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To: rdias@jpb.pi

19-Jan-2011

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Thank you very much for your fine contribution.

Sincerely,

Prof. Dr. Wilhelm Oppermann
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[E-Mail reference DL-SM-1]
Modeling Studies on the Synthesis of Superabsorbent Hydrogels using Population Balance Equations

<table>
<thead>
<tr>
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<th><em>Macromolecular Symposia</em></th>
</tr>
</thead>
<tbody>
<tr>
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Modeling Studies on the Synthesis of Superabsorbent Hydrogels using Population Balance Equations

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Summary:
The synthesis of super-absorbent hydrogels is simulated using a kinetic model based upon population balance equations of generating functions. Dynamics in a batch reactor of properties such as the weight fraction of gel or average molecular weights of the soluble fraction can be predicted. This kinetic model neglects intramolecular cyclization reactions for simplicity (hence predictions can be valid only for very small amounts of crosslinker) but it can accommodate the operation with different kinds of crosslinking agents, namely bifunctional (e.g. N,N’-methylenebisacrylamide), trifunctional (e.g. trimethylolpropane triacrylate) and tetrafunctional (e.g. tetraallyloxyethane). The influence of the use of such different kinds of crosslinkers on the dynamics of gelation is discussed. It is also assessed the impacts of the rate propagation coefficient of the monofunctional monomer (typically acrylic acid), of the reactivity of the pendant double bonds (PDB) and of the initial composition on the dynamics of gel production. Some crucial details concerning the numerical solution of the two-point boundary value problems (TPBVP) associated with this simulation tool are also presented. Predictions of the proposed kinetic approach are compared with those obtained using the Theory of the Branching Processes which is not strictly valid with kinetically controlled polymerization systems such as those here considered. Important differences between the predictions of the two approaches are shown. Superabsorbent hydrogels were synthesized with a 2.5 L batch reactor and the experimental data are used to show that the simple kinetic model developed is able to capture the main features of this polymerization system.

Keywords: hydrogels; kinetics (polymerization.); modeling

Introduction
Superabsorbent polymers (SAP) are hydrophilic gels that are able to retain, at a high absorption rate, huge amounts of water (up to 1000 g/g relatively to the dry weight). Thanks to these unique properties, SAPs have many important applications in hygienic-sanitary industries, agriculture, environment, separation process and other chemical engineering operations. Nowadays, SAPs or other related polymer networks (generically named hydrogels) are also used in biology and medicine, namely in controlled drug delivery. According to the provenience of the materials used in the synthesis, SAPs can be divided in two groups: synthetic SAP that are obtained through the copolymerization of petrochemical-based monomers and those SAP obtained from the grafting of natural polymers such as polysaccharides (e.g starch) or polypeptides.1–3

Synthetic SAPs are mainly obtained through the polymerization of acrylic acid (AA) with different kinds of crosslinkers such as N,N’-methylenebisacrylamide (MBA), trimethylolpropane triacrylate (TMPTA) or tetraallyloxyethane (TAO). Water-phase polymerizations are generally carried out and therefore the low solubility of some crosslinkers in aqueous medium should be accounted for.4 This problem can be overcome by using an organic solvent and conventional crosslinkers (e.g. divinylbenzene or ethylene-glycol-dimethacrylate) at the expenses of introducing in the products chemicals hindering the direct use of the materials for some applications. In practice, SAPs are produced using
the aforementioned kinds of crosslinkers at levels in the range 0.01 to 2 wt% (considering TMPTA as a model crosslinker\textsuperscript{[4]} in order to obtain materials with a high swelling ratio (which is attained at a low crosslinker content) and a low soluble fraction (which is more easily fulfilled using a higher crosslinker content).\textsuperscript{[4]} The mole fraction of crosslinker ($Y_C$) used in the production of such materials can therefore be as lower as 0.0025% to 0.5%.

Thermal, redox or even photo initiation are used to carry out the free radical copolymerization of acrylic acid aqueous solutions in the presence of crosslinkers. Aqueous solutions of AA salts (obtained through the neutralization of AA with a base such as NaOH) are also usually considered in SAP production. Reaction temperatures in the range 40 to 70 °C are often considered in these synthesis process. Note that in several kinetic studies concerning the polymerization of acrylic and methacrylic acid (namely using PLP), much lower temperature ranges have been considered (e.g. 2 °C to ambient temperature). Nevertheless, in order to assure high reaction rates (and almost complete monomer conversion) in industrial processes, higher temperatures must be used. Other parameters such as the degree of neutralization and monomer concentration have a strong impact on the polymerization of these ionic monomers.\textsuperscript{[5–25]}

Lack of reaction control often associated with aqueous solution production of SAPs (fast exothermic reaction and high viscosity with a concomitant temperature raise) can be overcome using inverse suspension polymerization which also allows the direct synthesis of powder products or microspheres.\textsuperscript{[26–32]} Porous hydrogels composites with improved properties can also be synthesized changing the conventional procedure through the introduction of inorganic fillers and a porogen.\textsuperscript{[33]}

The complex kinetics inherent to the aqueous homopolymerization of acrylic monomers and non-linear copolymerization acrylic/polyvinyl monomers has been studied the last few years with the main goal of elucidating the influence of key operation parameters (e.g. temperature and pH) on the reaction rate of such chemical systems. Another important class of works on the same subjects is devoted to the characterization of properties of the final products (e.g. their swelling ratio) and on the influence of the chosen polymerization medium (e.g. solution/suspension) on important features of the synthesized materials. Nevertheless, only scarce information can be found in literature concerning the prediction/measurement of the dynamics (time evolution) of important properties of acrylic superabsorbent materials during their synthesis process.

Thanks to an extension of the method of moments which the authors started developing since the early nineties and has been much improved in more recent years,\textsuperscript{[34–44]} it is possible to predict (before and after gelation) important properties of non-linear polymers (MWD, sequences distributions, z-average radius of gyration) when their synthesis is kinetically controlled. This approach has been applied in the modeling before gelation of chemical systems concerning the free radical polymerization (FRP) of styrene/divinylbenzene, acrylate/diacrylate and methacrylate/dimethacrylate monomers. Such studies have also been extended to the controlled radical polymerization (CRP), namely of the nitroxide mediated (NMRP) and atom transfer (ATRP) of the same classes of monomers.\textsuperscript{[45–50]} Still more recently, the dynamics of gel production in the suspension copolymerization of styrene/divinylbenzene\textsuperscript{[51]} was experimentally and theoretically studied.

Modeling capabilities of this kinetic approach are here illustrated considering the synthesis of superabsorbent hydrogels (mostly based on acrylic acid) as a case study. A simplified kinetic model is developed and used to predict the dynamics, before and after gelation, of key polymer properties associated with the synthesis of such materials in a batch reactor. The dependence of this dynamics on kinetic parameters such as the rate propagation coefficient of the monofunctional monomer (e.g.
acrylic acid), the reactivity ratio of pendant double bonds, the initial mole fraction of crosslinker or the functionality of the crosslinker is illustrated is this work. Important features of the synthesis of super-absorbent hydrogels can be captured by this simple kinetic model which should help the management of such processes making easier the design of new production conditions. Note that in the framework of the present kinetic approach much more complex models can be created but it is not easy to measure the required kinetic parameters for water soluble monomers, as discussed below.

These polymerization processes are kinetically controlled and therefore the classical Theory of Branching Process (TBP) is not strictly valid for their description. This issue becomes also evident in this work by comparing predictions of the proposed kinetic model with those obtained using the TBP. The occurrence of important dissimilarities between the predictions of the two approaches will be shown below. Experimental data obtained by this research team in the synthesis of acrylic acid/TMPTA SAP (in a 2.5 L batch reactor) are compared with the predictions of the proposed kinetic approach and a fair agreement is observed.

**Kinetic Modeling**

A very simple kinetic scheme describing the copolymerization of acrylic acid (or other acrylic monomer) with a multifunctional crosslinker (C) is presented in Eqs. (1)-(9). A generic crosslinker with functionality \( \alpha \) (number of active double bonds) is here considered. N,N’-methylenebisacrylamide (MBA), with \( \alpha = 2 \), and trimethylolpropane triacrylate (TMPTA), with \( \alpha = 3 \), tetraallyloxyethane \( (\alpha = 4) \) are examples of such crosslinkers which are industrially used in the preparation of acrylic super-absorbents. A linear copolymerization results if a chemical system including a second monomer with a single active double bond \( (\alpha = 1) \) is considered.

In Eqs. (1)-(9), \( P_{k,m,n} \) represent the ensemble of polymer molecules bearing \( k \) radicals, \( m \) pendant double bonds and \( n \) repeating units. This simplified description of the polymerization system is adopted in order to keep this presentation within a manageable size. Nevertheless, as shown in previous works, this kinetic approach was conceived in order to deal with much more detailed descriptions of non-linear polymerization systems. Consideration of different kinds of polymer radicals (different reactivities), different kinds of pendant double bonds (generically macromonomers with different reactivities) and discrimination of different structural repeating units (e.g. moieties derived from vinyl and multivinyl monomers) are some examples of peculiarities that can be accommodated by this method. The automation of the simulation tool developed allows the analysis of these more complex systems without rewriting all the involved equations. This feature will be explored below in the present work when discussing, for instance, the influence of the reactivity of the two PDBs of TMPTA on the dynamics of gelation.

- **Initiator Thermal Decomposition:**

  \[
  I \xrightarrow{k_i} 2fR_0 \tag{1}
  \]

- **acrylic acid (AA) Initiation:**

  \[
  R_0 + AA \xrightarrow{k_{i1}} P_{1,0,1} \tag{2}
  \]

- **Crosslinker Initiation:**

  \[
  R_0 + C \xrightarrow{k_{i2}} P_{1,\alpha-1,1} \tag{3}
  \]
• Pendent Double Bonds (PDB) initiation:

\[ R_0 + P_{k,m,n} \xrightarrow{k_{ln}} P_{k+1,m-1,n} \]  

(4)

• AA Propagation:

\[ P_{k,m,n} + AA \xrightarrow{k_{p1}} P_{k,m,n+1} \]  

(5)

• Crosslinker Propagation:

\[ P_{k,m,n} + C \xrightarrow{k_{p2}} P_{k,m+\alpha-1,n+1} \]  

(6)

• PDB Propagation (crosslinking):

\[ P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{p3}} P_{k+k',m+m'-1,n+n'} \]  

(7)

• Termination by combination:

\[ P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{tc}} P_{k+k'-2,m+m',n+n'} \]  

(8)

• Termination by disproportionation:

\[ P_{k,m,n} + P_{k',m',n'} \xrightarrow{k_{td}} P_{k-1,m,n} + P_{k'-1,m,n} \]  

(9)

In the kinetic scheme above presented, I represents a thermal initiator (e.g. V50) decomposing into a pair of primary radicals \( R_0 \) with an associated efficiency \( f \). Three different initiation steps arising from the reaction of primary radicals with acrylic acid, crosslinker and PDBs are considered and similarly three different propagation mechanisms related to the reaction of polymer radicals with these same species are also considered. Termination by combination (dominant in acrylates) and termination by disproportionation are also included in the kinetic scheme. Due to their relative low impact on the dynamics of gelation (e.g. comparatively to polymerization of PDBs) and also for the sake of simplicity, chain transfer reactions (e.g. to solvent or monomer) are not included in this analysis. Kinetic parameters (rate coefficients) involved in mechanisms described by Eqs. (1)-(9) play an important role when predictions of the dynamics of polymerization are desired. Estimates for these kinetic parameters, available in other published research works, are below discussed.

The kinetic approach here considered uses generating functions (GF) of polymer populations, that for the present case study transforms the ensemble of polymer molecules \( P_{k,m,n} \) in a 3-dimensional GF:

\[ G(s_R, s_B, s) = \sum_{k=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P(k, m, n)s_R^k s_B^m s^n \]  

(10)

Generally speaking, the dimension of the GF to be used depends of the degree of complexity considered to describe the polymer population. Three-dimensional GF presented in Eq. (10) bears the minimum number of dimensions (simplest possible description) allowing the analysis of a vinyl/multivinyl...
copolymers. For instance, a new dimension should be added if the two PDBs of a crosslinker with \( \alpha = 3 \) (such as TMPTA) are distinguished (e.g. due to eventual different reactivities).

For a batch reaction starting with the premixed monomers and initiator and assuming that the polymerization system stays in a single phase, the required PBE of polymer in terms of the aforementioned GF is described by the first-order partial differential equation below:

\[
\frac{\partial G}{\partial t} = k_{p1} M_1 (s - 1) \frac{\partial G}{s_R} + k_{p2} M_2 (s_{B}^{\alpha - 1} s - 1) \frac{\partial G}{s_B} + k_{p3} \left( \frac{1}{s_B} \frac{\partial G}{s_R} - B \frac{\partial G}{s_B} - R \frac{\partial G}{s_B} \right) + k_{c} \left[ 2 \frac{1}{s_R} \left( \frac{\partial G}{s_R} \right)^2 - 2R \frac{\partial G}{s_R} \right]
\]

\[
+ 2k_d R \left( \frac{1}{s_R} - 1 \right) \frac{\partial G}{s_R} + k_{i3} R_0 \left( \frac{s_R}{s_B} - 1 \right) \frac{\partial G}{s_B}
\]

\[
+ k_{i1} R_0 M_1 s_R s + k_{i2} R_0 M_2 s_R s_B^{\alpha - 1} s
\]

\[
G_{t=0} = 0
\]

Transfers to polymer

Acrylate polymerizations are known to be affected by inter- and intra-molecular transfer reactions (the back-biting reaction) described by Eqs. (13) and (14) leading respectively to long and short branches which can be detected by C-13 NMR\(^{[52]}\) and tertiary radical sites \( R_T \) showing propagation rate constants \( k_p^T \) which are 2 to 3 powers of ten less than the main secondary sites:\(^{[53]}\)

- Intermolecular transfer to polymer:
  
  \[
P_{k,m,n,j} + P_{k',m',n',j'} \xrightarrow{k_{p}} P_{k-1,m,n,j} + P_{k',m',n',j'+1}
  \]

- Backbiting:
  
  \[
P_{k,m,n,j} \xrightarrow{k_{b}} P_{k-1,m,n,j+1}
  \]

- Propagations with tertiary radicals (e.g.):
  
  \[
P_{k,m,n,j} + P_{k',m',n',j'} \xrightarrow{k_{p}^T} P_{k+k'+1,m+m'-1,n+n',j+j'-1}
  \]

In order to take into account this more complex scheme, the count \( j \) of tertiary radical sites per molecule must be followed. It may also be useful to introduce the counts of long branches \( n_{lb} \) and short branches \( n_{sb} \), with related dummy Laplace variables \( s_{lb} \) and \( s_{sb} \). Thus \( P_{k,m,n,j,n_{lb},n_{sb}} \) becomes the ensemble of polymer molecules carrying the above described moieties (secondary radicals, pendant double bonds and repeating units), plus the count of tertiary free radical sites per molecule \( j \) with a related dummy Laplace variable \( s_T \) and the two kinds of branches. Taking into account the additional reactions in Eqs. (13)-(15) and neglecting the differences in termination rate constants between secondary and tertiary radical sites, Eq. (11) becomes now Eq. (16):

\[
\frac{\partial G}{\partial t} = \frac{\partial G}{s_R} \left[ k_{p1} M_1 (s - 1) + k_{p2} M_2 (s_{B}^{\alpha - 1} s - 1) \right] + k_{p3} \left( \frac{1}{s_B} \frac{\partial G}{s_R} - B \frac{\partial G}{s_B} - R \frac{\partial G}{s_B} \right) + k_c \left[ \frac{1}{s_R} \left( \frac{\partial G}{s_R} \right)^2 - 2R \frac{\partial G}{s_R} \right]
\]

\[
+ 2k_d R \left( \frac{1}{s_R} - 1 \right) \frac{\partial G}{s_R} + k_{i3} R_0 \left( \frac{s_R}{s_B} - 1 \right) \frac{\partial G}{s_B}
\]

\[
+ k_{i1} R_0 M_1 \frac{s_R}{s} + k_{i2} R_0 M_2 \frac{s_{B}^{\alpha - 1} s}{s}
\]

\[
+ k_{p} X \frac{\partial G}{\partial \log s} \left( \frac{1}{s_R} - 1 \right) + R \frac{\partial G}{\partial \log s} \left( \frac{s_T s_{lb}}{s} - 1 \right)
\]
\begin{align}
&+ k_{tc} \left[ \left( \frac{1}{s_R} \frac{\partial G}{\partial s_R} + \frac{1}{s_T} \frac{\partial G}{\partial s_T} \right)^2 - 2 \left( R + R_T \right) \left( \frac{\partial G}{\partial s_R} + \frac{\partial G}{\partial s_T} \right) \right] \\
&+ 2k_{td} \left( R + R_T \right) \left[ \left( \frac{1}{s_R} - 1 \right) \frac{\partial G}{\partial s_R} + \left( \frac{1}{s_T} - 1 \right) \frac{\partial G}{\partial s_T} \right] \\
&+ k_{l1} R_0 M_1 s_R s + k_{l2} R_0 M_2 s_R s_B^{g-1} + k_{l3} R_0 \left( \frac{s_R}{s_B} - 1 \right) \frac{\partial G}{\partial s_B} + k_{lb} \left( \frac{s_T s_{sb}}{s_R} - 1 \right) \frac{\partial G}{\partial s_R}
\end{align}

Note that the dummy Laplace variable \( s \) above concerns only the repeating units \( X \) containing a transfer site. The added long branching according to the aforementioned reaction should be taken into account when the amount of added crosslinker is very low and at high temperature and polymer concentration.\textsuperscript{[47–49]} Only a minor effect on the network structure of intramolecular chain transfer is also expected in a crosslinking process at high dilution and at relative low temperature.\textsuperscript{[47–49]} Owing to the absence in literature of measured kinetic parameters applicable to acrylic acid polymerizations according to this model, we will not carry out its discussion further in this work, although this is likely to be an important feature of these processes particularly at higher temperatures.

**Kinetic Parameters**

Despite the technical importance of poly(acrylic acid) and poly(methacrylic acid), scarce information concerning the kinetics of polymerization of these monomers in aqueous phase could be found in the literature up to about one decade ago. In the last years, this challenging problem was studied by a few research groups aiming at measuring propagation and termination rate coefficients of these monomers, specially in aqueous phase and considering different synthesis conditions (showing the effect of temperature, concentration, pH, ionic strength, etc). A short review concerning this issue is presented in Tables 1 to 4 where the correspondent bibliographic sources and main remarks concerning the measurements are also described.

Among other important issues, PLP-SEC measurements for water soluble monomers are difficult because SEC analysis can not be carried out using THF as eluent and this well established technique is not directly feasible. This issue can be partially circumvented by performing a prior modification of poly(acrylic acid) generating the related methyl ester which can be afterwards analyzed using the conventional PLP-SEC with THF as eluent. A similar procedure can be used with poly(methacrylic acid). Nevertheless, polymer modification can introduce non negligible errors in molecular weight measurements and so to rate coefficient estimates. A detailed discussion concerning this issue and other important features associated with measurements of rate coefficients of water soluble monomers can be found in the references presented in Tables 1 to 4.

To sum up, propagation and termination rate coefficients, besides temperature, also depend (at least) on:

- Monomer/solvent concentration ratio with non-ionic systems. A decrease of about one order of magnitude in \( k_p \) was observed upon increasing monomer concentration.
- Degree of ionization. At low monomer concentration, a decrease in \( k_p \) of about one order of magnitude was measured when the degree of ionization was changed from 0 to 100%.
- Opposite variations were observed when the two effects (monomer concentration and ionization) are present: a weaker drop of \( k_p \) with monomer concentration was found when the monomer is partially ionized. For a fully ionized monomer, \( k_p \) increases when monomer concentration is also increased.
Occurrence of Trommsdorff effect is another issue complicating the kinetics of these polymerization systems.

It is therefore difficult to establish a fully reliable set of kinetic parameters valid for the different conditions to be considered in the synthesis of water soluble homopolymers based on acrylic or methacrylic acids or related super-absorbent hydrogels. The aim of the present work is the development of a simple kinetic model being able to capture the essential features of SAP production considering particular operation conditions with an associated set of kinetic parameters. Conversely this method can be used to predict the influence of the change of operating conditions (change in temperature, pH, and so on, and the concomitant change in the kinetic parameters) on the dynamics of gelation. These aspects are illustrated in the next section where simulations performed with different sets of kinetic parameters are presented.

Table 1: Some reported values of the propagation rate constant ($k_p$) of acrylic acid (AA) in water.

<table>
<thead>
<tr>
<th>$k_p$ (L mol$^{-1}$ s$^{-1}$)</th>
<th>T (°C)</th>
<th>pH</th>
<th>[M]</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 500 to ~2000</td>
<td>Room</td>
<td>2.2-9.9</td>
<td>30%wt AA</td>
<td>Minimum at pH~6.5 $k_p$ ↓ with ↑ conversion $k_p$ ↓ with ↑ ionic strength</td>
<td>[5]</td>
</tr>
<tr>
<td>~ 30000 to ~60000</td>
<td>20</td>
<td>N.N.</td>
<td>0.83-0.90 mol/L</td>
<td>$k_p$ ↓ with ↑ [M]</td>
<td>[6]</td>
</tr>
<tr>
<td>~ 40000 to ~70000</td>
<td>25</td>
<td>N.N.</td>
<td>0.90-1.37 mol/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ln k_p = 16.30 \pm 0.29 - \frac{1337\pm85}{T(K)}$</td>
<td>2.3-25</td>
<td>N.N.</td>
<td>30%wt AA</td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>($k_p = 88926@20^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ln k_p = 16.00 \pm 0.39 - \frac{168\pm112}{T(K)}$</td>
<td>2.3-28.5</td>
<td>N.N.</td>
<td>40%wt AA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($k_p = 59264@20^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ln k_p = 20.40 \pm 0.60 - \frac{2022\pm171}{T(K)}$</td>
<td>2.5-19.5</td>
<td>N.N.</td>
<td>1%wt AA</td>
<td>2%, 5% AA also included</td>
<td>[8]</td>
</tr>
<tr>
<td>($k_p = 131804@20^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ln k_p = 20.00 \pm 0.64 - \frac{2313\pm179}{T(K)}$</td>
<td>2.8-24.7</td>
<td>N.N.</td>
<td>3%wt AA</td>
<td>Maximum $k_p$ at ~ 3% AA</td>
<td></td>
</tr>
<tr>
<td>($k_p = 163311@20^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td>-Solvent equality effects</td>
<td></td>
</tr>
<tr>
<td>$\ln k_p = 18.00 \pm 0.74 - \frac{1848\pm209}{T(K)}$</td>
<td>2.1-20.1</td>
<td>N.N.</td>
<td>10%wt AA</td>
<td>-Association of AA with polymer/radicals.</td>
<td></td>
</tr>
<tr>
<td>($k_p = 119711@20^\circ$C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>112000</td>
<td>6</td>
<td>10% N.</td>
<td>0.69 mol/L</td>
<td>[M] corresponds to ~5%wt AA. A model for the dependence of $k_p$ with neutralization is presented.</td>
<td>[9]</td>
</tr>
<tr>
<td>82000</td>
<td>6</td>
<td>50% N.</td>
<td>0.69 mol/L</td>
<td></td>
<td></td>
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<tr>
<td>16700</td>
<td>6</td>
<td>95% N.</td>
<td>0.69 mol/L</td>
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<td>59900</td>
<td>6</td>
<td>110% N.</td>
<td>0.69 mol/L</td>
<td></td>
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<tr>
<td>38667</td>
<td>55</td>
<td>65% N.</td>
<td>33% solids (AA) (~ 25%wt AA)</td>
<td>Estimated from experimental. data in Ref.[22]</td>
<td>[21]</td>
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<tr>
<td>650</td>
<td>23</td>
<td>7.9</td>
<td>1.2 mol/L AA</td>
<td></td>
<td>[19,20]</td>
</tr>
<tr>
<td>6600</td>
<td>23</td>
<td>11</td>
<td>1.2 mol/L AA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td>23</td>
<td>13.6</td>
<td>1.2 mol/L AA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>50</td>
<td>N.N.</td>
<td>Bulk</td>
<td></td>
<td>[18]</td>
</tr>
</tbody>
</table>

Without estimation of $k_p$, important kinetic data concerning the aqueous polymerization of AA or AA/TMPTA is presented in Refs.[4,22–24]. The effect of neutralization of AA and solids content (dilution related) was extensively studied in these works in the temperature range 55 to 85 °C.

Simulation Results Using the Proposed Kinetic Approach

Figure 1 depicts the predicted dynamics of the weight fraction of gel ($w_g$) and monomer conversion.
Table 2: Some reported values of the propagation rate constant \((k_p)\) of methacrylic acid (MAA) in water.

<table>
<thead>
<tr>
<th>(k_p) (L mol(^{-1}) s(^{-1}))</th>
<th>T (°C)</th>
<th>pH</th>
<th>[M]</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ln k_p = 14.36 \pm 0.47 - \frac{1899\pm145}{T[K]})</td>
<td>18-89</td>
<td>N.N.</td>
<td>15% wt MAA</td>
<td>(k_p \downarrow) with ↑[M]</td>
<td>[16]</td>
</tr>
<tr>
<td>((k_p = 3241 @ 20^\circ C))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\ln k_p = \ln 4.62 \times 10^6 - \frac{16.5\pm0.5}{10^{-3}RT[K]})</td>
<td>20-80</td>
<td>N.N.</td>
<td>5% wt MAA</td>
<td>15%, 30%, 60 % MAA also included</td>
<td>[10]</td>
</tr>
<tr>
<td>((k_p = 5284 @ 20^\circ C))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\ln k_p = \ln 0.63 \times 10^6 - \frac{15.3\pm1.1}{10^{-3}RT[K]})</td>
<td>23-80</td>
<td>N.N.</td>
<td>45% wt MAA</td>
<td>- Intermolecular interactions between (H_2O, MAA) and transition state structures</td>
<td></td>
</tr>
<tr>
<td>((k_p = 1179 @ 20^\circ C))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\ln k_p = \ln 0.38 \times 10^6 - \frac{16.1\pm1.6}{10^{-3}RT[K]})</td>
<td>25-60</td>
<td>N.N.</td>
<td>100% wt MAA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((k_p = 512 @ 20^\circ C))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\ln k_p = 14.3 \pm 0.2 - \frac{1801\pm43}{T[K]})</td>
<td>18-89</td>
<td>N.N.</td>
<td>15% wt MAA</td>
<td>IUPAC benchmark.</td>
<td>[14]</td>
</tr>
<tr>
<td>((k_p = 3475 @ 20^\circ C))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7700</td>
<td>50</td>
<td>N.N.</td>
<td>10% MAA</td>
<td>(k_p \downarrow) with ↑[M]</td>
<td>[16]</td>
</tr>
<tr>
<td>4900</td>
<td>50</td>
<td>N.N.</td>
<td>20% MAA</td>
<td>(k_p \uparrow) with ↑ conversion</td>
<td></td>
</tr>
<tr>
<td>3300</td>
<td>50</td>
<td>N.N.</td>
<td>30% MAA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6602</td>
<td>60</td>
<td>70% N.</td>
<td>5% MAA</td>
<td>Other measurements were performed. Variation of (k_p) with (T, [M]) and N. is available.</td>
<td>[17]</td>
</tr>
<tr>
<td>4229</td>
<td>60</td>
<td>70% N.</td>
<td>20% MAA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2702</td>
<td>60</td>
<td>70% N.</td>
<td>40% MAA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2477</td>
<td>80</td>
<td>100% N.</td>
<td>40% MAA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Increase of \(k_p\) with increasing MAA concentration for fully monomer ionization and \(T=40\) °C is reported in Ref.[12] Ionic and hydrogen-bonded intermolecular interactions between the activated state and the molecular environment can be at the source of the variation of \(k_p\) with monomer concentration and degree of ionization. Increase of \(k_p\) with conversion was observed in Ref.[13] \(R=8.314\) J mol\(^{-1}\) K\(^{-1}\)

Table 3: Some reported values of the termination rate constant \((k_t)\) of acrylic acid (AA) in water.

<table>
<thead>
<tr>
<th>(k_t) (L mol(^{-1}) s(^{-1}))</th>
<th>T (°C)</th>
<th>pH</th>
<th>[M]</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sim 3\times10^3) to (\sim 5\times10^4)</td>
<td>Room</td>
<td>2.2-9.9</td>
<td>30% wt AA</td>
<td>Minimum at pH~6.5 (k_t \downarrow) with conversion (k_t \downarrow) with ionic strength</td>
<td>[5]</td>
</tr>
<tr>
<td>(k_t \downarrow) at high conversion (~ 0.9) and pH=6.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\frac{k_p}{k_t} = 25) to 40</td>
<td>70</td>
<td>75% N.</td>
<td></td>
<td>Inverse Suspension</td>
<td>[25]</td>
</tr>
<tr>
<td>(3\times10^8)</td>
<td>55</td>
<td>65% N.</td>
<td>33% solids (AA) (~ 25% wt AA)</td>
<td>Estimated from experimental. data in Ref.[22]</td>
<td>[21]</td>
</tr>
</tbody>
</table>
Table 4: Some reported values of the termination rate constant ($k_t$) of methacrylic acid (MAA) in water.

<table>
<thead>
<tr>
<th>$k_t$ ($L \cdot mol^{-1} \cdot s^{-1}$)</th>
<th>T (°C)</th>
<th>pH</th>
<th>M</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease from $\sim 10^7$ to $\sim 1.8 \times 10^3$</td>
<td>50</td>
<td>N.N.</td>
<td>30%wt MAA</td>
<td>$k_t \downarrow$ with conversion, P=200 bar</td>
<td>[15]</td>
</tr>
<tr>
<td>Decrease from $\sim 6 \times 10^5$ to $\sim 10^5$</td>
<td>50</td>
<td>N.N.</td>
<td>60%wt MAA</td>
<td>$k_t \downarrow$ with conversion, P=200 bar</td>
<td></td>
</tr>
<tr>
<td>$k_t = \frac{1}{1/k_{t,SD} + \exp\left(C_{w,MAA}^0 / k_{t,TD} \right) + C_{RD} (1-p) k_p}$</td>
<td>N.N.</td>
<td>N.N.</td>
<td>$w_0^{MAA}$</td>
<td>Change of $k_t$ with conversion ($p$) for different initial weight fraction of MAA ($w_0^{MAA}$).</td>
<td></td>
</tr>
<tr>
<td>$k_{t,SD} = 7.9 \times 10^6$, $k_{t,TD} = 10^9$</td>
<td>N.N.</td>
<td>N.N.</td>
<td>$w_0^{MAA}$</td>
<td>Same expression for change of $k_t$ with $p$ used in Ref.[15] was considered.</td>
<td>[16]</td>
</tr>
<tr>
<td>$C_{\eta} = 39$, $C_{RD} = 77.5$</td>
<td>50</td>
<td>N.N.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{t,SD} = 3.53 \times 10^7 \pm 8.47 \times 10^5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{t,TD} = 2.79 \times 10^8 \pm 4.52 \times 10^8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{\eta} = 10.9 \pm 4.72$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{RD} = 517 \pm 212$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

($p$) during a batch SAP production. Simulations were carried out considering the synthesis with a trifunctional crosslinker (TMPTA used as case study) at an initial mole fraction in the monomer mixture $Y_C = 0.0025\%$ (around the lower limit used in practice)[4]. In these simulations three different values of the rate coefficient for the homopropagation of acrylic acid ($k_{pl}$) were considered, in a range that is plausible for this monomer in these particular conditions (see Table 1 and Ref.[21]). An initial mole ratio between initiator and monomer $Y_I = 0.3\%$, and a rate coefficient for initiator unimolecular decomposition $k_d = 8.4 \times 10^{-6} s^{-1}$ valid for V50 (2,2'-Azobis(2-methylpropionamidine)dihydrochloride) at $T = 50^\circ$ have been assumed. Initial volumetric fraction of acrylic acid in the aqueous phase was set as $v_{AA} = 15\%$. The reactivity ratio for acrylic acid/TMPTA was considered to be $r_1 = \frac{k_{pl}}{k_{pA}} = 0.77$ as previously measured for this chemical systems in similar conditions.[4] Note that, for the sake of simplicity, polymer radicals derived from the two monomers were not distinguished in the present analysis and by consequence $r_2 = \frac{k_{pA}}{k_{pI}} = 1/r_1$ corresponds to an ideal copolymerization (note that the reactivity ratio for TMPTA is very difficult to measure[4]). The reactivity of pendant double bonds is another parameter of a very difficult experimental estimation.[4] In simulations presented in Figure 1 the value $r^* = \frac{k_{pA}}{k_{pl}} = 1$ was chosen, which corresponds to an equal reactivity of PDB and acrylic acid (under these conditions, reactivity of PDBs is higher than individual double bonds of TMPTA: $r_{PDB} = \frac{k_{pA}}{k_{pA}/(k_{pA}/3)} = 2.31$). To the termination rate coefficient was assigned the value $k_t = 5 \times 10^7$ L $\cdot$ mol$^{-1}$ $\cdot$ s$^{-1}$ which is also in the range of the values considered in other works concerning also the kinetics of acrylic acid polymerization.[21] Equality between initiation and propagation rate coefficients ($k_{pj} = k_{tj}$) was also considered along this work. Results presented in Figure 1 show the important impact of the rate coefficient of acrylic acid (i.e. temperature, pH, concentration, ionic strength) in gel formation during super-absorbent hydrogels production. With higher values of $k_{pl}$, the primary chain length increases with concomitant higher gel formation.

Figure 2 shows the predicted dynamics of the weight average molecular weight ($\bar{M_w}$) for the the same systems described in Figure 1. The ability of the present method to predict polymer properties before and after gelation becomes here evident. Besides MWD and its averages, $z$-average radius of gyration ($\bar{O}$) state and sequences distributions can also be computed before and after gelation as before shown.[34–51]
The effect of the reactivity of pendant double bonds on the predicted dynamics of the weight fraction of gel ($w_g$) and monomer conversion ($p$) for batch SAP production using a trifunctional crosslinker is presented in Figure 3. The following parameters (according to the above discussion) were now fixed: $Y_C = 0.0025\%$, $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{s}^{-1}$, $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $k_{p1} = 20000 \text{L mol}^{-1} \text{s}^{-1}$, $k_i = 5 \times 10^7 \text{L mol}^{-1} \text{s}^{-1}$. Under these conditions, the reactivity of pendant double bonds (quantified by the parameter $r^*$ or equivalently by $r_{PDB}$) has a huge effect on the dynamics of gel formation. As expected, low gel content is predicted if the reactivity of PDBs is much lower than for the initial double bonds of the crosslinker (e.g. $r_{PDB} = 0.58$) and increases with the value of this parameter. Due to the low content of crosslinker in the polymerization system, the overall monomer conversion is almost insensitive to this parameter. Simulations like those presented in Figure 3 can be used to estimate the reactivity of PDBs using experimental measurements of the dynamics of gel formation.

The effect of the initial mole fraction of crosslinker on the dynamics of the weight fraction of gel is illustrated in Figure 4. This parameter can be readily used to manipulate the properties of the final products, as depicted in that figure. Simulations for $Y_C$ ranging from the lower limit used in practice (around 0.0025%) to ten times this value show the change of $w_g$ from around 0.4 to 1. Remaining parameters fixed in these simulations are described in the legend of Figure 4. Operation with the higher limit of $Y_C$ (around 0.25%) is illustrated in Figure 5. Under these conditions, gelation is predicted to occur within some hundredths of seconds and the weight fraction of gel in the polymer rises very fast to around 1. However, in practice, polymerization must be prolonged in order to reach high monomer conversion.

The ability to numerical calculate the characteristics of Eqs (11-12) is a crucial step for the prediction of gel properties using generating functions of population balance equations, as here proposed. Development of very sharp numerical boundary layers is a special feature of these problems making very difficult the treatment of the associated two point boundary value problems (TPBVP), as discussed before.$^{35-38}$ These aspects are illustrated for the present chemical systems in Figure 6 and Figure 7. Note that the solution of this kind of problems in the context of this theory plays a role equivalent to the calculation of the extinction probabilities in the framework of the Theory of the Branching Processes, as discussed in the next section.

Another possible way to manipulate the dynamics of gelation is the choice of the functionality of the crosslinker, as depicted in Figure 8. Three different synthesis processes, correspondent to the use of crosslinkers with different functionalities (2, 3 and 4) by considering N,N'-methylenebisacrylamide ($\alpha = 2$), trimethylolpropane triacrylate ($\alpha = 3$) and tetraallyloxyethane ($\alpha = 4$) as case studies, were simulated. As expected, in the same conditions, the use of a crosslinker with higher functionality generates a higher amount of gel at a much higher pace. Substitution effects changing the reactivities of the different pendant double bonds of the crosslinker and possible low solubility of the crosslinker in the aqueous phase are some issues complicating the simple analysis here performed.

**Comparison between the Kinetic Approach and the Theory of the Branching Process**

Three main classes of theoretical approaches are used to describe the formation and to predict the structure of super-absorbent networks:$^2,54-58$

- Statistical Models
- Kinetic Models
- Kinetic Gelation Simulations
Figure 1: Predicted dynamics of the weight fraction of gel ($w_g$) and monomer conversion ($p$) in batch SAP production using a trifunctional crosslinker with $Y_C = 0.0025\%$. Different values of the rate coefficient for the homopropagation of acrylic acid ($k_{p1}$) were considered. Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$ ($T = 50^\circ \text{C}$ for V50), $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 1$ ($\tau_{PD} = 2.31$), $k_l = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.

Figure 2: Predicted dynamics of the weight average molecular weight ($\langle M \rangle_w$) in batch SAP production using a trifunctional crosslinker with $Y_C = 0.0025\%$. Different values of the rate coefficient for the homopropagation of acrylic acid ($k_{p1}$) were considered. Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$ ($T = 50^\circ \text{C}$ for V50), $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 1$ ($\tau_{PD} = 2.31$), $k_l = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.
Figure 3: Predicted dynamics of the weight fraction of gel ($w_g$) and monomer conversion ($p$) in batch SAP production using a trifunctional crosslinker with $Y_C = 0.0025\%$. Different values of the reactivity of pendant double bonds were considered, as quantified by the parameter $r^*$ (or $r_{PDB}$). Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$ ($T = 50^\circ \text{C}$ for V50), $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $k_{p1} = 20000 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_t = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.

Figure 4: Predicted dynamics of the weight fraction of gel ($w_g$) in batch SAP production considering different initial mole fraction of trifunctional crosslinker ($Y_C$). Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$ ($T = 50^\circ \text{C}$ for V50), $v_{AA} = 15\%$, $k_{p1} = 20000 \text{ L mol}^{-1} \text{ s}^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 0.433$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.
Figure 5: Predicted time evolution of monomer conversion and weight gel fraction during acrylic acid/triacylate copolymerization with $Y_C = 0.25\%$. Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6}$ s$^{-1}$ ($T = 50^\circ$ for V50), $v_{AA} = 15\%$, $k_{p1} = 30000$ L mol$^{-1}$ s$^{-1}$, $r_1 = 1/3$, $r_2 = 3$, $r^* = 1$ ($r_{PDB} = 1$), $k_I = 5 \times 10^7$ L mol$^{-1}$ s$^{-1}$.

Figure 6: Numerical solution of the characteristics (vector $s$) correspondent to the SAP synthesis using the conditions described in Figure 5. For illustration purposes the chosen polymerization time was $t_f = 203.6$ s. Solution of the problem of the characteristics is a crucial step for the prediction of gel properties using generating functions of Population Balance Equations.
Figure 7: Numerical solution of the characteristics (vector $G$) correspondent to the SAP synthesis using the conditions described in Figure 5. For illustration purposes the chosen polymerization time was $t_f = 203.6$ s. Solution of the problem of the characteristics is a crucial step for the prediction of gel properties using generating functions of Population Balance Equations.

Figure 8: Predicted dynamics of the weight fraction of gel ($w_g$) in batch SAP production considering three different synthesis processes correspondent to the use of three crosslinkers with different functionalities (bi-, tri- and tetrafunctional, considering N,N’-methylenebisacrylamide ($\alpha = 2$), trimethylolpropane triacrylate ($\alpha = 3$) and tetraallyloxyethane ($\alpha = 4$) as case studies). Parameters considered in the simulations: $Y_C = 0.005\%$, $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6}$ s$^{-1}$ ($T = 50^\circ$ for V50), $v_{AA} = 15\%$, $k_{pl} = 20000$ L mol$^{-1}$ s$^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = r_2/\alpha$ ($r_{PDB} = 1$), $k_l = 5 \times 10^7$ L mol$^{-1}$ s$^{-1}$. 
Statistical models provide important details concerning the structure/properties of the gel (a crucial information in the field of super-absorbent materials) but face enormous difficulties if history (time) dependent effects must be accounted for in the calculations. This issue can be overcome by this kinetic approach which is nevertheless unable to include spatial effects with have a particular importance in highly crosslinked networks (the mean-field approximation is inherent to statistical and kinetic approaches). It is usually accepted that simple kinetic models cannot offer a deep description of gel structure, namely when compared with statistical methods. Kinetic gelation theories are able to deal with spatial heterogeneities resulting from topological constraints occurring with highly crosslinked networks but on the other hand present deficiencies with lightly crosslinked systems due to the failure to account for monomer and polymer mobility. A comprehensive comparison between these different approaches can be found in a paper by A.B. Kinney and A.B. Scranton.\footnote{Kinney, A.B.; Scranton, A.B. J. Polym. Sci. Polym. Phys. Ed. 1978, 16, 1757.}

Formation of super-absorbent gels are kinetically controlled irreversible process (non-equilibrium kinetics) involving very small amounts of crosslinker and therefore generating lightly crosslinked materials. Advantages of kinetic modeling are therefore fulfilled for these polymerization systems. It is here shown that important differences between predictions obtained using this kinetic approach and a simplified statistical method (the theory of the branching process) are observed because the history of network formation is not preserved with the latter approach. Note that results above presented shown that it is actually possible to predict gel properties using a kinetic modeling.

Calculations using TBP are based on the introduction of link probability generating functions (PGF). Expressions for these PGF have already been written for chemical systems similar to the one here considered, with an analysis restricted to a bifunctional crosslinker:\footnote{Kinney, A.B.; Scranton, A.B. J. Polym. Sci. Polym. Phys. Ed. 1978, 16, 1757.}

\[
F_{01}(s) = 1 - x + x \left\{ 1 - \gamma + \gamma \left[ (1 - Y_D)s_1^- + Y_D s_2^- \right] \right\} \times \left\{ (1 - \gamma) \left[ 1 - \alpha_{tc} + \alpha_{tc} \left[ (1 - Y_D)s_1^- + Y_D s_2^- \right] \right] + \gamma \left[ (1 - Y_D)s_1^+ + Y_D s_2^+ \right] \right\} \tag{17}
\]

\[
F_{02}(s) = F_{01}^4(s) \tag{18}
\]

with \(F_{01}(s)\) representing the link probability generating function for the zero-th generation corresponding to the vinyl monomer and \(F_{02}(s)\) depicting the similar function for the divinyl monomer (crosslinker). The conversion of double bonds is denoted by \(x\), the probability that a growing radical add a new monomer unit instead of terminating by \(\gamma\) (\(\gamma = \text{probability of propagation} = \frac{R_p}{R_p + R_t + R_{tr}}\)) and the fraction of initial double bonds belonging to the divinyl monomer by \(Y_D\). The fraction of termination by combination is here represented by \(\alpha_{tc}\). In the dummy variables of the generating functions subscripts and superscripts are used \((s_i^\pm)\). The lower index identifies the kind of bond to which the root is linked in the next generation (1 for monovinyl monomer and 2 for crosslinker). The superscript + is used when a bond is issued to the next generation in the direction of propagation while – identify a bond issued in the opposite direction. The distinction between the directions of reaction is needed when both mechanisms of termination (combination and disproportionation) are considered.\footnote{Kinney, A.B.; Scranton, A.B. J. Polym. Sci. Polym. Phys. Ed. 1978, 16, 1757.}


Link probability generating functions for generations higher than zero should account for the four statistically different kinds of bonds that can be formed with the next generations.\footnote{Kinney, A.B.; Scranton, A.B. J. Polym. Sci. Polym. Phys. Ed. 1978, 16, 1757.}

These PGF are:

\[
F_1^-(s) = 1 - \gamma + \gamma \left[ (1 - Y_D)s_1^- + Y_D s_2^- \right] \tag{19}
\]
\[ F_1^+(s) = (1 - \gamma) \left[ 1 - \alpha tc + \alpha tc \left[ (1 - Y_D)s_1^- + Y_D s_2^- \right] + \gamma \left[ (1 - Y_D)s_1^+ + Y_D s_2^+ \right] \right] \]  

\[ F_2^-(s) = F_1^-(s) F_01(s) \]  

\[ F_2^+(s) = F_1^+(s) F_01(s) \]

Extinction probabilities (probability that a bond has no connection to the infinite network) are crucial to calculate the gel properties and for this system they are the smallest positive roots of the following non-linear system with four unknowns:

\[ \nu_i^j = F_i^j(v) \quad i = 1, 2 \quad j = -, + \]

After solving this problem, the weight fraction of gel is calculated using the following equation:

\[ w_g = 1 - w_{AA} F_01(v) - w_C F_{02}(v) \]

with \( w_{AA} \) and \( w_C \) representing the weight fraction of monofunctional monomer and crosslinker, respectively, in the initial monomer mixture.

A numerical algorithm to obtain the solutions of the expressions above presented was implemented in order to be able to compare the predictions of TBP with those of the kinetic modeling developed in this work, as shown in Figure 9. Besides the initial mole fraction of double bonds belonging to the crosslinker (which is related with \( Y_C \) by \( Y_D = \frac{2Y_C}{1+Y_C} \)), parameters needed in TBP simulations are the fraction of termination by coupling (fixed in \( \alpha tc = 1 \) as in kinetic simulations) and the probability of propagation, \( \gamma \). Calculations have shown that, besides \( Y_C \), the parameter \( \gamma \) also has a strong effect on the gelation process. The simulation results presented in that same figure were performed with \( \gamma = 0.9999 \), which is an average value correspondent to kinetic calculations. Note that this parameter is not strictly constant during the polymerization.

The huge differences between predictions presented in Figure 9 illustrate the dissimilarities between the two approaches. As the present processes are kinetic controlled, the direct application of the classical TBP seems to be incorrect and more elaborated models based on this theory must be developed in order to be valid.\(^{[58]}\)

**Comparison with Experimental Results**

The aqueous solution homopolymerization of acrylic acid was performed in batch reactor in order to have some insight concerning the kinetics of polymerization of this monomer in conditions similar to those used to synthesize SAP materials. These polymerizations were in-line monitored using a FTIR-ATR probe which allows the measurement of monomer conversion. The same experimental set-up, a reactor with maximum capacity of 2.5 L for which a detailed description has been presented elsewhere,\(^{[45-50]}\) was used to synthesize SAP materials based on acrylic acid/trimethylolpropane triacrylate copolymerization. In order to extend the process to the post-gelation period, maintaining good agitation and heat dissipation conditions, these experiments were performed in inverse suspension. In the continuous phase, toluene and/or cyclohexane were used as organic diluents and Span 60 and/or ethylcellulose as oil-suspending agents. The ratio oil-phase/water-phase in the reactor was 5/1 and the agitation speed of 400 rpm. Volume fraction of acrylic acid in the aqueous phase was \( \nu_A = 15\% \) and a similar composition was used in the solution homopolymerization of acrylic acid.
Figure 9: Comparison between the predictions of the Theory of Branching Process (TBB) and the proposed kinetic approach for the weight fraction of gel in the copolymerization of a vinyl monomer with a bifunctional crosslinker (two initial compositions were considered using acrylic acid + N,N’-methylenebisacrylamide as case study). Parameters considered in the simulations with TBP: $\alpha_{lc} = 1$, $\gamma = 0.9999$. Parameters considered in the simulations with the Kinetic Approach: $Y_t = 0.3\%$, $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$ ($T = 50^\circ \text{C}$ for V50), $v_{AA} = 15\%$, $k_{pl} = 20000 \text{ L mol}^{-1} \text{ s}^{-1}$, $r_1 = 0.5$, $r_2 = 1/r_1 = 2$, $r^* = r_2/2 = 1$ ($r_{PB} = 1$), $k_l = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ (with $\alpha_{lc} = 1$).

In Figure 10 are compared the experimental results of representative experiments performed in this context with predictions obtained using the kinetic model developed in this work. Only a noisy trend of the monomer conversion could be obtained with the in-line FTIR-ATR monitoring technique. This noise is probably due to the effect of the reactor agitation which causes the misalignment of the FTIR-ATR apparatus. Nevertheless, the experimental trend for monomer conversion presented in Figure 10 seems to confirm the reasonableness of the kinetics used. Dynamics of the weight fraction of gel was also experimentally measured by collecting from the reactor samples at different polymerization time. Insoluble (gel) mass fraction in these samples was later measured and, in all samples, a fraction of gel close to 1 was observed, as presented in Figure 10. In the synthesis of SAP materials performed in this work, the initial mole fraction of crosslinker (TMPTA) used is close to the upper limit considered for practical applications ($Y_C = 0.25\%$). In these conditions a very fast gelation with gel weight fraction $w_g$ close to 1 after around one minute of polymerization is predicted by the kinetic model and this behavior was experimentally confirmed. Main features of this polymerization systems could therefore be captured by the simple kinetic model here considered. Additional experimental work with a much lower initial mole fraction of crosslinker (and also different kinds of crosslinkers) should be performed in order to confirm the good foundations of this theory. Estimates of the reactivity of pendant double bonds of the crosslinkers can also eventually be obtained by comparison of these new experimental results with model predictions.

**Conclusion**

A simple kinetic model in the framework of population balance equations of generating functions was developed and applied to simulate the synthesis of super-absorbent hydrogels. Predictions concerning the dependence of the dynamics of gelation on the following kinetic/operation parameters were
Figure 10: Comparison between experimentally observed and predicted dynamics of monomer conversion and weight fraction of gel during the homopolymerization of acrylic acid and its crosslinking with trimethylolpropane triacrylate at $T = 50^\circ$ C. Homopolymerization of acrylic acid was performed in water solution with $v_{AA} = 15\%$ and $Y_l = 0.1\%$. Crosslinking copolymerization was performed in inverse suspension considering similar composition of the aqueous phase and $Y_G = 0.25\%$. Other parameters considered in the simulations: $k_d = 8.4 \times 10^{-6}$ s$^{-1}$, $k_{p1} = 30000$ L mol$^{-1}$ s$^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 0.433 (r_{PDB} = 1)$, $k_t = 5 \times 10^7$ L mol$^{-1}$ s$^{-1}$.

presented:

- Propagation rate coefficient of monovinyl monomer (acrylic acid).
- Reactivity ratio of the pendant double bonds of the crosslinker.
- Initial mole fraction of the crosslinker.
- Functionality of the crosslinker (bi-, tri- and tetrafunctional were considered).

The Theory of the Branching Processes (TBP) was also used to predict the evolution of the weight fraction of gel during the polymerization and important differences between the predictions of the two approaches were found. Usefulness of the proposed kinetic approach becomes evident because TBP is not strictly valid under kinetic controlled conditions such as those correspondent to superabsorbent hydrogels production. Comparison between predictions of the proposed kinetic method and measurements performed in the acrylic acid/trimethylolpropane triacrylate copolymerization show that this simple model is able to capture the main features of this polymerization system.

Future developments of this kinetic approach should allow the inclusion of intramolecular cyclizations in the kinetic schemes in order to quantify its impact on product properties. Nevertheless (in contrast to styrene/divinylbenzene copolymers and similar), the impact of intramolecular cyclizations in superabsorbent hydrogels production should be weak due to the very low content of crosslinker used and the high values of the primary chain lengths involved. Important developments should also be carried out in order to predict the elastic properties of the gel using a kinetic approach. Improvements of the method proposed by the authors in the early nineties[34] should be performed in order to achieve this goal.
Notation

- $[AA]$ - acrylic acid concentration.
- $B$ - total concentration of polymer pendant double bonds.
- $[C]$ - crosslinker concentration.
- $f$ - initiator decomposition efficiency.
- $F_{01}$ - link probability generating function for the zero-th generation corresponding to the vinyl monomer (in the framework of the TBP).
- $F_{02}$ - link probability generating function for the zero-th generation corresponding to the divinyl monomer (in the framework of the TBP).
- $F^{-}_1$ and $F^{+}_1$ - link probability generating functions for generations higher than zero (in the framework of the TBP), associated with monovinyl monomer.
- $F^{-}_2$ and $F^{+}_2$ - link probability generating functions for generations higher than zero (in the framework of the TBP), associated with divinyl monomer.
- $G(s_R, s_B, s)$ - generating function of the distribution of mole concentrations of polymer species according to their counts of radicals, PDB and repeating units.
- $I$ or $[I]$ - concentration of initiator.
- $M_k$ or $[M]_k$ - concentration of monomer or macromonomer of the kind $k$.
- $[M]$ - global monomer concentration.
- $\bar{M}_w$ - weight-average relative molecular mass.
- $n_{lb}$ - count of long branches in polymer molecules.
- $n_{sb}$ - count of short branches in polymer molecules.
- $k_{bb}$ - rate coefficient of the unimolecular backbiting reaction.
- $k_d$ - rate coefficient of the unimolecular thermal initiator decomposition.
- $k_{ij}$ - rate coefficient of the initiation of monomer or macromonomer of the kind $j$.
- $k_p$ - homopropagation rate coefficient.
- $k_{pj}$ - rate coefficient of the propagation of monomer or macromonomer of the kind $j$.
- $k_{ij}^{(f)}$ - rate coefficient of the propagation of tertiary radicals with a monomer or macromonomer of the kind $j$.
- $k_{ij}^{(g)}$ - rate coefficient of the global radical termination.
- $k_{ij}^{(c)}$ - rate coefficient of the radical termination by combination.
- $k_{ij}^{(d)}$ - rate coefficient of the radical termination by disproportionation.
- $k_{ij}^{(P)}$ - rate coefficient of the intermolecular chain transfer to polymer.
- $p$ - monomer conversion.
- $P(k, m, n)$ - concentration of polymer molecules bearing $k$ radicals, $m$ PDB and $n$ repeating units.
- $r_i$ - polymerization reactivity ratio (ideal polymerization).
- $r_1 = k_{p1}/k_{p2}$ - reactivity ratio of the monovinyl monomer.
- $r_2 = k_{p2}/k_{p1}$ - reactivity ratio of the crosslinker ($r_2 = 1/r_1$, ideal copolymerization considered in this work).
- $r^* = k_{p3}/k_{p1}$ - reactivity ratio of PDB as compared to the double bonds of the monovinyl monomer; with equal reactivity of PDB: $r^* = (k_{p2}/\alpha)/k_{p1} = r_2/\alpha$.
- $r_{PDB} = k_{p3}/(k_{p2}/\alpha) = \alpha r^* r_1$ - reactivity ratio of PDB comparatively to the double bonds of the crosslinker monomer; for ideal copolymerization and equal reactivity of PDB: $r_{PDB} = \alpha (r_2/\alpha)r_1 = 1$.
- $R_0$ - concentration of primary radicals.
- $R$ - total concentration of polymer radicals.
- $R_p$ - rate of propagation.
$R_t$ - rate of termination by coupling and/or disproportionation.

$R_T$ - concentration of tertiary radical sites.

$R_{tr}$ - rate of termination by chain transfer.

$s$ - vector of dummy variables of generating functions (see eg. Equation (17)).

$s$ - Laplace parameter of the generating function associated with the count of the number of repeating units.

$s_B$ - Laplace parameter of the generating function associated with the count of the number of PDB.

$s_R$ - Laplace parameter of the generating function associated with the count of the number of polymer radicals.

$s_{lb}$ - Laplace parameter of the generating function associated with the count of long branches in polymer molecules.

$s_{sb}$ - Laplace parameter of the generating function associated with the count of short branches in polymer molecules.

$s_T$ - Laplace parameter of the generating function associated with the count of tertiary radical sites in polymer molecules.

$s_j^d$ - dummy variables of the generating functions used in the framework of the TBP, which are associated with bonds of different kinds.

$t$ - time.

$T$ - temperature.

$v$ - vector of extinction probabilities defined by Equation (23).

$v_{AA} = \frac{v_{AA}}{v_{AA} + v_W}$ - initial volume fraction of monovinyl monomer (acrylic acid) using water content as reference.

$v_j^d$ - extinction probability associated with bonds of the kind $s_j^d$.

$w_g$ - weight fraction of gel.

$w_{AA}$ - initial weight fraction of monovinyl monomer in monomer mixture.

$w_C$ - initial weight fraction of divinyl monomer in monomer mixture.

$x$ - double bonds conversion.

$X$ - concentration of repeating units containing a transfer to polymer site.

$Y_C = \frac{[C]}{[C] + [AA]}$ - mole fraction of crosslinker in the initial monomers mixture.

$Y_D = \frac{2Y_C}{1 + Y_C}$ - mole fraction of initial double bonds belonging to the crosslinker.

$Y_I = \frac{I}{[AA]}$ - initial mole ratio of initiator comparatively to monovinyl monomer.

**Greek variables**

$\alpha$ - crosslinker functionality.

$\alpha_{le}$ - relative rate of radical termination by combination.

$\alpha_{id}$ - relative rate of radical termination by disproportionation.

$\gamma = \frac{R_p}{R_p + R_t + R_{tr}}$ - propagation probability.

**Subscripts**

$n$ - number average.

$w$ - weight average.

$z$ - z-average.

$o$ - initial.
Abbreviations

AA - acrylic acid.
AM - acrylamide.
ATR - Attenuated Total Reflection.
ATRP - atom transfer radical polymerization.
CRP - controlled radical polymerization.
FRP - free radical polymerization.
FTIR - Fourier Transform Infra-Red.
GF - generating function.
MMA - methacrylic acid.
MBA - N,N'-methylenebisacrylamide.
MWD - molecular weight distribution.
NMRP - nitroxide-mediated radical polymerization.
PBE - population balance equation.
PDB - pendent double bond.
PGF - Probability generating function.
PLP - pulsed laser polymerization.
SAP - super-absorbent polymers.
SEC - size exclusion chromatography.
Span 60 - sorbitan monostearate.
TAO - tetraallyloxyethane.
TBP - theory of the branching processes.
TMPTA - trimethylolpropane triacrylate.
TPBVP - two point boundary value problem.
THF - tetrahydrofuran.
V50 - 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (thermal initiator).

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| Keywords:         | gels, kinetics (polym.), modeling |
Kinetic Modeling of the Suspension Copolymerization of Styrene/Divinylbenzene with Gel Formation

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Summary: Experimental and theoretical studies concerning the suspension copolymerization of styrene with divinylbenzene are reported. Experiments were carried out in a batch stirred reactor, at 1.2 dm³ scale, and extended beyond gelation in order to synthesize insoluble material. In order to obtain real time information concerning the building process of such materials, these polymerizations were In-line monitored using a FTIR-ATR immersion probe. Polymer samples collected before and after gelation were Off-line characterized using a SEC/RI/MALLS system allowing the measurement of monomer conversion, average molecular weights, MWD and also the z-average radius of gyration. The weight fraction of insoluble material (gel) was measured for samples with different reaction times. The experimental program has included the study of the influence of key polymerization parameters on the dynamics of gelation and some properties of the resulting networks, namely the initial mole fraction of crosslinker and the initial proportions between monomers and inert diluent. Variable n-heptane/toluene mixtures were used as inert diluent. These experimental observations were complemented with theoretical studies using a general kinetic approach allowing the prediction of MWD and z-average radius of gyration before and also after gelation. Comparison of the experimental measurements with these predictions is being exploited to develop modeling tools useful for the design of operating conditions allowing the improvement of the performance of the final products.

Keywords: gels; kinetics (polym.); modeling

Introduction

A few insoluble polymer networks can be used as advanced materials due to the sensitivity of their microscopic properties to external stimulations. These polymers are often classified as stimuli responsive or smart polymers. Applications of these kinds of materials in biomedicine or bionanotechnology is nowadays a subject attracting considerable research efforts. Huge swelling ratios are also observed in many gels which is explored to produce superabsorbent materials. Formation of macroporous structures in polymer networks also makes possible their use as particles and membranes for many separation processes.

Styrene/divinylbenzene gels (S/DVB) are well-known for that purpose, usually after chemical derivatizing, such as for the ubiquitous ion-exchange resins. The formation of insoluble networks based on these monomers was studied by Staudinger and Huseman¹ at the very beginning of the development of polymer science.¹² Three stages can be identified in the time-line concerning the improvement of the production of S/DVB gel beads:

- Studies on the manipulation of the swelling ratio of the particles by adjusting the amount of DVB in the polymerization system.

- Improved materials with a macroporous structure were obtained by suspension polymerization of S/DVB in the presence of an inert diluent. Phase separation during this process is the main source for the formation of pores in the resulting materials, even in the dry state.¹
Macrosyneresis (macroscale) and microsyneresis (microscale) phase separation during the crosslinking process depend on the synthesis conditions. This can be exploited in order to design the porous structures of the materials. Specially important in this context are the works of K. Dusek and co-workers (see [2] and references therein), which have lead to major contributions to the knowledge of the macroporous networks based on the crosslinking of vinyl/divinyl monomers.

- The study of the formation of elastically ineffective crosslinks due to cyclization and multiple crosslinks, existence of trapped radicals and the role of pendant vinyl groups, among others.[2]

Nowadays, these issues are still being actively investigated by different research groups.

As above described, several important research works concerning the synthesis of gel beads through the conventional radical polymerization of S/DVB were carried out along the last decades. An extensive list of works dealing with this subject can be found in the review by O. Okay.[2] The present work is focused in the dynamics of formation of such gel beads in a batch reactor, with the goal of obtaining new insights in the polymer reaction engineering of such processes. The experimental program has covered the synthesis and characterization of polymer networks, both in the pre- and post-gelation periods. Final materials were also characterized by SEM. These experiments are complemented with kinetic modeling studies in the framework of a general theory which can be used before and after gelation.[7–16] Recent studies of this research team concerning the modeling of FRP and CRP of vinyl/divinyl monomers leading to soluble materials[17–20] are now extended with experiments on the post-gelation period here reported for the first time.

Experimental
Materials
Styrene of 99% purity stabilized with 0.005% w/w 4-tert-butylcatechol, commercial grade of divinylbenzene of 80% purity stabilized with 0.1% w/w 4-tert-butylcatechol, AIBN of 98% purity, toluene of 99.7% purity and n-heptane of 99% purity were purchased from Sigma Aldrich and used as received. Commercial DVB used in the present work is a mixture of isomers: 56.2% m-divinylbenzene, 24.2% p-divinylbenzene plus 19.6% of ethylvinylbenzene. Poly(vinyl alcohol) (PVA) with \(M_w\) of 85000-124000, 87-89% hydrolyzed, also from Sigma-Aldrich was used as a dispersant. Suspensions were prepared using deionized water.

Suspension Polymerizations
A detailed description of the experimental set-up used in this work can be found elsewhere.[17] An excess of aqueous phase, containing PVA, was previously prepared by dissolving the appropriated amount of surfactant in deionized water, at room temperature, using a magnetic stirrer. The concentration of PVA in aqueous phase was set using the total monomer weight as reference. In all experiments 0.09% of PVA by total monomer weight was used, similarly to the reported in related works.[3] The desired quantity of aqueous phase (around 913 mL) was charged to the reactor and brought to the polymerization temperature (60 °C) with the mechanical stirrer working at 400 rpm. The polymerization medium was purged with argon at a flow rate of 40 cm³/min before and during the operation. The organic phase was prepared by forming a solution involving the required amounts of chemicals, namely: styrene, divinylbenzene, AIBN, n-heptane and toluene, as detailed in Table 1. This solution was prepared immediately before the polymerization, at room temperature, in order to minimize the thermal decomposition of AIBN. When the temperature set-point for the aqueous phase was reached, the proper amount of organic phase (around 287 mL) was charged to the reactor defining the start of the polymerization. Product samples were collected from the reactor at prescribed
polymerization times. All polymerizations were stopped after 6 hours of reaction.

**In-line FTIR-ATR monitoring**

These polymerizations were *in-line* monitored using an Attenuated Total Reflection (ATR) immersion probe coupled to a Fourier Transform Infra-Red (FTIR) spectrophotometer. The following instruments were used: Axiom Analytical immersion probe, model DRR207 (ZnSe element, spectral cutoff at 600 cm$^{-1}$, maximum pressure and temperature operation 60 bar and 280 °C, respectively) and an ABB Bomem Fourier Transform Infra-Red (FTIR) spectrophotometer, model FTLA2000-104. The probe and the spectrophotometer are connected by a three arms light guide and an ABB Bomem, Mercury-Cadmium Telluride (MCT) detector (model D10B), cooled with liquid nitrogen, equips the spectrometer in order to increase the sensitivity of the analysis. These ATR-FTIR measurements were performed using the spectrum of air taken at room temperature as the reference background being the optical system continuously flushed with argon. A resolution of 4 cm$^{-1}$ was used for the spectra that were taken over the full MIR range from 600 cm$^{-1}$ to 4000 cm$^{-1}$. Each spectrum was calculated from 128 interferograms.

**SEC/RI/MALLS products characterization**

Samples collected from the reactor at different polymerization times, including aqueous and organic phases, were collected in a decanting ampoule containing a large quantity cold water in order to stop the reaction. After decanting, most of the organic phase was diluted in a large amount of methanol in order to precipitate the polymer (soluble and insoluble fractions). For samples collected before gelation, a small amount of organic phase was directly diluted in THF and analysed by SEC/RI/MALLS. With samples containing gel, the soluble fraction analyzed by SEC/RI/MALLS was obtained after the immersion of the global material in THF, during one day, as described below. The same instruments described in our past works$^{17–20}$ were here used for this purpose. Time evolution of polymer molecular weight and $z$-average radius of gyration of the soluble fraction were thus measured, before and after gelation, for the set of experiments performed.

**Measurement of the weight fraction of gel**

Polymer samples (soluble and insoluble fractions) obtained by precipitation in methanol were filtrated and dried in vacuum overnight. Afterwards, they were washed several times (during one week) in large amounts of THF in order to collect the insoluble network. The time evolution of the insoluble weight fraction of polymer (gel) during the polymerizations was thus measured.

**Swelling ratio measurements**

For each run, the final suspension, correspondent to 6 hours of polymerization, was processed as above described in order to isolate the produced gel beads. The swelling ratio of the dried gel beads was estimated by weighing around 1 g of material which was afterwards immersed in a large amount of THF. After 24 hours, the swollen gel beads were weighed again and the ratio between swollen and dried weights was used to estimate the swelling ratio of these materials.

**Scanning Electron Microscopy (SEM)**

The dried gel beads above described were also analyzed by Scanning Electron Microscopy (SEM) in the Centro de Microscopia da Universidade do Porto (CEMUP). Th influence of the synthesis conditions in the structure of the produced materials (e.g. macroporous formation) could thus be assessed.

**Kinetic Modeling**

The kinetic scheme considered in the modeling studies here performed is described by Equations (1)-
Table 1: Description of a set of experiments performed in the study of the suspension copolymerization of Styrene/divinylbenzene at 60°C.

<table>
<thead>
<tr>
<th>Run</th>
<th>( V_T ) (dm³)</th>
<th>( f_{OR} )</th>
<th>( f_M )</th>
<th>( f_{DVB} )</th>
<th>( 100 \times f_I )</th>
<th>( f_{HEP} )</th>
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<tr>
<td>1</td>
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<td>0.24</td>
<td>0.5</td>
<td>0.2</td>
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<td>0.00</td>
</tr>
<tr>
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<td>0.24</td>
<td>0.5</td>
<td>0.2</td>
<td>1.25</td>
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</tr>
<tr>
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<td>0.5</td>
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<td>0.1</td>
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<td>0.5</td>
<td>0.1</td>
<td>1.25</td>
<td>0.50</td>
</tr>
</tbody>
</table>

(12) with I representing the initiator (AIBN), \( R_0 \) the primary radicals and \( M_1, M_2 \) and \( M_3 \) the three monomers (styrene, \( m \)-divinylbenzene and \( p \)-divinylbenzene, respectively). Polymer molecules bearing \( k \) radicals, \( m \) pendant double bonds (PDB) and \( n \) repeating units or monomer moieties (degree of polymerization) are represented by \( P_{k,m,n} \); the counts of the repeating units derived from the three monomers have been lumped. This simple description of the polymer chains structure is used in order to keep this presentation within a manageable size. The general kinetic approach used in the present work\(^{7-16}\) is able to accommodate more complex descriptions of non-linear polymerization systems, namely the simultaneous consideration of several different kinds of polymer radicals and other reaction sites, encompassing also the detailed prediction of the molecular architecture of polymer chains. These distinctive features of this theoretical approach were recently applied to the analysis of different non-linear polymerization systems involving styrenic, acrylate and methacrylate monomers and in the framework of classical and controlled radical polymerization, namely NMRP and ATRP\(^{17-20}\)

Despite the simplicity of the kinetic scheme here considered, it is shown below that the most important features of the present polymerization system can be captured by the simulations performed. The lack of explicit consideration of intramolecular cyclization reactions (mostly propagations and terminations) is the major drawback of this kinetic scheme, as also discussed below.

AIBN decomposition:

\[
I \xrightarrow{k_i} 2fR_0 \tag{1}
\]

Styrene initiation:

\[
R_0 + M_1 \xrightarrow{k_{11}} P_{1,0,1} \tag{2}
\]

\( m \)-divinylbenzene initiation:

\[
R_0 + M_2 \xrightarrow{k_{21}} P_{1,1,1} \tag{3}
\]

\( p \)-divinylbenzene initiation:

\[
R_0 + M_3 \xrightarrow{k_{31}} P_{1,1,1} \tag{4}
\]

PDB initiation:

\[
R_0 + P_{k,m,n} \xrightarrow{k_{14}} P_{k+1,m-1,n} \tag{5}
\]

Styrene propagation:

\[
P_{k,m,n} + M_1 \xrightarrow{k_{01}} P_{k,m,n+1} \tag{6}
\]

\( m \)-divinylbenzene propagation:

\[
P_{k,m,n} + M_2 \xrightarrow{k_{02}} P_{k,m+1,n+1} \tag{7}
\]
$p$-divinylbenzene propagation:

\[ P_{k,m,n} + M_3 \xrightarrow{k_{p3}} P_{k,m+1,n+1} \]  \hspace{1cm} (8)

PDB propagation (crosslinking):

\[ P_{k,m,n} + P'_{k',m',n'} \xrightarrow{k_{p4}} P_{k+k',m+m'-1,n+n'} \]  \hspace{1cm} (9)

Chain transfer to solvent:

\[ P_{k,m,n} + S \xrightarrow{k_s} P_{k-1,m,n} + R_0 \]  \hspace{1cm} (10)

Termination by combination:

\[ P_{k,m,n} + P'_{k',m',n'} \xrightarrow{k_{tc}} P_{k+k'-2,m+m'-2,n+n'} \]  \hspace{1cm} (11)

Termination by dismutation:

\[ P_{k,m,n} + P'_{k',m',n'} \xrightarrow{k_{td}} P_{k-1,m,n} + P'_{k'-1,m,n} \]  \hspace{1cm} (12)

Most of the kinetic parameters used in the simulations have been collected from other research works, namely for what concerns the decomposition rate of AIBN at 60 °C, \( k_d = 9.6 \times 10^{-6} \text{ s}^{-1} \) with \( f=0.6 \) and styrene polymerization, \( k_{p1} = 340 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \), of which detailed bibliographic sources have been presented elsewhere.\(^{[17]}\) Specially important in the present context are the reactivity ratios of \( m- \) and \( p- \) divinylbenzene with styrene, and the values \( r_{12} = k_{p1}/k_{p2} = 0.43 \), \( r_{13} = k_{p1}/k_{p3} = 0.24 \), previously measured for these pairs were also here considered.\(^{[21]}\) Chain transfer to solvent and termination were quantified using the same kinetic parameters before used for the solution polymerization of the same chemical system: \( C_S = k_S/k_{p1} = 0.12 \times 10^{-4} \), \( k_{p1}/\sqrt{k_t} = 0.035 \) (dm\(^3\)mol\(^{-1}\)s\(^{-1}\))\(^{1/2} \), \( \alpha_{tc} = k_{tc}/k_t = 0.95.\(^{[17]}\) The rate constants of initiation reactions were considered to be equal to the correspondent propagation steps: \( k_{ij} \approx k_{pj} \). The rate constant for the propagation of pendant double bonds (\( k_{pd} \)) was used as the single fitting parameter because, in the absence of intramolecular cyclizations, the crosslinking is the major mechanism governing the properties of the polymer networks, as it has been shown in previous works.\(^{[17-20]}\)

Applying the principles of the general kinetic approach we have been developing\(^{[7-16]}\) with the kinetic scheme described by Equations (1)-(12), the Population Balance Equation (PBE) in terms of Generating Functions (GF) below written is obtained:

\[ \frac{\partial G}{\partial t} = k_{p1}M_1(s-1) \frac{\partial G}{\partial s_R} + k_{p2}M_2(s_{BS}-1) \frac{\partial G}{\partial s_B} + k_{p3}M_3(s_{BS}-1) \frac{\partial G}{\partial s_R} + k_{p1} \left( \frac{1}{s_B} \frac{\partial G}{\partial s_R} - B \frac{\partial G}{\partial s_B} - R \frac{\partial G}{\partial s_R} \right) + k_{tc} \left[ \frac{1}{s_R^2} \left( \frac{\partial G}{\partial s_R} \right)^2 - 2R \frac{\partial G}{\partial s_R} \right] + 2k_{td}R \left( \frac{1}{s_R} - 1 \right) \frac{\partial G}{\partial s_R} + k_S S \left( \frac{1}{s_R} - 1 \right) \frac{\partial G}{\partial s_B} + k_{I1}R_0M_1s_{RS} + k_{I2}R_0M_2s_{RS} + k_{I3}R_0M_3s_{RS} + k_{I4}R_0 \left( \frac{s_R}{s_B} - 1 \right) \frac{\partial G}{\partial s_B} \]  \hspace{1cm} (13)

The generating function of mole concentrations of polymer species with respect to the counts of chemical groups is here defined by:

\[ G(s_R, s_B, s) = \sum_{k=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P(k, m, n) s_R^k s_B^m s^n \]  \hspace{1cm} (14)
Laplace parameters of the GF of polymer population named $s_R$, $s_B$ and $s$ are associated with the counts of radicals in polymer molecules ($k$), of PDB ($m$) and repeating units ($n$), respectively. In PBE Equation (13), $R$ and $B$ represent the total concentration of polymer radicals and pendant double bonds, respectively. As no polymer exists in the system when the reaction starts, the initial condition of Equation (13) is:

$$G_{h=0} = 0$$  \(15\)

Solution of PBEs of the kind of Equation (13) can be obtained by the method of the characteristics.[7–16] Before gelation, the problem reduces to a system of ordinary differential equations with initial conditions (IVP) and gelation point is located through the divergence of the solution of this IVP problem. After gelation, two-point boundary value problems (TPBVP) must be solved in order to obtain the properties of soluble and non-soluble fractions. The techniques described elsewhere[7–16] were used to obtain the results presented below.

**Results and Discussion**

Figure 1 shows the predicted and observed time evolution of the weight average molecular weight ($\bar{M}_w$) during the suspension copolymerization of S/DVB at 60 °C (see Table 1). Experimental values were measured before and after gelation by SEC/RI/MALLS, as above described. The effect of the mole fraction of DVB in the initial monomer mixture ($f_{DV}$=10 and 20%) on the dynamics of $\bar{M}_w$ in batch reactor is clearly put into evidence, namely for what concerns the delay in gelation time. This dynamics was also predicted before and after gelation using the aforementioned calculation techniques. A good agreement between measurements and predictions can be obtained if the reactivity of PDB is used as a fitting parameter. In this context the following reactivity ratios of PDB comparatively to styrene were estimated: $C_{pDB} = k_{p1}/k_{p2} = 0.555$ for $f_{DV}=20\%$ and $C_{pDB} = 0.07$ for $f_{DV}=10\%$. These unrealistic low values obtained by the fitting procedure are a consequence of neglecting intramolecular cyclizations, which are a competitive kinetic mechanism decreasing crosslinking efficiency, as previously shown.[17–20] The slightly different values of the reactivity ratios of PDB estimated for $f_{DV}=20\%$ and $f_{DV}=10\%$ are also probably a result of the different impact of intramolecular cyclizations which, for the same dilution, should increase with the initial mole fraction of DVB. Simple attempts to include intramolecular cyclizations in the framework of the present kinetic approach have already been performed[12] but a lot more additional theoretical developments are needed in this context. Despite this limitation, results presented in Figure 1 show that some important features of gel formation can be captured by the simple kinetic here considered.

Figure 2 shows a comparison between the predicted and measured time evolution of the weight fraction of gel ($w_g$) during the suspension copolymerization of S/DVB. In this case, high deviations between the measured values and predictions are observed for both initial compositions. The same kinetic parameters resulting from the fitting studies described in Figure 1 were used in the calculation of $w_g$ considering a non-ideal crosslinking process ($C_{pDB} < 1$). The ideal behavior correspondent to $C_{pDB} = 1$ (ideal crosslinking in the absence of intramolecular cyclizations) is also presented in Figure 2. Experimental measurements are confined between the predictions correspondent to these two simulation systems, confirming the modeling limitations before described (intramolecular cyclizations not included). In fact, the produced gels were several times washed in THF and only small amounts of sol are expected to be entrapped in the final products given the not so large molecular weight. Therefore, deficient gel washing can not explain the huge differences observed. Formation of microgel and inhomogeneous gel structures along polymerization can be at the source of such discrepancies, with intramolecular cyclizations playing a major role. These phenomena were not taken in to account in the present modeling studies (complex developments are needed) and the predicted...
Figure 1: Predicted and measured time evolution of the weight average molecular weight ($M_w$) during the suspension copolymerization of S/DVB at 60 °C. The effect of the mole fraction of DVB in the initial monomer mixture ($f_{DVB}$=10 and 20%) over the dynamics of $M_w$ in batch reactor is observed. This dynamics was predicted and measured before and also after gelation.

gel fraction is underestimated for the non-ideal system and overestimated for the ideal crosslinking behavior. In the presence of very high contents of DVB (10 and 20%) and due to the relative small length of primary chains (namely when compared with non-linear acrylic systems), intramolecular cyclizations phenomena are likely to occur in the formation of S/DVB networks. It is a relevant result from this work the finding that a simplistic model assuming reduced pendant bond reactivity is unable to predict both sol average molecular weight or radius of gyration and also sol fraction.

The influence of the synthesis conditions in the end-use properties of S/DVB gel beads was extensively studied in the last decades.[3–6] Experimental studies concerning the effects of initiator concentration, temperature, stirring speed, concentration of crosslinking agent, diluent concentration and thermodynamic affinity are reported in these works. The influence of these parameters in the gel beads appearance, namely concerning fusion and coalescence was also studied.[3] The morphology of the products obtained in the present research was also studied by Scanning Electron Microscopy (SEM) as shown in Figure 3, where the micrographs of S/DVB gel beads synthesized in different conditions (see Table 1) are presented. Comparison of Figures 3(a) and (b) puts into evidence the effect of the DVB content in bead formation. Higher DVB amounts seems to promote the formation of such structures, avoiding the synthesis of clustered and fused products.[3] The effect of the thermodynamic affinity of the diluents[4] with the copolymer can be observed by comparison of Figures 3(c) and (d) where runs with very different $n$-heptane/toluene ratios are analyzed. Gel beads prepared with a large fraction of bad solvent in the diluent ($n$-heptane in the present work) show very rough surfaces as observed in Figure 3(d). When the thermodynamic affinity of the diluent increases (higher proportion of toluene) gel beads produced have a smoother surface, characteristic of non-porous materials, as observed in Figure 3(c). Other details of the morphology of such materials can be observed in Figures 3(e) and (f) where a cavity and a macroporous structures are showed by SEM.
Figure 2: Predicted and measured time evolution of the weight fraction of gel ($w_g$) during the suspension copolymerization of S/DVB at 60 °C. The effect of the molar fraction of DVB in the initial monomer mixture ($f_{DVB}=10$ and 20%) over the dynamics of $w_g$ is observed. Experimental measurements are confined between the predictions correspondent to the ideal crosslinking ($C_{PDB} = 1$, absence of intramolecular cyclizations) and the non-ideal behavior ($C_{PDB} < 1$) considering the same reactivity ratios obtained from the fitting of average molecular weight.

Figure 4 depicts the measured swelling ratio for S/DVB gel beads synthesized using different proportions of n-heptane/toluene in the organic phase and different initial mole fractions of DVB in the monomer mixture, as detailed in Table 1. Note that the amount of DVB in the initial mixture and the diluent composition plays an important role in this end-use property of the gel beads. With the materials synthesized in the present work, a maximum swelling ratio around 11 was measured for gel beads produced with $f_{DVB} = 10\%$ and $f_{HEP} = 0.5$. The dependency of the swelling ratio of S/DVB gel beads on diluent, styrene and DVB concentrations used in the synthesis process has also been previously reported in other research works.[3]

In-Line FTIR-ATR monitoring of vinyl monomer polymerization has been investigated in the last years driven by the need for improvement in product quality. The establishment of feed policies of monomers in semi-batch co-terpolymerizations, with an expected impact on the molecular architecture of linear polymers is such an application of In-Line FTIR-ATR monitoring. The determination of the reactivity ratios for different groups of vinyl monomers is also an important application of this technique. Several works reporting the In-Line FTIR-ATR monitoring of homo-, co-, terpolymerizations using different operational conditions, namely emulsion and solution processes, can be found in the literature.[22–30] Suspension crosslinking copolymerizations performed in the present work were also monitored by In-Line FTIR-ATR, as previously described. Typical results obtained with that technique are presented in Figure 5. Our main goal with such in-line monitoring is to obtain real-time information concerning the building process of the synthesized non-linear materials. The reactivity ratios of the involved vinyl monomers, divinyl monomers and PDBs are a valuable information in such context, as above discussed. Results presented in Figure 5 show the occurrence of a phe-
nomenon similar to "catastrophic coagulation" reported for instance in the in-line monitoring of butyl acrylate/vinyl acetate emulsion copolymerization.[28] With emulsion processes, this phenomenon is due to unstable polymerization conditions which seems also to occur at the gel point for the suspension crosslinking polymerization performed in the present work. For the operation conditions used in the present work, gelation occurs at low monomer conversion (around 10% with $f_{DVB} = 10\%$, as estimated by SEC/RI/MALLS) and by consequence "catastrophic coagulation" precluded the obtainment by In-Line FTIR-ATR of reliable quantitative information concerning the reactivity of the different monomers/pendant double bonds involved. Besides "catastrophic coagulation", is possible that the spectra observed with In-Line FTIR-ATR can also be a result of the coating of the ATR crystal during the polymerizations. Further experiments with different operation conditions (e.g. changing the kind of stabilizer, its concentration and agitation speed) must be performed to elucidate this issue with suspension polymerization. On other hand, In-Line FTIR-ATR monitoring of emulsion polymerization of vinyl monomers is reported in previous research works without apparent occurrence of coating of the ATR crystal.[22,28] However, given its very different initiation mechanism and likely occurrence of space separation of radicals, emulsion polymerization is very different from the suspension polymerization operation here studied and major modeling changes would have to be discussed. Use of confocal Raman spectroscopy (with a higher penetration depth) should overcome the coating of the ATR crystal in both circumstances (suspension/emulsion), but this requires major changes on the experimental set-up here used.

Conclusion
Suspension copolymerization of styrene/divinylbenzene with gel formation was experimentally studied by performing a set of different runs in a batch reactor. The dynamics of product molecular properties was measured by SEC/RI/MALLS. These reactions were also In-Line monitored by FTIR-ATR. The produced gel beads were analyzed by scanning electron microscopy (SEM) and the impact on the morphology of these materials of parameters such as the proportion of bad/good solvents in the diluent was studied. The dynamics of the gel fraction in batch reactor was followed and the swelling ratio of the resulting gel beads was also quantified. A general kinetic approach allowing predictions before and also after gelation was used in the modeling studies of this non-linear copolymerization system.

It was shown that the main features of this crosslinking process can be captured by the kinetic model developed using as a single fitting parameter the relative reactivity of the pendant double bonds. Under these circumstances, with the same set of kinetic parameters, it is possible obtain good predictions of the dynamics of $M_w$ before and also after gelation, which is a major contribution of this work for the polymer reaction engineering of such processes. Nevertheless, the unrealistic low values of reactivity estimated (around 6% of styrene reactivity) should be mostly an effect of neglecting intramolecular cyclizations in the model.

SEM characterization of these gel beads confirmed the formation of macroporous structures if appropriated synthesis conditions are used, namely concerning the thermodynamic affinity of the diluent mixture. In the present work, different proportions of n-heptane/toluene (bad/good solvents) were considered for this purpose. Measured swelling ratios of these gel beads are also in line with previous works and a maximum swelling ratio of 11 was here observed.

In-Line FTIR-ATR monitoring of the crosslinking process here performed showed the occurrence of "catastrophic coagulation" at the gel point which precluded the intended in-line measurement of the building parameters of the polymer networks. A new design operating conditions should be carried
Figure 3: (a) SEM of S/DVB gel beads obtained in run 3 with magnification of 250 ×. (b) Gel beads of run 6 with magnification of 250 ×. (c) Run 1 with magnification of 50000 ×. (d) Run 5 with magnification of 50000 ×. (e) Run 2 with magnification of 2500 ×. (f) Run 3 with magnification of 20000 ×.
Figure 4: Measured swelling ratio for S/DVB gel beads synthesized using different proportions of \textit{n}-heptane/toluene in the organic phase and different initial mole fraction of DVB in the monomer mixture (see Table 1). The amount of DVB in the initial mixture and the diluent composition plays an important role in this end use property of the gel beads.

Figure 5: FTIR-ATR spectra observed in the \textit{in-line} monitoring of the suspension copolymerization of S/DVB using \textit{n}-heptane and toluene as diluents of the organic phase. The figure shows spectra with wavelength number from 700 to 1800 cm\textsuperscript{-1}. Changes in the spectrum due to "\textit{catastrophic coagulation}" are also here visible.
out in order to avoid this phenomenon so that this spectroscopic technique can be fully exploited.

The present work paves the way to further studies concerning the design and production of gel beads by means of different radical polymerization systems, namely nitroxide mediated radical polymerization (NMRP) of styrene/divinylbenzene. The exploitation of the distinctive features of the general kinetic approach here considered to improve properties of gels produced by CRP is an expected outcome of this research line. These new studies should go in parallel with the theoretical developments allowing the proper consideration of intramolecular cyclizations in the kinetic schemes, an issue which has once again been clearly identified in this work. Ongoing studies concerning the kinetic prediction of elastic properties of gels should also be specially useful in this context.

Notation

$B$ - total concentration of polymer pendant double bonds.
$C_S = k_S/k_p$ - reactivity ratio for chain transfer to solvent.
$C_{PDB} = k_{pA}/k_{p1}$ - reactivity ratio for polymerization of PDB.
$f$ - initiator decomposition efficiency.
$f_{DBB}$ - initial mole fraction of divinylbenzene in the total monomer content.
$f_{HEP}$ - volumetric fraction of $n$-heptane in the diluent mixture ($n$-heptane + toluene).
$f_1$ - initial mole ratio between initiator and total amount of monomers double bonds.
$f_M$ - initial volumetric fraction of monomers (styrene + divinylbenzene) in the organic phase (styrene + divinylbenzene + $n$-heptane + toluene).
$f_{OR}$ - initial volumetric fraction of organic phase in the total liquid content (organic phase + water).
$G(s_R, s_B, s)$ - generating function of the distribution of mole concentrations of polymer species according to their counts of radicals, PDB and repeating units.
$I$ - concentration of initiator.
$M_k$ - concentration of monomer or macromonomer of the kind $k$.
$\bar{M}_w$ - weight-average relative molecular mass.
$k_d$ - rate coefficient of the unimolecular thermal initiator decomposition.
$k_{ij}$ - rate coefficient of the initiation of monomer or macromonomer of the kind $j$.
$k_{pj}$ - rate coefficient of the propagation of monomer or macromonomer of the kind $j$.
$k_S$ - rate coefficient of the chain transfer to solvent.
$k_t$ - rate coefficient of the global radical termination.
$k_{tc}$ - rate coefficient of the radical termination by combination.
$k_{td}$ - rate coefficient of the radical termination by disproportionation.
$P(k, m, n)$ - concentration of polymer molecules bearing $k$ radicals, $m$ PDB and $n$ repeating units.
$r_{ij}$ - polymerization reactivity ratio.
$R_0$ - concentration of primary radicals.
$R$ - total concentration of polymer radicals.
$s$ - Laplace parameter of the generating function associated with the count of the number of repeating units.
$s_{PDB}$ - Laplace parameter of the generating function associated with the count of the number of PDB radicals.
t - time.
$T$ - temperature.
$V_T$ - total liquid volume in the reactor, including water and organic phase.
$w_g$ - weight fraction of gel.
Greek Characters

\( \alpha_{tc} \) - relative rate of radical termination by combination.
\( \alpha_{td} \) - relative rate of radical termination by disproportionation.

Subscripts

n - number average.
w - weight average.
z - z-average.
0 - initial.

Abbreviations

AIBN - 2,2'-azobis(2-methylpropionitrile).
ATR - Attenuated Total Reflection.
ATRP - atom transfer radical polymerization.
CRP - controlled radical polymerization.
DMF - N,N-dimethylformamide.
DVB - divinylbenzene.
FRP - free radical polymerization.
FTIR - Fourier Transform Infra-Red.
GF - generating function.
IVP - initial value problem.
\( M_k \) - monomer or macromonomer of the kind k.
MCT - mercury-cadmium-telluride detector.
MIR - medium Infra-Red.
MWD - molecular weight distribution.
NMRRP - nitroxide-mediated radical polymerization.
ODE - ordinary differential equation.
PBE - population balance equation.
PDB - pendent double bond.
PDE - partial differential equation.
PVA - poly(vinyl alcohol).
\( P_{k,m,n} \) - polymer molecule bearing \( k \) radicals, \( m \) PDB and \( n \) repeating units.
R0 - primary radical.
S - styrene.
SEC/RI/MALLS - size exclusion chromatography with refractive index and multi-angle laser light scattering detection.
SEM - scanning electron microscopy.
TPBVP - two point boundary value problem.

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