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

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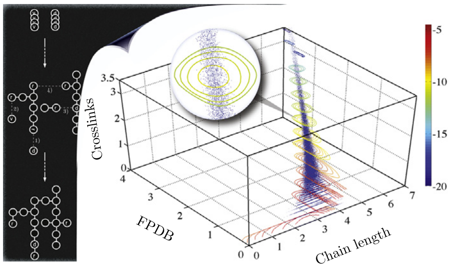
HIGHLIGHTS

- Radical polymerisation in a continuously stirred tank reactor was studied.
- The polymerisation results in cross-linked polymer network and eventually, gel.
- The system was described by a four-dimensional population balance model.
- Results include chain length, FPDB, and crosslink distributions and correlations.
- The role of multiradicals in formation of polymer network was studied.

GRAPHICAL ABSTRACT



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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.

1. Introduction

Copolymerisation 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 (Wang et al., 2009).

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 (1993), already accounted for two dimensions: chainlength and radical centres. More recently, Hernández-Ortiz et al. considered detailed models in three (Hernández-Ortiz et al., 2014a, 2012; Espinosa-Pérez et al., 2014; López-Domínguez et al., 2014) and five (Hernández-Ortiz et al., 2014b) dimensions. Lazzari et al. (2014), Lazzari and Storti (2013) focused on the issue of multiradicals importance employing models of three parametric dimensions. With no exceptions, the level of

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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. (2014, 2013), and a percolation model was considered by Lattuada et al. (2013). Despite 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 (2013, 2014a,b).

In our previous work (Kryven et al., 2013) 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 (Li et al., 2004; Li and McCoy, 2004) 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 (Kryven and Iedema, 2013a) allows us 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 (Kryven and Iedema, 2013a); a three-dimensional PBM has been employed by Kryven and Iedema (2014a) 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 by Kryven and Iedema (2014b).

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 (Wattis, 2006), 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 employs 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 (Li et al., 2004; Li and McCoy, 2004; Kizilel et al., 2007; Teymour and Campbell, 1994) (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.

2. The mathematical model

2.1. 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 (Kryven and Iedema, 2014b). In the current paper, we study the polymerisation in a CSTR including the following reaction mechanisms:

$$
\begin{aligned}
& I_2 \overset{k_d}{\rightarrow} 2I. \\
& I + M_1 \overset{k_i}{\rightarrow} R_{1,0,0,1}, \\
& I + M_2 \overset{k_{i2}}{\rightarrow} R_{1,1,0,1}, \\
& R_{x,y,c,z} + M_1 \overset{zk_{p1}}{\rightarrow} R_{x+1,y,c,z}, \\
& R_{x,y,c,z} + M_2 \overset{zk_{p2}}{\rightarrow} R_{x+1,y+1,c,z}, \\
& R_{x_1,y_1,c_1,z_1} + R_{x_2,y_2,c_2,z_2} \overset{y_1 z_2 k_c}{\rightarrow} R_{x_1+x_2,y_1+y_2-1,c_1+c_2+1,z_1+z_2}, \\
& R_{x_1,y_1,c_1,z_1} + R_{x_2,y_2,c_2,z_2} \overset{z_1 z_2 k_{td}}{\rightarrow} R_{x_1,y_1,c_1,z_1-1} + R_{x_2,y_2,c_2,z_2-1}, \\
& R_{x_1,y_1,c_1,z_1} + R_{x_2,y_2,c_2,z_2} \overset{z_1 z_2 k_{tc}}{\rightarrow} R_{x_1+x_2,y_1+y_2,c_1+c_2,z_1+z_2-2}.
\end{aligned}
\tag{1}
$$

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 Fig. 1.

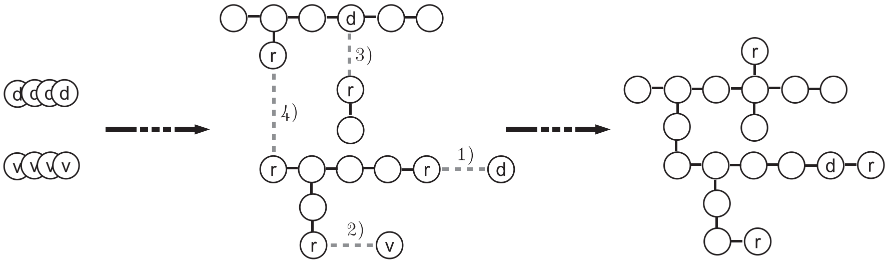

Fig. 1. Monomer units as appearing in the topology are labelled according to chemical context; v: monovinyl, d: divinyl, r: radical site. The figure illustrates a possible polymerisation scenario. *Left*: mono-vinyl and divinyl monomers present initially; *centre*: an intermediate branched topology formed 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.