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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

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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[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).[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 trough 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.[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.[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.[33]

The complex kinetics inherent to the aqueous homopolymerization of acrylic monomers and non-linear copolymerization acrylic/polyvinyl monomers has been studied is 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 super-absorbent 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,[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.[45–50] Still more recently, the dynamics of gel production in the suspension copolymerization of styrene/divinylbenzene[51] was experimentally and theoretically studied.

Modeling capabilities of this kinetic approach are here illustrated considering the synthesis of super-absorbent 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[45–50] 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 dissimilitudes 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 Equation (1)–(9). A generic crosslinker with functionality α (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 superabsorbents. A linear copolymerization results if a chemical system including a second monomer with a single active double bond ($\alpha = 1$) is considered.

In Equation (1)–(9), $P_{k,m,n}$ represent the ensemble of polymer molecules bearing k radicals, m pendent 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:

$$I \xrightarrow{k_d} 2fR_0 \tag{1}$$

- 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:

$$\mathrm{R}_0 + \mathrm{P}_{\mathrm{k,m,n}} \xrightarrow{k_{I3}} \mathrm{P}_{\mathrm{k+1,m-1,n}} \tag{4}$$

- AA Propagation:

$$\mathrm{P}_{\mathrm{k,m,n}} + \mathrm{AA} \xrightarrow{k_{p1}} \mathrm{P}_{\mathrm{k,m,n+1}} \tag{5}$$

- Crosslinker Propagation:

$$\mathrm{P}_{\mathrm{k,m,n}} + \mathrm{C} \xrightarrow{k_{p2}} \mathrm{P}_{\mathrm{k,m+\alpha-1,n+1}} \tag{6}$$

- PDB Propagation (crosslinking):

$$\mathrm{P}_{\mathrm{k,m,n}} + \mathrm{P}_{\mathrm{k',m',n'}} \xrightarrow{k_{p3}} \mathrm{P}_{\mathrm{k+k',m+m'-1,n+n'}} \tag{7}$$

- Termination by combination:

$$\mathrm{P}_{\mathrm{k,m,n}} + \mathrm{P}_{\mathrm{k',m',n'}} \xrightarrow{k_{tc}} \mathrm{P}_{\mathrm{k+k'-2,m+m',n+n'}} \tag{8}$$

- Termination by disproportionation:

$$\begin{aligned}\mathrm{P}_{\mathrm{k,m,n}} + \mathrm{P}_{\mathrm{k',m',n'}} &\xrightarrow{k_{td}} \mathrm{P}_{\mathrm{k-1,m,n}} \\ &+ \mathrm{P}_{\mathrm{k'-1,m,n}}\end{aligned} \tag{9}$$

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[34–44] uses generating functions (GF) of polymer populations, that for the present case study transforms the ensemble of polymer molecules $\mathrm{P}_{\mathrm{k,m,n}}$ in a 3-dimensional GF:

$$G(s_R, s_B, s) = \sum_{k=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P(k,m,n) s_R^k s_B^m s^n \tag{10}$$

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 copolymerization. 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:

$$\begin{aligned}\frac{\partial G}{\partial t} = {} & k_{p1} M_1 (s-1) \frac{\partial G}{\partial \log s_R} \\ & + k_{p2} M_2 (s_B^{\alpha-1} s - 1) \frac{\partial G}{\partial \log s_R} \\ & + k_{p3} \left(\frac{1}{s_B} \frac{\partial G}{\partial \log s_R} \frac{\partial G}{\partial \log s_B} \right. \\ & \left. - B \frac{\partial G}{\partial \log s_R} - R \frac{\partial G}{\partial \log s_B} \right) \\ & + k_{tc} \left[\frac{1}{s_R^2} \left(\frac{\partial G}{\partial \log s_R} \right)^2 - 2R \frac{\partial G}{\partial \log s_R} \right] \\ & + 2 k_{td} R \left(\frac{1}{s_R} - 1 \right) \frac{\partial G}{\partial \log s_R} \\ & + k_{I1} R_0 M_1 s_R s + k_{I2} R_0 M_2 s_R s_B^{\alpha-1} s \\ & + k_{I3} R_0 \left(\frac{s_R}{s_B} - 1 \right) \frac{\partial G}{\partial \log s_B}\end{aligned} \tag{11}$$

$$G_{|t=0} = 0 \tag{12}$$

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:

$$\mathrm{P}_{\mathrm{k,m,n,j}} + \mathrm{P}_{\mathrm{k',m',n',j'}} \xrightarrow{k_{tP}} \mathrm{P}_{\mathrm{k-1,m,n,j}} + \mathrm{P}_{\mathrm{k',m',n',j'+1}} \tag{13}$$

- Backbiting:

$$\mathrm{P}_{\mathrm{k,m,n,j}} \xrightarrow{k_{bb}} \mathrm{P}_{\mathrm{k-1,m,n,j+1}} \tag{14}$$

- Propagations with tertiary radicals (e.g.):

$$\mathrm{P}_{\mathrm{k,m,n,j}} + \mathrm{P}_{\mathrm{k',m',n',j'}} \xrightarrow{k_p^T} \mathrm{P}_{\mathrm{k+k'+1,m+m'-1,n+n',j+j'-1}} \tag{15}$$

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, pendent 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 Equation (13)–(15) and neglecting the differences in termination rate constants between secondary and tertiary radical sites, Equation (11) becomes now Equation (16):

$$\begin{aligned}
\frac{\partial G}{\partial t} = {} & \frac{\partial G}{\partial \log s_R}\left[k_{p1}M_1(s-1) + k_{p2}M_2(s_B^{\alpha-1}s-1)\right] \\
& + k_{p3}\left(\frac{1}{s_B}\frac{\partial G}{\partial \log s_R}\frac{\partial G}{\partial \log s_B} - B\frac{\partial G}{\partial \log s_R} - R\frac{\partial G}{\partial \log s_B}\right) \\
& + \frac{\partial G}{\partial \log s_T}\left[k_{p1}^T M_1\left(\frac{s_R s}{s_T}-1\right) + k_{p2}^T M_2\left(\frac{s_B^{\alpha-1}s_R s}{s_T}-1\right)\right] \\
& + k_{p3}^T\left(\frac{s_R}{s_T s_B}\frac{\partial G}{\partial \log s_T}\frac{\partial G}{\partial \log s_B} - B\frac{\partial G}{\partial \log s_T} - R_T\frac{\partial G}{\partial \log s_B}\right) \\
& + k_{tP}\left[X\frac{\partial G}{\partial \log s_R}\left(\frac{1}{s_R}-1\right) + R\frac{\partial G}{\partial \log s}\left(\frac{s_T s_{lb}}{s}-1\right)\right] \\
& + k_{tc}\left[\left(\frac{1}{s_R}\frac{\partial G}{\partial \log s_R} + \frac{1}{s_T}\frac{\partial G}{\partial s_T}\right)^2 - 2(R+R_T)\left(\frac{\partial G}{\partial \log s_R} + \frac{\partial G}{\partial \log s_T}\right)\right] \\
& + 2k_{td}(R+R_T)\left[\left(\frac{1}{s_R}-1\right)\frac{\partial G}{\partial \log s_R} + \left(\frac{1}{s_T}-1\right)\frac{\partial G}{\partial \log s_T}\right] \\
& + k_{I1}R_0M_1s_Rs + k_{I2}R_0M_2s_Rs_B^{\alpha-1}s + k_{I3}R_0\left(\frac{s_R}{s_B}-1\right)\frac{\partial G}{\partial \log s_B} \\
& + k_{bb}\left(\frac{s_T s_{sb}}{s_R}-1\right)\frac{\partial G}{\partial \log s_R}
\end{aligned} \tag{16}$$

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.[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.[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 Table 1 to 4 where the correspondent bibliographic sources and main remarks concerning the measurements are also described.

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

k_p (L mol^{-1} s^{-1})	T (°C)	pH	[M]	Remarks	Ref.
~500 to ~2000	Room	2.2-9.9	30%wt AA	Minimum at pH~6.5 $k_p \downarrow$ with $\uparrow$ conversion $k_p \downarrow$ with $\uparrow$ ionic strength	[5]
~30000 to ~60000	20	N.N.	0.83–0.90 mol/L	$k_p \downarrow$ with $\uparrow$ [M]	[6]
~40000 to ~70000	25	N.N.	0.90–1.37 mol/L		
$\ln k_p = 16.30 \pm 0.29 - \frac{1437 \pm 83}{T(K)}$ ($k_p = 88926$@20°C)	2.3–25	N.N.	30%wt AA		[7]
$\ln k_p = 16.00 \pm 0.39 - \frac{1468 \pm 112}{T(K)}$ ($k_p = 59264$@20°C)	2.3–28.5	N.N.	40%wt AA	$k_p \downarrow$ with $\uparrow$ [M]	
$\ln k_p = 20.40 \pm 0.60 - \frac{2523 \pm 171}{T(K)}$ ($k_p = 131804$@20°C)	2.5–19.5	N.N.	1%wt AA	2%, 5% AA also included	[8]
$\ln k_p = 20.00 \pm 0.64 - \frac{2343 \pm 179}{T(K)}$ ($k_p = 163311$@20°C)	2.8–24.7	N.N.	3%wt AA	Maximum k_p at ~3% AA	
$\ln k_p = 18.00 \pm 0.74 - \frac{1848 \pm 209}{T(K)}$ ($k_p = 119711$@20°C)	2.1–20.1	N.N.	10%wt AA	-Solvent equality effects -Association of AA with polymer/radicals.	
112000	6	10% N.	0.69 mol/L	[M] corresponds to ~5%wt AA. A model for the dependence of k_p with neutralization is presented.	[9]
82200	6	50% N.	0.69 mol/L		
16700	6	95% N.	0.69 mol/L		
59900	6	110% N.	0.69 mol/L		
38667	55	65% N.	33% solids (AA) (~25%wt AA)	Estimated from experimental. data in Ref. [22]	[21]
650	23	7.9	1.2 mol/L AA		[19,20]
6600	23	11	1.2 mol/L AA		
2500	23	13.6	1.2 mol/L AA		
5000	50	N.N.	Bulk		[18]

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. R = 8.314 J mol^{-1} K^{-1}.

Table 2.
Some reported values of the propagation rate constant (k_p) of methacrylic acid (MAA) in water.

k_p(L mol^{-1} s^{-1})	T (°C)	pH	[M]	Remarks	Ref.
$\ln k_p = 14.36 \pm 0.47 - \frac{1839 \pm 145}{T(K)}$ $(k_p = 3241@20°C)$	18–89	N.N.	15%wt MAA	$k_p \downarrow$ with $\uparrow$ [M]	[6]
$\ln k_p = \ln 4.62 \times 10^6 - \frac{16.5 \pm 0.5}{10^{-3}RT(K)}$ $(k_p = 5284@20°C)$	20–80	N.N.	5%wt MAA	15%, 30%, 60% MAA also included	[10]
$\ln k_p = \ln 0.63 \times 10^6 - \frac{15.3 \pm 1.1}{10^{-3}RT(K)}$ $(k_p = 1179@20°C)$	23–80	N.N.	45%wt MAA	$k_p \downarrow$ with $\uparrow$ [M] -Intermolecular interactions between H_2O, MAA and transition state structures	
$\ln k_p = \ln 0.38 \times 10^6 - \frac{16.1 \pm 1.6}{10^{-3}RT(K)}$ $(k_p = 512@20°C)$	25–60	N.N.	100%wt MAA		
$\ln k_p = 14.3 \pm 0.2 - \frac{1801 \pm 43}{T(K)}$ $(k_p = 3475@20°C)$	18–89	N.N.	15%wt MAA	IUPAC benchmark.	[14]
7700	50	N.N.	10% MAA		[16]
4900	50	N.N.	20% MAA	$k_p \downarrow$ with $\uparrow$ [M]	
3300	50	N.N.	30% MAA	$k_p \downarrow$ with $\uparrow$ conversion	
6602	60	70% N.	5% MAA	Other measurements were performed. Variation of k_p with T, [M] and N. is available.	[17]
4229	60	70% N.	20% MAA		
2702	60	70% N.	40% MAA		
2477	80	100% N.	40% MAA		

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] $R = 8.314\,J\,mol^{-1}\,K^{-1}$.

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

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

k_t(L mol^{-1} s^{-1})	T (°C)	pH	[M]	Remarks	Ref.
$\sim 3 \times 10^3$ to $\sim 5 \times 10^4$ Very low values ($k_t = 0.1$ to 1) at high conversion ($\sim$0.9) and pH = 6.5	Room	2.2–9.9	30%wt AA	Minimum at pH$\sim$6.5 $k_p \downarrow$ with conversion $k_p \downarrow$ with ionic strength	[5]
$\frac{k_p}{\sqrt{k_t}} = 25$ to 40	70	75% N.		Inverse Suspension	[25]
3×10^8	55	65% N.	33% solids (AA) ($\sim$25%wt AA)	Estimated from experimental. data in Ref. [22]	[21]

Table 4.
Some reported values of the termination rate constant (k_t) of methacrylic acid (MAA) in water.

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

associated with measurements of rate coefficients of water soluble monomers can be found in the references presented in Table 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.

Simulation Results Using the Proposed Kinetic Approach

Figure 1 depicts the predicted dynamics of the weight fraction of gel (w_g) and monomer conversion (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_{p1}) were considered, in a range that is plausible for this monomer in these particular conditions (see Table 1 and

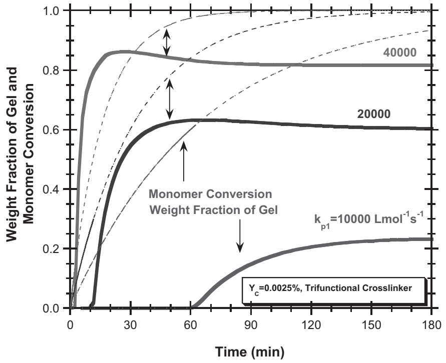

Figure 1.

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: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} s^{-1}$ ($T = 50^\circ$ for V50), $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 1$ ($r_{PDB} = 2.31$), $k_t = 5 \times 10^7 \, L\,mol^{-1}\,s^{-1}$.

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 $r_1 = \frac{k_{p1}}{k_{p2}} = 0.77$ 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 $r_2 = \frac{k_{p2}}{k_{p1}} = 1/r_1$ 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 $r^* = \frac{k_{p3}}{k_{p1}} = 1$ 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: $r_{PDB} = \frac{k_{p3}}{(k_{p2}/3)} = 2.31$).

To the termination rate coefficient was assigned the value $k_t = 5 \times 10^7\ L\,mol^{-1}\,s^{-1}$ 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 ($k_{pj} = k_{Ij}$) 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 superabsorbent hydrogels production. With higher values of k_{p1}, the primary chain length increases with concomitant higher gel formation.

Figure 2 shows the predicted dynamics of the weight average molecular weight ($\overline{M}_w$) 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 (Θ 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

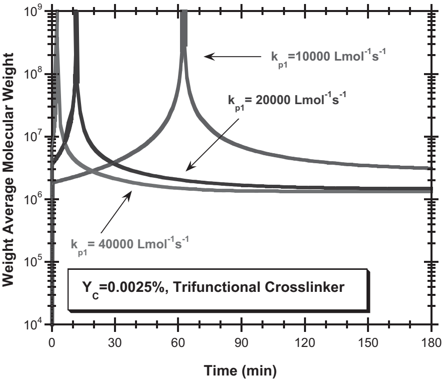

Figure 2.

Predicted dynamics of the weight average molecular weight ($\overline{M}_w$) 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: $Y_I = 0.3\%$, $k_d = 8.4\times 10^{-6} s^{-1}$ ($T = 50^\circ$ for V50), $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 1$ ($r_{PDB} = 2.31$), $k_t = 5 \times 10^7\,L\,mol^{-1}\,s^{-1}$.

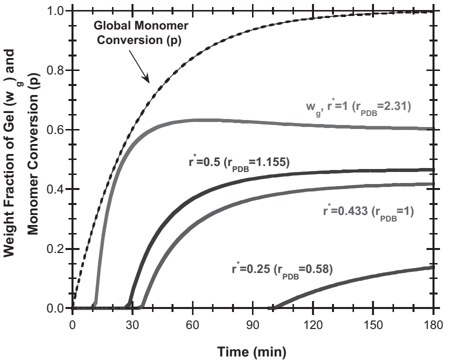

Figure 3.
Predicted dynamics of the weight fraction of gel (w_g) and monomer conversion (p) in batch SAP production using a trifunctional crosslinker with $Y_C = 0.0025\%$. Different values of the reactivity of pendant double bonds were considered, as quantified by the parameter r^* (or r_{PDB}). Other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

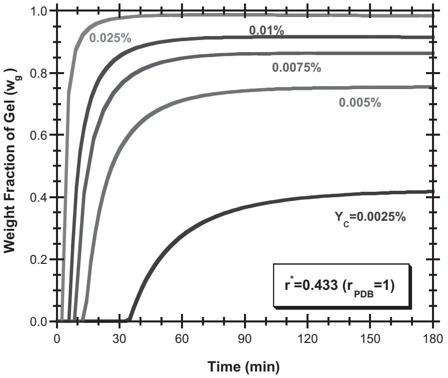

Figure 4.
Predicted dynamics of the weight fraction of gel (w_g) in batch SAP production considering different initial mole fraction of trifunctional crosslinker (Y_C). Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} s^{-1}$ ($T = 50°$ for V50), $v_{AA} = 15\%$, $k_{p1} = 20000\ L\,mol^{-1}s^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 0.433$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7\ L\,mol^{-1}s^{-1}$.

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: $Y_C = 0.0025\%$, $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6}\ s^{-1}$, $v_{AA} = 15\%$, $r_1 = 0.77$, $r_2 = 1/r_1$, $k_{p1} = 20000\ L\,mol^{-1}\,s^{-1}$, $k_t = 5 \times 10^7\ L\,mol^{-1}\ s^{-1}$. 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 Equation (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

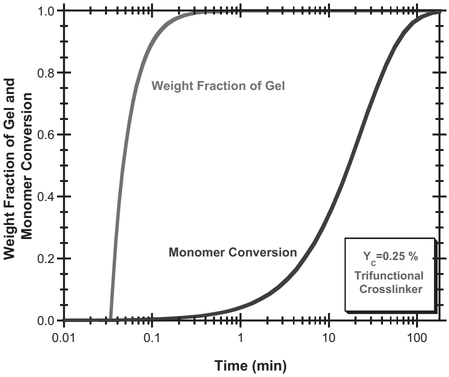

Figure 5.
Predicted time evolution of monomer conversion and weight gel fraction during acrylic acid/triacrylate copolymerization with $Y_C = 0.25\%$. Other parameters considered in the simulations: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6} s^{-1}$ (T = 50° for V50), $v_{AA} = 15\%$, $k_{p1} = 30000\ L\,mol^{-1}\,s^{-1}$, $r_1 = 1/3$, $r_2 = 3$, $r^* = 1$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7\ L\,mol^{-1}\,s^{-1}$.

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.

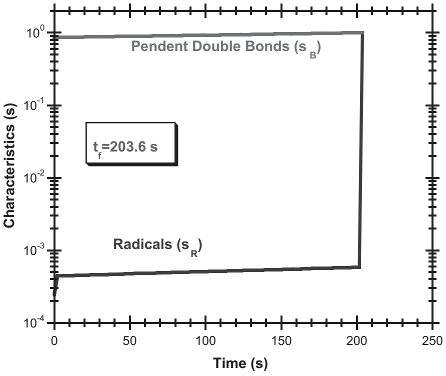

Figure 6.
Numerical solution of the characteristics (vector s) correspondent to the SAP synthesis using the conditions described in Figure 5. For illustration purposes the chosen polymerization time was $t_f = 203.6$ s. Solution of the problem of the characteristics is a crucial step for the prediction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

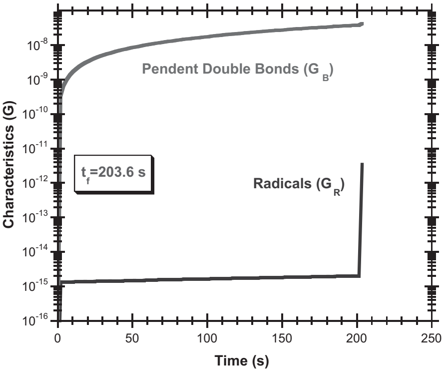

Figure 7.
Numerical solution of the characteristics (vector G) correspondent to the SAP synthesis using the conditions described in Figure 5. For illustration purposes the chosen polymerization time was $t_f = 203.6$ s. Solution of the problem of the characteristics is a crucial step for the prediction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

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

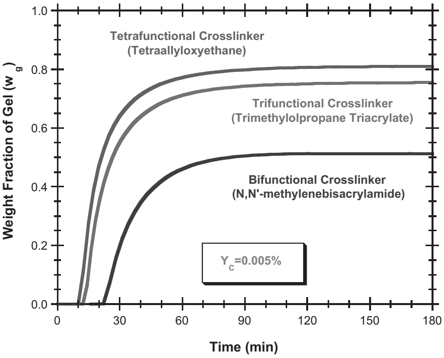

Figure 8.
Predicted dynamics of the weight fraction of gel (w_g) in batch SAP production considering three different synthesis processes correspondent to the use of three crosslinkers with different functionalities (bi-, tri- and tetrafunctional, considering N,N′-methylenebisacrylamide ($\alpha = 2$), 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° for V50), $v_{AA} = 15\%$, $k_{p1} = 20000\ L\,mol^{-1}\,s^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = r_2/\alpha$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7\ L\,mol^{-1}\,s^{-1}$.

crosslinkers with different functionalities (2, 3 and 4) by considering N,N′-methylene-bisacrylamide ($\alpha = 2$), 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 functionally 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

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 spacial 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.[2]

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:[55]

$$\begin{aligned} F_{01}(\mathbf{s}) = {} & 1 - x + x\{1 - \gamma + \gamma[(1 - Y_D)s_1^- \\ & + Y_D s_2^-]\} \times \{(1 - \gamma)[1 - \alpha_{tc} \\ & + \alpha_{tc}[(1 - Y_D)s_1^- + Y_D s_2^-]] \\ & + \gamma[(1 - Y_D)s_1^+ + Y_D s_2^+]\} \end{aligned} \tag{17}$$

$$F_{02}(\mathbf{s}) = F_{01}^2(\mathbf{s}) \tag{18}$$

with $F_{01}(\mathbf{s})$ representing the link probability generating function for the zero-th generation corresponding to the vinyl monomer and $F_{02}(\mathbf{s})$ 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 γ (γ=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 α_{tc}. In the dummy variables of the generating functions subscripts and superscripts are used (s_i^j). 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.[54,55] The influence of reaction directionality and termination by combination was introduced in the statistical treatment of linear free-radical polymerizations by H. Galina.[59]

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.[55]

These PGF are:

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

$$F_1^+(\mathbf{s}) = (1-\gamma)\left[1 - \alpha_{tc} + \alpha_{tc}\left[(1 - Y_D)s_1^- + Y_D s_2^-\right]\right] + \gamma\left[(1 - Y_D)s_1^+ + Y_D s_2^+\right] \tag{20}$$

$$F_2^-(\mathbf{s}) = F_1^-(\mathbf{s})F_{01}(\mathbf{s}) \tag{21}$$

$$F_2^+(\mathbf{s}) = F_1^+(\mathbf{s})F_{01}(\mathbf{s}) \tag{22}$$

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 nonlinear system with four unknowns:

$$v_i^j = F_i^j(\mathbf{v}) \quad i = 1,2 \quad j = -,+ \tag{23}$$

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

$$w_g = 1 - w_{AA}F_{01}(\mathbf{v}) - w_C F_{02}(\mathbf{v}) \tag{24}$$

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, γ. Calculations have shown that, besides Y_C, the parameter γ 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.

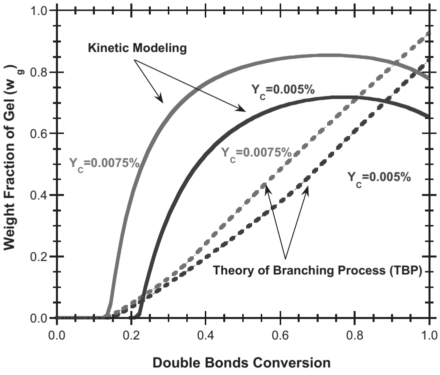

Figure 9.

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: $\alpha_{tc} = 1$, $\gamma = 0.9999$. Parameters considered in the simulations with the Kinetic Approach: $Y_I = 0.3\%$, $k_d = 8.4 \times 10^{-6}\ s^{-1}$ (T = 50° for V50), $v_{AA} = 15\%$, $k_{p1} = 20000\ L\,mol^{-1}\ s^{-1}$, $r_1 = 0.5$, $r_2 = 1/r_1 = 2$, $r^* = r_2/2 = 1$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7\ L\,mol^{-1}s^{-1}$ (with $\alpha_{tc} = 1$).

The huge differences between predictions presented in Figure 9 illustrate the dissimilitudes 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 $v_{AA} = 15\%$ and a similar composition was used in the solution homopolymerization of acrylic acid.

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

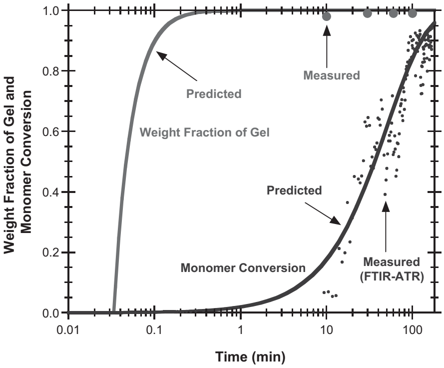

Figure 10.

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 °C. Homopolymerization of acrylic acid was performed in water solution with $v_{AA} = 15\%$ and $Y_1 = 0.1\%$. Crosslinking copolymerization was performed in inverse suspension considering similar composition of the aqueous phase and $Y_C = 0.25\%$. Other parameters considered in the simulations: $k_d = 8.4 \times 10^{-6}\ s^{-1}$, $k_{p1} = 30000\ L\,mol^{-1}\,s^{-1}$, $r_1 = 0.77$, $r_2 = 1/r_1$, $r^* = 0.433$ ($r_{PDB} = 1$), $k_t = 5 \times 10^7\ L\,mol^{-1}\,s^{-1}$.

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 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 tetrafuncional 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 super-absorbent 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 super-absorbent 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.
$\overline{M}_w$	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_{pj}^T	rate coefficient of the propagation of tertiary radicals with a monomer or macromonomer of the kind j.
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.
k_{tP}	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 asso-

	ciated 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_i^j	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_i^j	extinction probability associated with bonds of the kind s_i^j.
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

α	crosslinker functionality.
α_{tc}	relative rate of radical termination by combination.
α_{td}	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.
$_0$	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.
MAA	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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[1] F. L. Buchholz, A. T. Graham, *Modern Superabsorbent Polymer Technology*, Wiley-VCH, New York 1998.

[2] F. L. Buchholz, *N.A. Peppas Superabsorbent Polymers: Science and Technology*, ACS Symposium Series, American Chemical Society, Washington 1994.

[3] M. J. Zohuriaan-Mehr, K. Kabiri, *Iranian Polymer Journal.* **2008**, *17*, 451.

[4] D. J. Arriola, S. S. Cutié, D. E. Henton, C. Powell, P. B. Smith, *J. Appl. Polym. Sci.* **1997**, *63*, 439.

[5] K. S. Anseth, R. A. Scott, N. A. Peppas, *Macromolecules.* **1996**, *29*, 8308.

[6] F.-D. Kuchta, A. M. van Herk, A. L. German, *Macromolecules.* **2000**, *33*, 3641.

[7] I. Lacík, S. Beuermann, M. Buback, *Macromolecules.* **2001**, *34*, 6224.

[8] I. Lacík, S. Beuermann, M. Buback, *Macromolecules.* **2003**, *36*, 9355.

[9] I. Lacík, S. Beuermann, M. Buback, *Macromol. Chem. Phys.* **2004**, *205*, 1080.

[10] S. Beuermann, M. Buback, P. Hesse, I. Lacík, *Macromolecules.* **2006**, *39*, 184.

[11] M. Buback, T. Junkers, *Macromol. Chem. Phys.* **2006**, *207*, 1640.

[12] S. Beuermann, M. Buback, P. Hesse, S. Kukučková, I. Lacík, *Macromol. Symp.* **2007**, *248*, 23.

[13] S. Beuermann, M. Buback, P. Hesse, S. Kukučková, I. Lacík, *Macromol. Symp.* **2007**, *248*, 41.

[14] S. Beuermann, M. Buback, P. Hesse, F.-D. Kuchta, I. Lacík, A. M. Van Herk, *Pure Appl. Chem.* **2007**, *79*, 1463.

[15] S. Beuermann, M. Buback, P. Hesse, R. A. Hutchinson, S. Kukučková, I. Lacík, *Macromolecules.* **2008**, *41*, 3513.

[16] M. Buback, P. Hesse, R. A. Hutchinson, P. Kasák, I. Lacík, M. Stach, I. Utz, *Ind. Eng. Chem. Res.* **2008**, *47*, 8197.

[17] I. Lacík, L. Učňnoá, S. Kukučková, M. Buback, P. Hesse, S. Beuermann, *Macromolecules.* **2009**, *42*, 7753.

[18] J. J. Kurland, *J. Polym. Sci.* **1980**, *18*, 1139.

[19] V. A. Kabanov, D. A. Topchiev, T. M. Karaputadze, *J. Polymer Sci., Symposium* **1973**, *42*, 173.

[20] V. A. Kabanov, D. A. Topchiev, T. M. Karaputadze, *Eur. Polym. J.* **1975**, *11*, 153.

[21] R. Li, F. J. Schork, *Ind. Eng. Chem. Res.* **2006**, *45*, 3001.

[22] S. S. Cutié, D. E. Henton, C. Powell, R. E. Reim, P. B. Smith, T. L. Staples, *J. Appl. Polym. Sci.* **1997**, *64*, 577.

[23] D. E. Henton, C. Powell, R. E. Reim, *J. Appl. Polym. Sci.* **1997**, *64*, 591.

[24] S. S. Cutié, P. B. Smith, D. E. Henton, T. L. Staples, C. Powell, *J. Polym. Sci. B: Polym. Phys.* **1997**, *35*, 2029.

[25] B. Renard, T. F. McKenna, *Macromol. Symp.* **2000**, *150*, 251.

[26] H. Omidian, M. J. Zohuriaan-Mehr, H. Bouhendi, *European Polymer Journal.* **2003**, *39*, 1013.

[27] G. Wang, M. Li, X. Chen, *J. Appl. Polym. Sci.* **1997**, *65*, 789.

[28] S. K. Bajpai, M. Bajpai, L. Sharma, *Designed Monomers and Polymers.* **2007**, *10*, 181.

[29] H. Bodugöz, O. Güven, *J. Appl. Polym. Sci.* **2002**, *83*, 349.

[30] S. Kiatkamjornwong, P. Phunchareon, *J. Appl. Polym. Sci.* **1999**, *72*, 1349.

[31] H. Bahaj, R. Benaddi, M. Bakass, C. Bayane, *J. Appl. Polym. Sci.* **2010**, *115*, 2479.

[32] X. Chen, G. Shan, J. Huang, Z. Huang, Z. Weng, *J. Appl. Polym. Sci.* **2004**, *92*, 619.

[33] K. Kabiri, M. J. Zohuriaan-Mehr, *Macromol. Mater. Eng.* **2004**, *289*, 653.

[34] M. R. P. F. N. Costa, R. C. S. Dias, *Chem. Eng. Sci.* **1994**, *49*, 491.

[35] M. R. P. F. N. Costa, R. C. S. Dias, *Macromol. Theory Simul.* **2003**, *12*, 560.

[36] R. C. S. Dias, M. R. P. F. N. Costa, *Macromolecules.* **2003**, *36*, 8853.

[37] M. R. P. F. N. Costa, R. C. S. Dias, *Chem. Eng. Sci.* **2005**, *60*, 423.

[38] R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Theory Simul.* **2005**, *14*, 243.

[39] R. C. S. Dias, M. R. P. F. N. Costa, *Polymer.* **2005**, *46*, 6163.

[40] R. C. S. Dias, M. R. P. F. N. Costa, *Polymer.* **2006**, *47*, 6895.

[41] M. R. P. F. N. Costa, R. C. S. Dias, *Macromol. Symp.* **2006**, *243*, 72.

[42] M. R. P. F. N. Costa, R. C. S. Dias, *Polymer.* **2007**, *48*, 1785.

[43] R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. React. Eng.* **2007**, *1*, 440.

[44] R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Theory Simul.* **2010**, *19*, 323.

[45] M. A. D. Gonçalves, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2007**, *259*, 124.

[46] I. M. R. Trigo, M. A. D. Gonçalves, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2008**, *271*, 107.

[47] M. A. D. Gonçalves, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2010**, *289*, 1.

[48] M. A. D. Gonçalves, V. D. Pinto, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2010**, *296*, 210.

[49] M. A. D. Gonçalves, R. C. S. Dias, M. R. P. F. N. Costa, *Chem. Eng. Technol.* **2010**, *33*, 1797.

[50] M. A. D. Gonçalves, I. M. R. Trigo, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2010**, *291–292*, 239.

[51] M. A. D. Gonçalves, V. D. Pinto, R. C. S. Dias, M. R. P. F. N. Costa, *Macromol. Symp.* **2011**, *302*, 179.

[52] C. Plessis, G. Arzamendi, J. M. Alberdi, A. M. van Herk, J. R. Leiza, J. M. Asua, *Macromolecules.* **2000**, *33*, 4.

[53] A. Nikitin, R. A. Hutchinson, M. Buback, P. Hesse, *Macromolecules.* **2007**, *40*, 8631.

[54] A. B. Scranton, N. A. Peppas, *J. Polym. Sci.* **1990**, *28*, 39.

[55] A. B. Scranton, J. Klier, N. A. Peppas, *Macromolecules.* **1991**, *24*, 1412.

[56] R. J. J. Williams, C. I. Vallo, *Macromolecules.* **1988**, *21*, 2568.

[57] R. J. J. Williams, C. I. Vallo, *Macromolecules.* **1988**, *21*, 2571.

[58] N. A. Dotson, *Macromolecules.* **1992**, *25*, 308.

[59] H. Galina, *Eur. Polym. J.* **1986**, *22*, 665.