cdot 10^6$	disproportionation termination rate	$m^3 kmole^{-1} s^{-1}$
$m_{1 feed}$	9.995	initial concentration of vinyl	$kmole m^{-3}$
$m_{2 feed}$	0.005	initial concentration of divinyl	$kmole m^{-3}$
$c_{i2 feed}$	0.0013	initial concentration of initiator	$kmole m^{-3}$

Table 2: Reaction rates for comparison with Monte Carlo generated data from Ref. [16]

range of scaling factor values ξ between $1/32$ and 2 . The MC generated data was compared to the solutions obtained from the deterministic PBM employing rate coefficients as in Table 2. Figure 27 clearly shows that the deterministic PBE model gives rise to different FPDB distributions as obtained for the various values of ξ . They are at closest proximity to the MC generated data for $\xi = 0.5$. As a possible explanation for the difference shown in Figure 27 we suggest the fact that the MC simulations assume instantaneous growth of primary polymer chains. Although the connectivity results of MC implicitly account for multiradicals, the growing macroradical chains themselves are not described there. In our deterministic model, in contrast, we are forced to describe these properly. Figure 28 shows the radical distributions that are also strongly dependant on the value of the scaling factor ξ . The representation of a tridimensional distribution connecting the properties chain length, FPDB, and crosslinks, together with Monte Carlo generated data can be viewed in Figure 29. Each MC sample, corresponds to one molecule that has a particular length x , numbers of FPDBs y and crosslinks c , and is represented by a dot (x, y, z) in the figure. The MC method does not yield concentrations explicitly. The concentration associated to a sample (x, y, z) can be deduced from a relative frequency of its appearance according to the MC method, which in turn is strongly dependant on the method conversion that is hard to estimate. Therefore, there is no sound mechanism to transit from a finite ensemble of MC samples to exact values of concentrations, while the deterministic model naturally provides information on polymer concentrations.

In a qualitative sense, it can be concluded that the samples are scattered around the mean values in each crosslink slice of the distribution (see the enlarged part of Figure 29) and thus constitute a good match between deterministic and stochastic methods.

3. Conclusions

Crosslinking polymerisation in a CSTR has been studied by means of a four-dimensional population balance model. Both dynamic and steady state

Figure 28: Radical distribution as obtained for various ratios $\xi = 2^{-5, -4, \dots, 3}$ from simulations with 50 radical classes.

Figure 29: Level lines in slices of the tridimensional distribution $f(x, y, c)|_{c=c_i}$ connecting properties of chain length, FPDB, and crosslinks as compared to Monte Carlo generated data. Colour denotes concentration. A sample slice of the distribution, corresponding to $c = 100$, is enlarged for better visibility. Three distinct modes can be seen in the distribution: A) short linear polymer, no FPDB; B) linear and crosslinked polymer of intermediate length and FPDBs, intermediate length; C) large crosslinked polymer.

models were developed. The validity of the models covers the full range of residence times, including those that correspond to operating in the gel regime. The results are extremely detailed and exhibit a good match with Monte Carlo simulations for a large part of the chain length and FPDB range. Remarkably, different sets of kinetic parameters corresponding to one particular set of MC parameters turn out to lead to clear differences in the tails of the FPDB and chain length distributions and hence to discrepancies with the MC outcomes.

Special attention has been paid to the multiradicals issue. It has been shown that multiradicals are present in a narrow range of residence times and are expressed to a lesser extent when comparing with a batch reactor under similar conditions. The recombination termination reaction turns out to suppress the influence of the multiradicals on the final topological properties. By performing parametric studies with average residence time in the CSTR we observed the system switching between four successive modes:

- 1) Linear mode. Small residence time, the reactor produces linear polymer chains only;
- 2) Crosslinked mode. Intermediate residence time, the reactor produces crosslinked polymer, no gel can be detected. The crosslinking density and molecular weight increases with increasing residence time.
- 3) Gel mode. Residence time exceeds gelation time. Polymer product consists of sol and a gel parts. Further increase in the residence time leads to increasing crosslinking density in the gel while this property continues to decrease in sol phase.
- 4) Critical mode. Almost all polymer product present in the gel form. Remaining sol, if present, is linear again. Further increase in residence time does not change the properties of the sol product at all, while it may still lead to a more densely crosslinked gel.

The minimal residence time leading to gel formation is sensitive to divinyl content, it turns out to possess a simple algebraic relation with divinyl fraction.

Our CSTR model represents the first successful attempt to predict a wide range of topology related properties for crosslinking polymerisation in a *distribu-*

tional form. The multidimensional distributional representation of chain length, FPDBs, crosslinks, radicals, and their densities considerably improves detailed understanding of the crosslinking polymerisation process. For instance, non-trivial patterns in the evolution over time of average quantities (e.g. crosslink and FPDB densities, molecular weight, etc.) are reflections of a typical multimodal structure observed in the three-dimensional distribution. The strongly correlated behaviour of the main topological properties demonstrated by especially the long molecules at the gel point suggests the existence of possible self-similar structures developing in large polymer molecules. This would imply that their topologies are built according to fractal principles.

Even though the population balance model is required describing the state of the polymer by no less than a four dimensional distribution, an accurate solution is achieved in a reasonable computational time by applying an approximation scheme based on radial basis functions.

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Low molecular species	
m_1	monovinyl monomer concentration
m_2	divinyl (crosslinker) concentration
$c_{rd}, c_{rd sol}, c_{rd gel}$	total number of radicals: total, sol and gel parts
c_{i2}	initiator concentration
c_i	dissociated initiator concentration
$c_{db}, c_{db sol}, c_{db gel}$	total number of free pending double bonds: total, sol and gel parts
c_{cl}	total number of crosslinks
$c_m, c_{m sol}, c_{m gel}$	number of monomers: total, sol and gel parts
$\omega_{db}, \omega_{rd}, \omega_{cl}, \omega_m$	weight fractions of FPDB, radicals, crosslinks, and material in gel
$d_{db}(x, t)$	FPDB density as a function of chain length, and time
$d_{cl}(x, t)$	crosslink density as a function of chain length, and time
τ	residence time
χ, χ_1, χ_2	conversions: overall, of the first monomer, of the second monomer
$\bar{n}$	average primary polymer length for MC method
ρ_i, ρ_a	instantaneous and additional crosslinking density for MC method
f_a	fraction of active monomers
ξ	MC invariant scaling factor
Distributions	
$f(x, y, c, z)$	Relative frequency of polymer as a function of chain length, x , number of FPDB y , number of crosslinks c , and number of radicals z .
$f(x, y, z)$	Three dimensional marginal of $f(x, y, c, z)$: relative frequency of polymer as a function of chain length, x , number of FPDBs y , and number of radicals z .
$f(y, c, z)$	Three dimensional marginal of $f(x, y, c, z)$: relative frequency of polymer as a function of number of FPDBs y , number of crosslinks c , and number of radicals z .

Table 3: Adopted notations