



# Transition into the gel regime for free radical crosslinking polymerisation in a batch reactor



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## ABSTRACT

Crosslinking polymerization 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, for the first time and to a full extent resolves the crosslinking problem as formulated by Zhu et al. [1] and 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 model has been validated with data from an experimental crosslinking polymerization, Methyl Methacrylate with Ethylene Glycol Dimethacrylate. Non-trivial patterns in the time evolution of average quantities like crosslink densities, partly observed in prior studies [2–4], are naturally emerging from the model by computing marginals of the four-dimensional distribution possessing an interesting multimodal structure.

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## 1. Introduction

The crosslinking copolymerization of vinyl and divinyl monomer is a process that may lead to gel formation, but only few studies provide details of the transition zone from sol to gel. Monte Carlo studies, for instance those carried out by Hamzehlou et al. [5], reveal the main polymer morphological properties, but they remain rather qualitative as regards the precise behaviour of the molecular weight distribution (MWD) due to highly scattered data. The numerical fractionation approach introduced by Teymour and Campbell [4] and the generating functions approach [6] are the only two deterministic methods claimed to be capable to describe the crosslinking polymerization system on both sides of the gel point. Yet, the original formulation of the numerical fractionation approach relies on concepts like ‘generation’ and ‘pseudo-gel’ that are heuristic and hard to interpret in a chemically meaningful way. Although the generating function approach has a sound and clear mathematical formulation, the numerical implementation often suffers from the ill-posedness of an inverse integral transform that often results in a failure of the computations.

Remarkably, the full population balance equation describing the crosslinking polymerization system has already been formulated

20 years ago in the work of Zhu et al. [1], but until now no complete solution has been offered. In an almost unchanged manner the problem has been considered in a series of follow-up studies [4,3,2,7–9]. No alterations to the original model itself were proposed, since the studies [4,3,2,7–9] mainly targeted the development of a new mathematical toolbox relevant to the problem at hand. Regarding gelation phenomena from a deterministic modelling point of view one may observe that it has been addressed by a relatively simple coagulation model with a multiplicative kernel [10]. In this model one expects the total mass of particles to be conserved, however, explicit solutions show that this is not always true. It may happen that the total mass decreases after a finite time, an event that marks the formation of a cluster of infinite size [11].

The current paper for the first time and to a full extent resolves the crosslinking problem as formulated by Zhu et al. [1] employing the multidimensional population balance equation (PBE). The model describes the evolution of a four-dimensional distribution in time and resolves properties as chain length, number of free pending double bonds (FPDB), number of crosslinks, and number of radicals per molecule as dimensions of the distribution. 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. The PBE is designed to be valid in both pre-gel and gel regimes, it also capable of capturing the state of the polymerization system exactly at the gel point,

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where the numerical solution develops a shock. The approach is absolutely novel to the class of crosslinking polymerization problems and is neither relying on heuristic ideas, nor on numerically unstable algorithms.

As results we present various distributional data: chain length, FPDBs, crosslinks, radical sites and their evolution in 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 observed in the prior studies [2–4] (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. Some of the results are studied with respect to sensitivity to crosslinker and multiradical limitations.

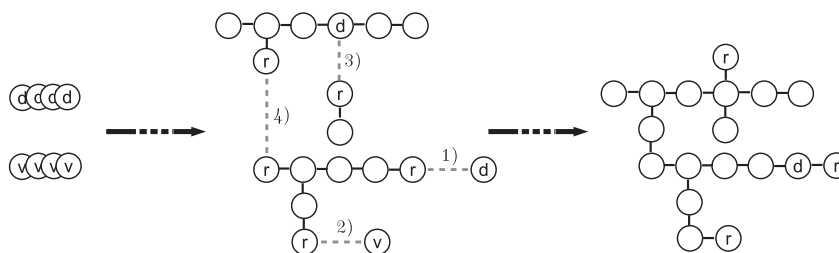
## 2. Random processes creating branched molecular topologies and gels in relation to reaction mechanisms

Gelation phenomena have been followed by the most basic random graph models, where gelation is called ‘giant component phase transition’. For instance, the  $G(n,p)$  model introduced by Erdos [12] considers  $n$  disconnected nodes that become connected with a probability  $p$  at each time point. Eventually, the gap in size between the largest component and the second largest component increases, since the two are very probable to become connected, and the giant component emerges, Fig. 2.

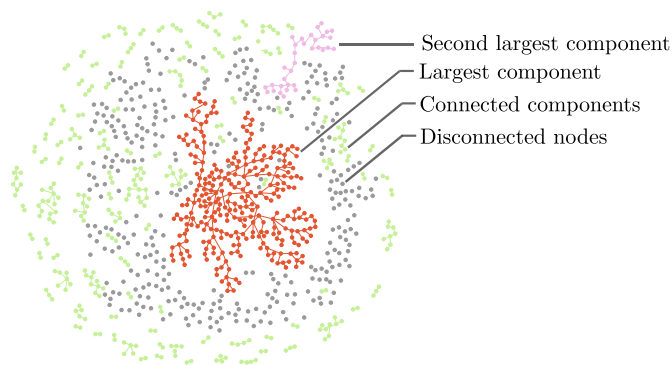
Although crosslinking copolymerization leading to gelation may be described by a random graph model in a relatively simple manner, analytical estimates are much harder to obtain, and require sophisticated numerical techniques. In order to deal with a large number of graph-like molecular topologies, we measure them according to the most important properties. This is done by employing one of the measures  $\mu_{full}$ ,  $\mu_x$ , and  $\mu_c$  that map a polymer topology to a corresponding three- or four-dimensional point,

$$\begin{aligned} \mu_{full}(\text{topology}) &\rightarrow (x, y, c, z) \in R^4; \\ \mu_x(\text{topology}) &\rightarrow (x, y, z) \in R^3. \\ \mu_c(\text{topology}) &\rightarrow (y, c, z) \in R^3. \end{aligned} \quad (1)$$

The measures (1) provide a way to describe the state of the whole polymer system as a multidimensional distribution; its kinetic as a population balance equation. Analogously to Ref. [13] where a polymer modification problem was addressed, we consider a 4-dimensional distribution  $R_{x,y,c,z}$  that denotes the relative frequency of polymers with total number of monomers  $x$ , number of FPDBs  $y$ , number of cross links  $c$ , and number of active radical sites  $z$ . We study an evolution of  $R_{x,y,c,z}$  driven by reactions kinetics, departing from only monomers and arriving, at full conversion, in a situation of one single gel molecule and non reactive sol. The reaction mechanisms considered in the current model are as follows.



**Fig. 1.** Monomers units as appearing in the topology, are labelled according to chemical context; v: monovinyl, d: divinyl, r: radical site. The figure illustrates a possible polymerization 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 indicated by numbers: 1) divinyl propagation; 2) vinyl propagation, 3) crosslinking 4) termination by disproportionation.



**Fig. 2.** A small random graph model, assuming equal probability for each arbitrary pair of nodes becoming connected, predicts the emergence of the ‘giant component’ i.e. a largest connected component that is much larger than the second largest one.

Initiator decomposition (I2 initiator, I initiator radical)



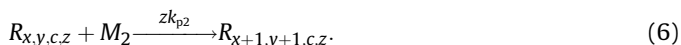
Monovinyl and divinyl initiation, reactions between initiator and monomer,



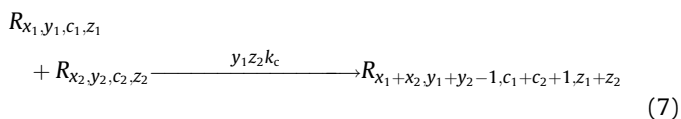
Monovinyl propagation, leads to increase of total amount of monomers by one,



Divinyl propagation, leads to increase in the number of FPDBs and total amount of monomers,



A cross-linking step is a reaction between a growing polymer molecule containing radicals and a free divinyl incorporated into another molecule, leading to a combined molecule having one more crosslink and one less free vinyl group:



Disproportionation leads to decrease in a number of radicals by one in each molecule,

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