Physical and chemical gels

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PHYSICAL AND CHEMICAL GELS

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. Sc. ETH Zurich)

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despite our ways are about to part. Thanks for your good mood, for the jokes and for reminding me to take things easier. Basti requires a special mention for the good time spent in San Francisco and for his brilliant sense of humor, I will miss it. Speaking of more recently met friends, I need to mention David, Lucrèce, Baptiste and Michael: besides science, it was a pleasure to share with you (in sparse order) music, conferences, exhibitions, chess, beers, movies and theatre.

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Abstract

In the present thesis the formation of chemical and physical gels is deepened. Chemical gels are constituted by polymeric macromolecules of large enough sizes to become insoluble. Such chains are formed in the presence of a multi-functional monomer (crosslinker) which causes the linking of chains, leading to a significant increase in the molecular weight. Once a critical size of the chain is reached, a new phase, termed gel, precipitates out of the reactive mixture. Such new phase can be visualized as a single, highly crosslinked macromolecule spanning the entire reaction locus. The formation of physical gels instead is mediated by the aggregation of pre-formed colloidal particles which build up macro-aggregates spanning throughout their vessel.

In the first part of the thesis, free-radical crosslinking copolymerization, which typically leads to the formation of chemical gels, has been studied employing different modelling approaches. Initially, a statistical/kinetic model has been employed to estimate the kinetic parameters for the industrially relevant copolymerization of acrylamide and N’N’-methylene-bisacrylamide, allowing to describe their gel properties such as their swelling and crosslinking density. Successively, a deterministic model has been developed to clarify the role of multiple active sites (multiradicals) in crosslinking copolymerization. Based on the methylmethacrylate/ethylene-glycol dimethacrylate system, a new quantitative criterion was proposed to decide whether or not such multiple active sites should be accounted for. The latter two models were then compared with a Kinetic Monte Carlo and another deterministic model, in order to clarify their strength and weaknesses and provide guidelines for their application.
In the second part of the thesis, the shear-stability of Inverse Latexes, i.e. polymer particles suspended in an oil phase, has been investigated experimentally by means of a rheometer. In these conditions the Inverse Latexes undergo gelation as a result of irreversible shear-induced particle aggregation, characterized by a significant increase in viscosity: a physical gel is formed. The experimental studies allowed identifying the key parameters affecting the shear-stability of Inverse Latexes both during as well as after the polymerization. It turned out that a competition between aggregation and coalescence regulates the gelation process. Finally, a deterministic model accounting for both aggregation and coalescence of such particles has been developed in order to provide a tool for quantifying their role.
Sommario

Nel presente lavoro di tesi si è approfondita la formazione di gel fisici e chimici. I gel chimici sono costituiti da macromolecole polimeriche di dimensione tali da risultare insolubili. Tali catene possono formarsi in presenza di un monomero multifunzionale (crosslinker) che causa l’interconnessione dalla catene, provocando un significativo incremento del peso molecolare. Raggiunta una dimensione critica di catena, funzione del solvente e del polimero, si assiste alla formazione di una nuova fase, detta gel, che precipita dalla miscela di reazione. Tale nuova fase può essere visualizzata come una singola macromolecola estremamente crosslinkata che si estende per tutto il luogo di reazione. La formazione di gel fisici invece è mediata dalla formazione di macroaggregati di particelle colloidali che si estendono per tutta la grandezza del vessel che li contiene.

Nella prima parte della tesi è stata studiata, mediante differenti approcci modellistici, la copolimerizzazione crosslinkata free-radical, che porta tipicamente alla formazione di gel chimici. Inizialmente si è utilizzato un modello statistico/cinetico per stimare i parametri cinetici della copolimerizzazione di acrilamide e metilen-bisacrilamide, che ha permesso di descrivere le proprietà di tali gel quali il loro swelling o la loro densità di crosslinking. Successivamente si è adoperato un modello deterministico per chiarire il ruolo di catene radicaliche aventi più siti attivi (multiradicali). Sulla base del sistema metil-metacrilato/etilen-glicole-dimetacrilato è stato proposto un nuovo criterio quantitativo mediante il quale decidere se trascurare o meno i multiradicali. I due modelli summenzionati sono stati poi confrontati con un approccio Monte Carlo cinetico e con un ulteriore modello deterministico in modo da chiarirne punti di forza e proporre delle linee guida per il loro utilizzo.
Nella seconda parte della tesi, la stabilitá in shear di lattici inversi, ossia di particelle polimeriche sospese in una fase oleosa, é stata investigata sperimentalmente mediante un reometro. Sotto shear i lattici inversi aggregano, formando cluster di particelle che causano la gelazione del sistema, evidenziata da un significativo incremento di viscositá: nel momento in cui le particelle formano un cluster percolante (che si estende cioè per tutto il vessel) si ha la formazione di un gel fisico. Lo studio sperimentale ha permesso di individuare i parametri chiave che influenzano al stabilitá in shear dei lattici inversi sia durante, sia dopo la polimerizzazione. Dallo studio si evince che é la competizione fra aggregazione e coalescenza a regolare il processo di gelazione. Da ultimo si é perció sviluppato un modello deterministico che contemplasse aggregazione e coalescenza di particelle colloidali, che rappresenta uno strumento per la quantificazione dei tempi caratteristici di aggregazione e coalescenza.
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1. Introduction

1.1. Chemical gels

The formation of a chemical gel occurs during polymerizations in which the polymer chains combine (i.e. crosslink) with each other till their size is so large that they become insoluble in the continuous medium and a new phase, termed (chemical) gel, arises. Such extremely large macromolecules typically span throughout their reaction locus and have therefore virtually “infinite” molecular weights. Polymer chains which instead are still soluble are termed sol chains; progressively, these chains will be taken up by the gel, till the whole system consists of one gigantic macromolecule, or polymer network. The transition from the situation where only sol chains are present, to the one where the first gel molecule is present is referred to as sol-gel transition, whereas the critical point where the gel arises is called gelation.\[^{[1]}\]

There are several ways for gelation to occur, both in step growth as well as in free-radical polymerization. In the first case, the copolymerization of multifunctional monomers (one of the two has to be at least tri-functional) may lead to the formation of a macroscopic network.\[^{[2]}\] In free-radical polymerization instead, two ways exist for the system to undergo gelation. The first one requires the presence of a di-functional monomer (e.g. di-vinyl-benzene) which, once polymerized, introduces a pendant double bond (PDB) along the chain. The latter can further react and link (i.e. crosslink) the chain with different ones, leading to the formation of the aforementioned network. The other possibility is that the polymer chains undergo transfer to polymer, which means that a hydrogen atom is abstracted from a terminated chain, which is re-
activated (typically with an active site along its backbone) and a branch is formed. Once this branched chain terminates by combination with another branched chain, a crosslink is formed and the re-iteration of this process leads eventually to the gelation of the system.\[^{[3]}\]

The resulting properties of the gel formed (i.e. its swelling by solvents and mechanical characteristics) are defined by the amount and types of crosslinkages formed. The larger the amount of such links between the chains, the stronger and less swelling the gel will result.\[^{[4]}\] This becomes of particular importance in the case of free-radical crosslinking copolymerization where the PDB can undergo several different reactions, as shown in Figure 1.1.

![Figure 1.1 Possible reactions for the pendant double bonds\[^{[4]}\)](image)

The larger the relevance of primary and secondary cyclization, the later the gelation will occur as these reactions consume PDB without linking two chains together (hence without promoting the network formation), but simply tightening the already existing chain. It is clear that understanding and properly estimating the rate of such reactions (in competition with the
crosslinking one) is of the utmost importance to define the gel final properties, and the degree of polymerization of crosslinked, yet soluble (i.e. not gelled) systems.

Another characteristic of crosslinking copolymerization is the possible formation of multiple active sites, also termed multiradicals. Such chains arise for instance if an active chain reacts with the PDB of another active chain. The presence of such multiple active sites is known to affect the correct prediction of the gelation onset and the average properties of the produced polymer.\[5\]

As can be inferred from the previous paragraphs, the description of chemical gels is relatively complex; the drive to deepen the understanding of the formation and properties of such materials is their great practical interest. Such polymer networks have a very large impact on the market, with products ranging from supports for cell culture, to superabsorbent materials, to tires, just to mention few examples.\[6\]

1.2. Physical gels

Colloidal systems are constituted of small particles ($1\text{nm-}1\mu\text{m}$) which are dispersed in a medium.\[7\] In particular, polymer particles suspended in a liquid phase are termed latexes, more specifically direct latexes if the continuous phase is water-based or inverse latexes if the medium is oil-based.

These latexes are typically referred to as kinetically stable: eventually they will undergo aggregation and rearrange into clusters. If this process continues, the clusters will further aggregate and interconnect, till a macrostructure spanning throughout the whole system arises and a physical gel is formed.\[7\] A distinction in a strong or weak physical gel is further possible
according to the strength of the structure formed: strong physical gels are irreversible, while weak physical gels can be re-dispersed in primary particles.

The gelation process and more generally the particle stability is regulated by the balance of attractive and repulsive forces the particles are exposed to. Attractive forces are for instance van der Waals forces (defined by the particle size and particles/medium interactions) and shear forces (related to the introduction of mechanical energy into the system), whereas repulsive forces are usually electrostatic or steric forces, induced by the presence of a surface active agent (i.e. a surfactant or emulsifier) typically adsorbed on the particles surfaces. Controlling the latex stability is of key importance in industrial applications: the destabilization of a system may be essential (e.g. in water clarification where destabilizing agents are introduced) or undesired (e.g. paints or drug delivery systems). More specifically, also the physical gelation of a colloidal system is of extreme interest: while preparing chromatographic supports for instance, a possible technique is the so-called reactive gelation, where the physical gelation of the system is a key prerequisite. On the other hand there are several situations where the gelation of a latex is undesired, namely during its production or processing phases. In these situations the particles undergo a significant extent of shear, which is known to accelerate gelation significantly. In those cases gelation leads not only to a non-homogeneous product, but also to the fouling or even clogging of reactors, vessels or pumps, which of course have a negative economic impact. Despite the huge amount of available literature on particles stability in general, room for improvement exists in terms of better understanding and controlling the physical gelation. This becomes especially true if the focus is on systems of industrial relevance, which reach concentrations by far larger than those typically studied in the literature: for such high-concentrated systems, significant deviations from the theory are known to occur.
1.3. **Outline of the present work**

The present thesis is structured into two main parts; the first dealing with chemical gels and the second one with physical gels. To get insights in the formation and characterization of these gels, the phenomena responsible for the gel build up and the parameters regulating those phenomena are investigated, employing both experimental and modelling techniques.

In chapters 2-4 the formation of chemical gels from bulk crosslinking copolymerization is studied from a modelling point of view: several models are compared with one another and different systems are analyzed, in an attempt to describe the formation mechanism of chemical gels and their properties.

In particular, in chapter 2 the solution copolymerization of acrylamide/N,N'-methylenebisacrylamide is simulated through a statistical/kinetic model: the comparison with experimental and literature data provided a complete set of kinetic parameter values suitable to describe this copolymerization system. Moreover, the dependency of primary cyclization on the system dilution and its impact on the gel properties is clarified.

In chapter 3, the system methyl methacrylate/ethylene glycol dimethacrylate is employed to study the role of active chains having multiple active sites (multiradicals) and their impact on the gel formation process. To do so, a multidimensional population balance equation is written and solved by means of the numerical fractionation. A literature criterion\[5\] to decide on the necessity of multiradicals has been revised and improved, taking into account diffusion limitations. As a result, a better comprehension of the gel formation is provided as well as an improved strategy to choose the most adequate modelling approach (mono- or multiradical).

The two models employed in chapters 2 and 3 were then compared in chapter 4 with two other more complex models (a kinetic Monte Carlo model and another deterministic model based
on the solution of the generating functions) in an attempt to clarify advantages and downsides of the different approaches. On the basis of two case studies, the predictions of the four models were compared both in terms of average properties and chain length distributions. A critical analysis of the proper degree of model complexity required for describing a crosslinking copolymerization is discussed in this frame.

Physical gels are dealt with in chapters 5-7, where focus is set on the key parameters regulating the shear-stability of inverse latexes during and after polymerization and on the possibility of modeling such systems.

In particular, the shear-stability of inverse latexes after their polymerization is deepened in chapter 5, where an experimental analysis involving rheological measurements allowed deepening the understanding of the gelation mechanisms of those systems. The competition between coalescence and aggregation was highlighted and suggestions on how to prevent the gelation by tuning the polymerization recipes are suggested.

A similar analysis is proposed in chapter 6 on inverse latexes during their polymerization; the stability of different systems was analyzed by means of a rheometer as a function of the monomer conversion. Once more the interplay of coalescence and aggregation was identified as a key parameter for the shear-stability, along with several other phenomena, related to the polymer composition and the particle concentration.

In chapter 7, a deterministic modeling approach based on population balance equations has been developed, aimed to describe the stability of aggregating and coalescing colloidal systems. The approach is based on a discretization technique employing Gaussian functions, which allow dealing with some usually cumbersome integrals in a relatively easy and elegant way.
Finally, in chapter 8 the main achievements of the present work are summarized and a short outlook is provided.
2. Modeling of Acrylamide/N,N’-methylenebisacrylamide Copolymerization

2.1. Introduction

Acrylamide (Am)/N,N’-methylenebisacrylamide (BAm) hydrogels are of paramount importance in a great variety of applications, ranging from superabsorbant materials, electrophoresis gels, supports for cell culture and artificial muscles. In several of the aforementioned applications, the hydrogel structure and molecular weights need to be tailor-made and well-controlled in order to meet the required specification. Mathematical models can be very helpful to design the reaction conditions in optimal way: as a matter of fact, a great deal of modeling tools to predict the properties of such complex nonlinear polymers have been introduced in the past years. The various modelling techniques have to take into account crosslinking and intramolecular reactions, due to the divinyl nature of the BAm. The interplay of these reactions is of utmost importance, as it regulates the material properties in terms of mechanical and swelling response, as well as the onset of the gel formation, after which the polymerization occurs in two phases, named sol and gel. While the sol contains soluble linear and branched chains, the gel phase contains insoluble, highly crosslinked chains, with a virtually infinite molecular weight.

The present chapter has been partially published as: S. Lazzari, D. Pfister, V. Diederich, A. Kern, G. Storti “Modeling of Acrylamide/N’N-Methylenebisacrylamide Solution Copolymerization”, Industrial and Engineering Chemical Research, in press. The experimental results presented in this chapter have been obtained by V. Diederich and presented in his PhD Thesis. The contribution of the author Stefano Lazzari is strictly limited to the modelling part.
Different modelling approaches have been reported in the literature for crosslinking copolymerization reactions, ranging from deterministic to stochastic and probabilistic ones. As a detailed description of the available crosslinking models is out of the scope of this work, the different approaches will be only briefly sketched. Kinetic models usually rely on the solution of population balance equations (PBE), which describe among other properties, the chain length distribution (CLD) of the polymer and the crosslinking density. In crosslinking copolymerization, multidimensional PBE are typically needed, as at least the numbers of units and pendant double bonds have to be employed as internal coordinates \(^{[17-19]}\). Despite the great deal of information these models provide, their numerical solution, especially when the entire chain length distribution is needed, requires a significant computational effort.

Stochastic Monte Carlo (MC) simulations based on the resolution of chemical master equations have also become popular in the last decades. MC strategies are a versatile tool that can handle complicated problems, as gelation phenomena, and still provide detailed structure of the gel polymer \(^{[20-24]}\). Unfortunately, stochastic methods, despite their relative apparent simplicity, require lengthy computing time to reach sufficient accuracy.

The first statistical approaches date back to the early 40’s, where Flory \(^{[25]}\) and Stockmayer \(^{[26, 27]}\) developed a theory of gelation, which is based on the concept of primary chains and on the crosslinking density, representing the probability for a monomer unit to form a link between two chains. The classical Flory-Stockmayer theory \(^{[25-29]}\) has been extended to free-radical crosslinking copolymerization by Tobita and Hamielec who provided a powerful model able to account for different types of intramolecular reactions, such as loop formation, primary and secondary cyclization. In other words, beside average properties, such as sol and gel fractions and sol average molecular weights, also effective and ineffective crosslinking densities can be estimated through this model.
All the aforementioned models require reliable values of the corresponding kinetic parameters for obtaining robust predictions. In the specific case of Am/BAm hydrogels, kinetic parameters concerning propagation and termination have been abundantly discussed in the literature [30]. On the other hand, only few papers can be found dealing with the estimation of intramolecular and crosslinking kinetic constants, despite their great importance. Tobita and Hamielec [31] found that with an overall weight fraction of monomer-crosslinker mixture \( (w_t) \) of 5.6% (w/w), about 80% of the pendant double bonds (PBD) are consumed by primary cyclization reactions; and this happens for crosslinker over total monomer mixture weight fraction \( (w_c) \) ranging from very large to fairly low values, i.e. from 28% down to 0.02%. A similar amount of PDB consumed by primary cyclization was found by Naghash and Okay [32] when performing experiments at \( w_t = 1.8\% \) with crosslinker weight fractions in the range \( w_c = 5-22\% \). On the other hand, Okay et al. [33] estimate the amount of PDB consumed by primary cyclization as large as 95%, performing experiments at \( w_t = 5\% \) with crosslinker contents varying between \( w_c = 2-15\% \). The discrepancy between these values could be attributed to the experimental techniques employed to determine the PDB conversion: in the cases of Tobita and Hamielec [31] and the first evaluation of Naghash and Okay [32], a titration was performed on the sol polymer, whereas swelling measurements of the obtained gel were used to calculate the amount of PDB consumed by cyclizations in the subsequent paper by Okay et al. [33] Moreover, the crosslinking kinetics has been quantified by Tobita and Hamielec only roughly, as explicitly stated by themselves. It turned out that secondary cyclization is 1000 times more effective than crosslinking in consuming PDB and that the combination of crosslinking and secondary cyclization is a factor 2-4 larger than the propagation kinetic constant. [31].
Given the aforementioned discrepancy on the primary cyclization and its expected dependency on the monomer concentration,\textsuperscript{[34]} affecting gel formation onset, mechanical and swelling properties, a further estimate for a broad range of monomer concentrations would be desirable.

In this frame, the aim of this work is to estimate the kinetic parameters describing the intramolecular reactions (primary and secondary cyclizations) as well as of the crosslinking reaction at various crosslinker contents and for several monomer concentrations by comparing model predictions with swelling experimental data. In particular, we employed the probabilistic model proposed by Tobita and Hamielec,\textsuperscript{[35]} which represents an excellent compromise between prediction accuracy and computational effort, thus making it an effective tool towards parameter evaluation. The model predictions are compared to literature data and our own experimental measurements, i.e. swelling ratios of Am/BAm copolymer hydrogels produced at various crosslinker contents \((w_c = 3–5\%)\) and different total monomer concentrations \((w_t = 3–16\%)\).

### 2.2. Materials and methods

#### 2.2.1. Chemicals

Acrylamide for electrophoresis, 99% was purchased from Sigma. \textit{N,N’-methylenebisacrylamide} for electrophoresis, 99% and ammonium persulfate (APS) for molecular biology, 98.0% were purchased from Fluka. \textit{N,N,N’,N’-tetramethyl ethane 1,2-diamine} (TEMED), 99.5% was purchased from Aldrich. All chemicals were used without any further purification. Throughout the study, either MilliQ water or distilled water stripped with nitrogen was used.
2.2.2. Preparation of the hydrogels

In a typical preparation, required amounts of Am and BAm were solubilized in water previously deoxygenated by nitrogen stripping for at least 20 minutes. The prepared monomer/water solution was again stripped with nitrogen for 10 to 15 minutes; all experiments were carried out at room temperature (25°C). TEMED was charged as such, whereas APS in solution (10% w/w in water). Reactions at different amounts of crosslinker \( w_c \) (3, 4 and 5% w/w, cf. equation (2.1)) and at different dilution ratios \( w_t \) (from 3 to 16% w/w of monomers, cf. equation (2.2)) were performed; the employed quantities of monomers and initiator are presented in Table 2.1. In all cases the polymerization duration was 8 hours, but gelation was usually already observed after several minutes. After the reaction, the hydrogel was immersed in excess water.

\[
w_c = \frac{m_{\text{crosslinker}}}{m_{\text{crosslinker}} + m_{\text{monovinyl}}} \quad (2.1)
\]

\[
w_t = \frac{m_{\text{crosslinker}} + m_{\text{monovinyl}}}{m_{\text{crosslinker}} + m_{\text{monovinyl}} + m_{\text{water}}} \quad (2.2)
\]
Table 2.1 Reaction recipes.

<table>
<thead>
<tr>
<th>Am</th>
<th>BAm</th>
<th>Tot TEMED/APS</th>
<th>Am</th>
<th>BAm</th>
<th>Tot TEMED/APS</th>
<th>Am</th>
<th>BAm</th>
<th>Tot TEMED/APS</th>
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<td>g</td>
<td>g</td>
<td>µL</td>
<td>g</td>
<td>g</td>
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<td>30.03 20/100</td>
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<td>3.7</td>
<td>30.08 20/100</td>
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<td>9.2</td>
<td>60.02 40/200</td>
<td>1.14</td>
<td>5.9</td>
<td>29.98 20/100</td>
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<tr>
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<td>59.99 40/200</td>
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<td>7.4</td>
<td>30.00 20/100</td>
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<td>9.1</td>
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<td>29.98 20/100</td>
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<tr>
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<td>14.6</td>
<td>60.01 40/200</td>
<td>4.60</td>
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<td>60.07 40/200</td>
<td>2.28</td>
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<tr>
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<td>30.11 20/100</td>
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<td>60.08 40/200</td>
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<td>22.5</td>
<td>30.03 20/100</td>
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<tr>
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<td>30.04 20/100</td>
<td>9.21</td>
<td>38.4</td>
<td>60.07 40/200</td>
<td>4.56</td>
<td>24.2</td>
<td>30.04 20/100</td>
</tr>
</tbody>
</table>

2.2.3. Equilibrium swelling ratio

After complete polymerization and immersion in excess water, samples were taken out and cut in 4 slices (between 0.25 and 1g of swollen polymer each). The slice surfaces were dried and weighted before further immersion in water (ca. 30 mL). The sample was weighted daily and subsequently water was changed until equilibrium swelling was achieved. The equilibrium volume fraction of crosslinked polymer \( \phi_p \) is determined gravimetrically assuming the additivity of volumes through equation (2.3):

\[
\phi_p = \left(1 + \frac{(q-1)d_p}{d_w}\right)^{-1}
\]  

(2.3)
where $q$ is the swelling ratio defined as $\frac{m_{\text{polymer}}}{m_{\text{polymer}}^{\text{dry}}}$. $d_p$ and $d_w$ are the densities of polymer and water, respectively, and $m_{\text{polymer}}^{\text{dry}}$ the mass of a dried slice of gel whereas $m_{\text{polymer}}$ is the mass of the same slice of gel after equilibrium swelling in water has been reached.

### 2.3. Model Summary

The chemical species involved in the model are mono- ($M_1$) and divinyl- ($M_2$) monomers, pendant double bonds (PDB) and their respective radical species, as clarified in Table 2.2. The kinetic scheme employed to describe the Am/BAm copolymerization, is detailed in Table 2.3, whereas the kinetic constants are presented in Table 2.4. Their estimation, wherever necessary, will be treated in detail in paragraph 2.4.

<table>
<thead>
<tr>
<th>Table 2.2 Chemical species involved in the model.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Radical</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 2.3 Free-radical copolymerization kinetic scheme.

<table>
<thead>
<tr>
<th>Kinetic Scheme</th>
<th>Equation</th>
<th>Reaction Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initiation</strong></td>
<td>$I_2 + 2M_1 \rightarrow 2R_{1,1,0}^{p_1}$</td>
<td><img src="Image" alt="Initiation Reaction" /></td>
</tr>
<tr>
<td></td>
<td>$I_2 + 2M_2 \rightarrow 2R_{2,1,1}^{p_2}$</td>
<td><img src="Image" alt="Initiation Reaction" /></td>
</tr>
<tr>
<td><strong>Propagation</strong></td>
<td>$R_{i,m,n} + M_1 \rightarrow R_{i,m+1,n}^{k_{n1}}$</td>
<td><img src="Image" alt="Propagation Reaction" /></td>
</tr>
<tr>
<td></td>
<td>$R_{i,m,n} + M_2 \rightarrow R_{2,m+1,n}^{k_{n2}}$</td>
<td><img src="Image" alt="Propagation Reaction" /></td>
</tr>
<tr>
<td></td>
<td>$R_{i,m,n} + D_{3,r,q} \rightarrow R_{3,m+r,n+q}^{k_{n3}}$</td>
<td><img src="Image" alt="Propagation Reaction" /></td>
</tr>
<tr>
<td><strong>Primary cyclization</strong></td>
<td>$R_{i,m,n} \rightarrow R_{3,m,n-1}^{\eta_p}$</td>
<td><img src="Image" alt="Primary Cyclization Reaction" /></td>
</tr>
<tr>
<td><strong>Secondary cyclization</strong></td>
<td>$R_{i,m,n} + D_{3,r,q} \rightarrow R_{3,m+r,n+q}^{\alpha}$</td>
<td><img src="Image" alt="Secondary Cyclization Reaction" /></td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$R_{i,m,n} + R_{j,r,q} \rightarrow \begin{cases} P_{m+r,n+q}^{p_1} \ P_{m,n}^{p_1} + P_{r,q}^{p_2} \end{cases}$</td>
<td><img src="Image" alt="Termination Reaction" /></td>
</tr>
</tbody>
</table>

$r = \text{radical type (1 = monovinyl, 2 = divinyl, 3 = pendant)}$

$m = \text{chain length}$

$n = \text{PDB}$
The Tobita and Hamielec model enables the calculation of weight fractions of sol and gel, crosslinking densities and average molecular weight between consecutive crosslinks by using three ordinary differential equations and one partial differential equation. The model is based on the calculation of primary chains, defined as those linear chains one would obtain by severing the crosslinkages between them (cf. to Figure 2.1) and on the crosslinking density \( \rho \) (defined as the fraction of crosslinked units over the total number of incorporated monomers) \(^{[25]}\).
The main model assumptions are: (1) quasi steady state assumption (QSSA) for the radicals, (2) monoradical assumption, (3) equality of the kinetic rate constants for sol and gel, (4) negligible penultimate effects, (5) PDB on primary chains consumed only by intramolecular reactions, (6) pseudo-kinetic constants and (7) equal crosslinking density for chains born at the same conversion. The QSSA is well-known and accepted in polymer science since the early work by Stockmayer\cite{43} and it has been proven to be a very reasonable assumption when combined with the monoradical one in the presence of crosslinking.\cite{5} Furthermore, the monoradical assumption is in the present case fully justified, being the $k_p/k_i$ ratio lower than $10^{-3}$.\cite{5, 44} Moreover, intramolecular cyclizations are known to be dominant in this system, reducing the amount of PDB available for multiradical formation (which in the present case is mediated by crosslinking only). Also assuming the same reactivity of sol and gel is a typical choice when it comes to crosslinking free-radical polymerization,\cite{17, 35} whereas assumptions (4)-(6) are typically employed in the present model.\cite{35, 45} As for the employment of pseudo-kinetic constants (assumption (6)), some literature works report the necessity to employing a chain-length dependent termination in the frame of polymer modification.\cite{46} Despite the present kinetic scheme is quite different, it is reasonable to assume that a proper chain length dependent termination mechanism is necessary. Nevertheless, to the authors’ knowledge, no such expression
validated for Am/BAm is provided in the literature, whereas pseudo-kinetic constants have been already successfully employed when modelling this same system.\cite{47} Finally, the relevance of assumption (7) has been studied by Zhu and Hamielec,\cite{48} who compared simulations results with and without this assumption. It turned out that these effects are important for very short primary chains (10^2 units), in the presence of unequal reactivity of the two monomers \((k_{p22}/k_{p11} \approx 5-10)\). As in the present systems the primary chains are known to be very long (10^5 units)\cite{31} and the reactivity of the two monomers differs by a factor 2 only (Table 2.4), it is expected that the assumption of equal crosslinking density for chains born at the same conversion is quite reasonable.

The model solution can be conveniently organized into three successive steps: i) calculation of the primary chains CLD, ii) estimation of the total crosslinking density \(\rho\) and iii) combination of the primary chains according to the crosslinking density to reconstruct sol and gel fractions as well as the average molecular weight between two consecutive crosslinks. Note that the monomer and PDB balances, as well as the pseudo-kinetic constants and the radical balances are reported in the appendix (equations (A1)-(A10)).

### 2.3.1. Primary Chains CLD

As previously mentioned, primary polymer chains are linear and therefore the number and weight CLDs at conversion \(\theta\) are derived from equations (2.4) and (2.5) valid for linear chains\cite{49}:

\[
 f_n(n,\theta) = \frac{\alpha(\theta)}{(1+\alpha(\theta))^n} \left[ \frac{\tau(\theta)+0.5\alpha(\theta)\beta(\theta)(n-1)}{\tau(\theta)+0.5\beta(\theta)} \right]^{\tau(\theta)+0.5\beta(\theta)} \quad (2.4)
\]
2.3.2. Crosslinking density

The crosslinking density of a polymer network depends on the reaction of a radical of one chain with a PDB of another chain, leading to the formation of one effective crosslinkage. Several intramolecular reactions, such as primary and secondary cyclizations,\(^{[35]}\) consume PDB without the formation of effective crosslinkages and need to be accounted for. To clarify the different nature of primary, secondary cycles and crosslinks, consider Figure 2.2.

\[
f_n(n, \theta) = \frac{\alpha(\theta)}{(1 + \alpha(\theta))^{n+1}} \left[ \tau(\theta) + 0.5 \alpha(\theta) \beta(\theta)(n-1) \right] n
\]  

(2.5)

where \( \tau = \frac{k_{\text{int}}^* R_{\text{ext}}}{k_{p1}^* M_1 + k_{p2}^* M_2} \), \( \beta = \frac{k_{\text{int}}^* R_{\text{ext}}}{k_{p1}^* M_1 + k_{p2}^* M_2} \) and \( \alpha = \tau + \beta \).

All symbols are detailed in Appendix A.
Moreover, to correctly describe the kinetics of the crosslinkage formation, two time or conversion coordinates have been used, one corresponding to the chain birth and the other to the actual reaction extent, as already discussed by Tobita and Hamielec.\textsuperscript{[35]}

In particular, properties characterising the primary chains during their life are called “instantaneous” and properties evolving after chain termination “additional”. Such properties are function of the two coordinates: in terms of conversion, chain birth conversion, $\theta$, and actual conversion, $\psi$. As an example, at the actual conversion $\psi$, the total crosslinking density $\rho (\theta, \psi)$ of a primary chain born at conversion $\theta$ is the sum of the instantaneous crosslinking density $\rho_i (\theta)$ and the additional crosslinking density $\rho_a (\theta, \psi)$ accumulated after its “death”.

$$\rho (\theta, \psi) = \rho_i (\theta) + \rho_a (\theta, \psi) \quad (2.6)$$

It is worth noting that implicitly the same value of $\rho$ is assumed whatever the chain length.

2.3.2.1. Instantaneous properties

Crosslinking density – The propagation with PDB leads to the crosslinking of two previously independent chains increasing thus the crosslinking density. The global rate of the crosslinking reaction is:

$$r_{\text{cross}} = k_{p3}^* R_{\text{tot}} D_3 \quad (2.7)$$

$D_3$ being the PDB concentration, $R_{\text{tot}}$ the total radical concentration and $k_{p3}^*$ the pseudo-kinetic rate constant of crosslinking. The instantaneous crosslinking density is defined as the ratio between the PDB propagation rate and the total rate of monomer incorporation, as defined in (2.8).
Primary cyclization – This intramolecular reaction leads to the formation of primary cycles in the polymer network. Primary cycles are only closed by one crosslink and differ on this point from secondary cycles. The mechanism of cyclization was originally proposed by Jacobson and Stockmayer\textsuperscript{[50]} for linear polycondensation systems. Further modifications have been proposed by Tobita\textsuperscript{[47]} and Zhu et al.\textsuperscript{[51]} They pointed out the importance of properly estimating the cyclization rate in order to evaluate the gel point with accuracy. Indeed, intramolecular primary cyclization leads to the consumption of PDB without linking two primary chains, thus delaying gel formation. According to Landin and Macasoko\textsuperscript{[52]} the rate of cyclization is proportional to the rate of incorporation of divinyl monomers. The higher the rate of divinyl addition, the higher the number of PDB in the active chains and therefore, the probability of cyclization. This probability is taken into account by the additional coefficient $\eta_{cp}$, in the expression of the rate of primary cyclization:

$$r = \eta_{cp} \frac{dM_2}{dt} = \eta_{cp} k^*_{p2} M_2 R_{tot}$$

(2.9)

and the instantaneous primary cyclization density is given by:

$$\rho_{cp} (\theta) = \eta_{cp} \frac{k^*_{p2} M_2}{k^*_{p1} M_1 + k^*_{p2} M_2} = \eta_{cp} X_2$$

(2.10)

Notably $\eta_{cp}$ is influenced by many factors, such as flexibility of the chain, amount of crosslinker, primary chains length, quality of the solvent and absolute concentration. All these dependences should be accounted for in a genuinely predictive model: here, we limit ourselves to a constant, effective value, whose validity is therefore restricted to the specific set of operating conditions under examination.
Secondary cyclization – It is worth noting that this monomolecular reaction is assumed to be bimolecular when considering “primary chains”. Let us consider two primary chains (one active and the other terminated) already linked together. The radical can propagate with any type of monomers including its own PDBs: the proximity between the radical and the PDB makes the probability of secondary cyclization larger than that of the reaction with PDB of other chains. Consequently an adjustable quantity, the so-called secondary cyclization constant $\alpha_{cs}$, is introduced to enhance the corresponding rate constant. It can be greater than unity; moreover it is a function of length of the chains, distance between consecutive PDB, and accessibility of the double bonds entrapped in the polymer network. Because of the lack of understanding for most of these phenomena, also the value of this quantity is assumed to be constant. Despite its roughness, this zero-order approximation has already been proved to provide satisfactory results.\cite{47} The rate of secondary cyclization is expressed by:

$$ r_{cs} = \alpha_{cs} k_{p3} D_3 R_{tot} \tag{2.11} $$

and the instantaneous secondary cyclization density is given by:

$$ \rho_{cs,i}(\theta) = \alpha_{cs} \rho_i(\theta) \tag{2.12} $$

2.3.2.2. Additional properties

Additional crosslinking density – The maximum theoretical fraction of crosslinked units (i.e. the crosslinking density) would be equal to the fraction of incorporated divinyl monomer in the active chains ($X_z$) if no other reactions, apart from crosslinking, consumed them. Actually, the crosslinking density is lower than this maximum value, as several other reactions consume double bonds: primary cyclization and secondary cyclization. Therefore, a partial differential
equation describing the additional crosslinking density evolution with conversion has been proposed by Tobita\cite{47} as shown in equation (2.13):

\[
\frac{\partial \rho_{a}(\theta,\psi)}{\partial \psi} = \frac{k_{p3}^{*}(X_{2}(\theta) - \rho_{cs,a}(\theta,\psi) - \rho_{cp}(\theta) - \rho_{a}(\theta,\psi))}{(k_{p1}x_{1} + k_{p2}x_{2})(1-\psi)}
\]

where \(x_{1}\) and \(x_{2}\) are the monomer fractions corresponding to \(M_{1}\) and \(M_{2}\). In the frame of the zero-order approximation described above, \(\rho_{cs,a}\), the additional secondary cyclization, is assumed to be equal to the additional crosslinking density multiplied by \(\alpha_{cs}\):

\[
\rho_{cs,a}(\theta,\psi) = \alpha_{cs} \rho_{a}(\theta,\psi)
\]  

### 2.3.2.3. Overall crosslinking density

Given \(\rho(\theta,\psi)\), the overall crosslinking density of the entire polymer at conversion \(\psi\), is readily evaluated by integration above all possible values of birth conversion:

\[
\bar{\rho}(\psi) = \frac{1}{\psi} \int_{\psi}^{\theta} \rho(\theta,\psi) d\theta \quad \theta \leq \psi
\]

Through the overall crosslinking density it is possible to access other properties of the polymer network, such as the sol and gel partitioning and the molecular weight distribution between crosslinks, as briefly illustrated in the next section.

### 2.3.3. Sol and gel partitioning and molecular weight distribution between crosslinks

**Sol and gel partitioning** – Based on Flory’s model, Tobita proposed to calculate the weight fraction of sol at every birth conversion.\cite{47} Assuming that the crosslinking density is the
same for all the primary chains born at the same conversion, Flory’s original formula\textsuperscript{[25]} becomes equation (2.16):

\[
w_i(\theta, \psi) = \sum_{n=1}^{\infty} f_w(n, \theta) (1 - \rho(\theta, \psi) (1 - w_i(\theta, \psi)))^n
\]  \hspace{1cm} \text{(2.16)}

Considering a primary chain of length \(n\), this equation can be understood as follows:

- \((1 - w_i(\theta, \psi))\) represents the probability for a single unit of this chain not to be part of the sol (meaning to be part of the gel);
- multiplying by \(\rho(\theta, \psi)\), provides the probability for the same unit to be crosslinked and part of the gel;
- thus \((1 - \rho(\theta, \psi) (1 - w_i(\theta, \psi)))^n\) is the probability that all the units of this chain of length \(n\) are not crosslinked with the gel, meaning they are part of the sol.

By introducing \(f_w(n, \theta)\) from equation (2.5) into equation (2.16) and expanding the series, a polynomial equation was derived for \(w_i\)\textsuperscript{[47]}

\[
w_i(\theta, \psi) = AG_i [T + ABG_i]
\]  \hspace{1cm} \text{(2.17)}

with \(A = \alpha(\theta)/d(\theta, \psi), \quad T = \tau(\theta)/d(\theta, \psi), \quad B = \beta(\theta)/d(\theta, \psi), \quad d(\theta, \psi) = \alpha(\theta) + \rho(\theta, \psi) w_g(\theta, \psi)\) and \(G_i = 1 - \rho(\theta, \psi) w_g(\theta, \psi)\). The derivation of this equation is also reported by Sajjadi\textsuperscript{[45]}. Solving this equation at each value of \(\theta\), \(w_i(\theta, \psi)\) is calculated, and the weight fraction of gel is readily obtained as:

\[
w_g(\theta, \psi) = 1 - w_i(\theta, \psi)
\]  \hspace{1cm} \text{(2.18)}

From this equation the overall gel fraction at conversion \(\psi\), \(w_g(\psi)\), is evaluated by integration over all possible birth conversions, as already shown in equation (2.15).
**Molecular weight distribution between crosslinks** – Under the assumption of primary chains long enough to neglect end effects, Tobita [53] proposed the following equation for the molecular weight distribution between consecutive crosslinks:

\[
f_n^i (n, \theta, \psi) = n \left(1 - \rho_{el}^i (\theta, \psi)\right)^{n-1} \rho_{el}^i (\theta, \psi)^2
\]  

(2.19)

where \( \rho_{el}^i \) represents the elastic crosslinking density defined in terms of double bonds. In other words:

\[
\rho_{el}^i = \rho_{el}^f \left(1 + \rho_i + \rho_{cx,i} + \rho_{cy}\right)
\]  

(2.20)

\[
\rho_{el} (\theta, \psi) = \rho(\theta, \psi) + \rho_{cx} (\theta, \psi)
\]  

(2.21)

and \( \rho_{el} \) is defined as the sum of the total crosslinking density and the secondary cyclization density. When increasing the crosslinking density, the elasticity decreases and the elastic modulus increases. Nevertheless the elastic crosslinking density does not account for physical crosslinkages which may play a role in the elastic properties. Therefore, it is not directly related to Young’s elastic modulus characterizing the mechanical strength of the material.[54, 55] The zero and first-order moments of this distribution are readily evaluated from their definitions as:

\[
\mu_0^i (\theta, \psi) = \sum_{n=1}^{\infty} \left(1 - \rho_{el}^i (\theta, \psi)\right)^{n-1} \rho_{el}^i (\theta, \psi)^2
\]  

(2.22)

\[
\mu_1^i (\theta, \psi) = \sum_{n=1}^{\infty} f_n^i (n, \theta, \psi)
\]  

(2.23)

These are instantaneous quantities: their corresponding cumulated values \( \overline{\mu}_0^i (\psi) \) and \( \overline{\mu}_1^i (\psi) \) are calculated by integration over all birth conversion values. Finally, the number average molecular weight between two consecutive crosslinks is expressed as:
2.4. Parameter evaluation

The values of all model parameters used for the following simulations are listed in Table 2.4. The values of the kinetic parameters specific of the monomer/initiator system under examination (initiator dissociation rate constant $k_d$, crosslinking reactivity ratio $r_3$ and cyclization coefficients of primary ($\eta_{cp}$) and secondary cyclization ($\alpha_{cs}$)) were evaluated from experimental and literature data as explained below.

2.4.1. Initiator dissociation

The redox system TEMED/APS has been used in this work; despite the large popularity of this initiating system very few data are available in the literature. To estimate the initiator decomposition constant, a homopolymerization of Am in aqueous solution has been carried out. In particular, 2.5 mL solution with 10 % w/w of Am, 8.32 µL APS (10 % w/w solution) and 16.8 µL TEMED (10 % w/w solution) was polymerized at room temperature. The double bond consumption was monitored by UV spectroscopy at 286 nm as presented in Figure 2.3. Assuming the pseudo-steady state assumption and a first order reaction with respect to APS, the initiation rate constant is evaluated from the slope at zero conversion through equation (2.25):

$$\frac{d\psi}{dt}\bigg|_{t=0} = \frac{k_p}{\sqrt{k_i}} \left(2fk_dI_2 \right)^{1/2}$$  \hspace{1cm} (2.25)
Given $k_p^2 / k_c = 11.83 \, \text{L/mol/s}$ for Am$^{[38]}$ and assuming initiator efficiency $f$ equal to 0.5, the dissociation rate constant of APS in the presence of TEMED at APS:TEMED ratio of 1:4 has been estimated as $k_d = 2.77 \times 10^{-5} \, \text{s}^{-1}$. The advantage of employing such a decomposition rate constant is that all the elementary steps involved in the quite complex redox reaction involving APS and TEMED are lumped together.

![Figure 2.3 Conversion of Am during the polymerization reaction; consumption of double bonds monitored by UV spectroscopy.](image)

2.4.2. **Cross-propagation reaction**

To evaluate the cross-propagation rate constants, $k_{p_{12}}$ and $k_{p_{21}}$, the values of the reactivity ratios ($r_1$ and $r_2$) as well as of the homopropagation rate constants, $k_{p_{11}}$ and $k_{p_{22}}$, are needed. These values have been found in the literature; note that the reactivity ratios were evaluated from composition data$^{[30]}$ using the method of Kelen-Tudös.$^{[56]}$. Concerning the propagation of pendant radicals, due to the lack of experimental information, equal reactivity of the double
bonds has been assumed. This approximation, originally proposed by Flory,\cite{25} corresponds to
assume $k_{p1} = k_{p2}$ and $k_{p3} = k_{p1}$. When dealing with small amounts of crosslinker, these two
parameters do not play a decisive role because of the correspondingly small amounts of pendant radicals.

### 2.4.3. Crosslinking and secondary cyclization

The formation of a polymer network is mediated by two different reactions: the
intermolecular attack of a radical chain to the PDB of another chain, i.e. crosslinking and the
intramolecular secondary cyclization, where a backbone radical of one chain propagates till it
attacks a PDB of the same chain. Secondary cyclization is accounted for by the parameter $\alpha_{cs}$,
whereas crosslinking by the kinetic constants $k_{p1}, k_{p2}$ and $k_{p3}$. Employing the same hypothesis
introduced by Landin and Macosko and defining $r_j = k_{p_j} / k_{p_i}$, the following equality applies:\cite{52}

$$\frac{1}{r_{31}} = \frac{1}{2r_{32}} = r_{33} = \frac{r_{33}}{2} = r_3$$

(2.26)

As a consequence, only two kinetic parameters need to be estimated, namely $\alpha_{cs}$ and $r_3$. Their
evaluation procedure has been proposed by Landin and Macosko\cite{52} and relies on two types of
experimental data: PDB conversion and gel point conversion.

Clearly, several combinations of $\alpha_{cs}$ and $r_3$ can be used to fit one of the two experimental
information, but only one specific combination is able to satisfy both constraints at the same
time. Employing the PDB conversion (for $w_c = 14\%$ and $w_c = 28\%$) and the gel points (for
$w_c = 0.02\%$ and $w_c = 0.04\%$) reported by Tobita and Hamielec\cite{31} at 25°C, couples of $r_3$ and $\alpha_{cs}$
values were fitted to satisfy both conditions, namely comparing the predictions of gel point and
the PDB conversion\cite{57} (equations (2.27)-(2.29)) against the experimental data.
\[
\frac{dD_3}{d\psi} = \frac{dD_3 / dM_2}{1 + dM_1 / dM_2}
\]

(2.27)

\[
\frac{dM_1}{dM_2} = \frac{r_{12}M_1(M_1 + M_2 / r_{12} + D_1 / r_{23})}{r_{21}M_2(M_1 / r_{21} + M_2 + D_2 / r_{23})}
\]

(2.28)

\[
\frac{dD_3}{dM_2} = (1 + \alpha_{cr}) \frac{D_3 r_{23} (M_1 / r_{31} + M_2 / r_{23} + D_3)}{M_1 / r_{21} + M_2 + D_3 / r_{23}} - (1 - \eta_{cr})
\]

(2.29)

Notably, equations ((2.27)-(2.29)) are fully equivalent to those shown in the appendix ((A1)-(A3)) and were re-written in this form to highlight the parameters to be estimated.

The solutions satisfying both constraints simultaneously are shown in Figure 2.4 as the shaded area resulting from the intersection of the four calculated curves (PDB conversion for \( w_c = 28\% \) and \( w_c = 14\% \) and gel point constraints applied for both \( w_c = 0.02\% \) and \( w_c = 0.04\% \)). Ideally, the four curves should be two, one for the gel point and one for the PDB conversion, independent from the crosslinker amount, thus leading to only one single pair of values. However, due to the experimental error, a range of pair values is identified, highlighted by the shaded area shown in Figure 2.4: such area is quite narrow, allowing thus an accurate estimation of \( r_3 \) and \( \alpha_{cr} \). In particular, the following two values have been selected: \( r_3 = 5.76 \) and \( \alpha_{cr} = 7.61 \). It is worth noticing that this parameter evaluation has been carried out assuming the primary cyclization coefficient \( \eta_{cr} \) equal to 0.81. This value has been obtained by Tobita and Hamielec \[31\] and Naghash and Okay \[32\] by fitting their own experimental data at low conversion.
Figure 2.4 Graphical determination of $r_3$ and $\alpha_{cs}$ according to the procedure described by Landin and Macosko.\[^{52}\]

“Gel point conversion” (dashed lines) represent all the ($r_3$, $\alpha_{cs}$) pairs satisfying the constraints on the gel point conversion. “PDB conversion” (continuous lines) represent ($r_3$, $\alpha_{cs}$) pairs satisfying the constraint on the PDBs conversion. The shaded area obtained by the intersection of the four curves corresponds to the set of parameters $r_3$ and $\alpha_{cs}$ satisfying both constraints simultaneously.

It is worth mentioning that Tobita and Hamielec\[^{31}\] reported values of $r_3$ and $\alpha_{cs}$ in the order of $10^3$, hence quite different from those estimated here employing the mentioned fitting procedure,\[^{52}\] although the authors themselves consider their parameter evaluation quite poor. Despite the parameter discrepancy, the mechanism of Am/BAm network formation is invariably dominated by secondary cyclization (i.e. $\alpha_{cs} > 1$). Moreover, defining $k_{p3}^T = k_{p3}^s (1 + \alpha_{cs})$ as the sum of crosslinking and secondary cyclization and estimating the ratio $k_{p3}^T / (k_{p1}^s + k_{p2}^s)$, values in the order of $10^0$ are obtained, as also stated by Tobita and Hamielec: this confirms that the overall PDB consumption is predicted in the very same way despite the largely different absolute values of the parameters $r_3$ and $\alpha_{cs}$. 
To further confirm the reliability of our estimation, the gel fraction against conversion for \( w_c = 0.04\% \) calculated using our parameter values (continuous line) and Tobita and Hamielec parameter values \(^{[31]}\) (dashed line) is shown in Figure 2.5. Notably, the values of the initiation parameters have been found in the literature,\(^{[47]}\) whereas equation (2.16) has been employed to estimate the gel curve. While the gelation onset is predicted at 11% of conversion in the first case, in very good agreement with the experimental data by Tobita and Hamielec,\(^{[31]}\), no gelation at all is predicted using the larger \( r_3 \) and \( \alpha_{cs} \) values previously suggested in the literature. This can be explained considering that \( r_3 \approx 10^3 \) indicates crosslinking reactions 3 orders of magnitude slower than propagation, thus suppressing gel formation.

![Figure 2.5 Gel fraction against conversion predicted for the case \( w_c = 0.04\% \) employing \( \alpha_{cs} \) and \( r_3 \) values evaluated by fitting in this work (continuous line) and proposed by Tobita and Hamielec\(^{[31]}\) (dashed line). The experimental gel point reported by Tobita and Hamielec is at 11% of conversion.](image-url)
2.4.4. Intramolecular cyclization

The primary cyclization coefficient, $\eta_{cp}$, has been determined from swelling measurements, taking advantage of the well-known Flory-Rehner equation:

$$\ln\left(1 - \phi_p\right) + \phi_p + \chi\phi_p^2 = -\frac{v_m^0 d_p}{M_n^c} \left(\phi_p^{1/3} \phi_0^{2/3} - \frac{\phi_p}{2}\right)$$  \hspace{1cm} (2.30)

where $\phi_p$ is the volume fraction of the polymer in the mixture with the swelling solvent at equilibrium, $\chi$ is the Flory-Higgins interaction parameter, $v_m^0$ is the molar volume of the solvent, $\phi_0$ is the volume fraction of polymer at preparation and $d_p$ the polymer density. A simple equation to compute the average molecular weight between two consecutives crosslinks involving the primary cyclization coefficient has been proposed by Okay:

$$\frac{M_n^c}{M_n^a} = \frac{1}{2X \left(1 - \eta_{cp}\right)}$$  \hspace{1cm} (2.31)

with $X$ being the initial ratio between Am and BAm. Combining the last two equations, and making $\eta_{cp}$ explicit, the following relationship providing $\eta_{cp}$ as a function of the measurable quantity $\phi_p$ is finally obtained:

$$\eta_{cp} = 1 - \frac{M_n^a}{v_m^0 d_p} \frac{\ln\left(1 - \phi_p\right) + \phi_p + \chi\phi_p^2}{2X \left(\frac{\phi_p}{2} - \phi_p^{1/3} \phi_0^{2/3}\right)}$$  \hspace{1cm} (2.32)

This equation will be used in the next section to evaluate $\eta_{cp}$ from the swelling data summarized in Table 2.2.
2.4.5. Termination reaction

In the present model, diffusion-controlled termination rate constants have been considered; specifically, the kinetic expression suggested by Buback et al.[40] was selected:

\[
k_{i_0} = \frac{1}{k_{i_0}^{\text{chem}}} + \frac{\exp(C_{i_0}W_t\psi)}{k_{i_0}^0 k_{t,D_i}} + C_{RD,i} k_{p_0} (1 - \psi) \quad (2.33)
\]

Such equation has been applied for homo-terminations; the cross termination rate constants have been estimated as geometric averages:

\[
k_{i_0} = \sqrt{k_{i_x} k_{i_y}} \quad (2.34)
\]

Notably, the values of \(C_{i_0}, C_{RD,i}, k_{i_0}^0\) have been considered equal for all radicals and have been selected from the ranges suggested by Buback et al.,[40-42] as no estimates of those parameters were found in the literature for this specific system. In particular, \(C_{i_0} = 27\), (literature range: 10-27), \(C_{RD,i} = 250\) (literature range 94-1900) and \(k_{i_0}^0 = 2 \times 10^9\) L mol\(^{-1}\) s\(^{-1}\) were chosen.

Notably, these values were selected to give a termination rate constant at zero conversion which lies in between the termination rate constants of Am and BAm (Table 2.4).

Finally, since the values of the termination rate constants for the radicals on PDB are not easily accessible, the termination rate constant is set equal to the one of the monovinyl monomer, i.e.:

\[
k_{i_{3,3}} = k_{i_1} \quad (2.35)
\]
2.5. Results and discussion

2.5.1. Simulation of Am/BAm copolymerization

The comparison of the model predictions to the experimental data was done at different amounts of crosslinker (\( w_c = 3\%, 4\% \) and 5\%) and different monomer concentrations (\( w_i = 3-16\% \)). In addition to predicting quantities directly comparable to the experimental results, the model can be used to calculate properties not measured experimentally, such as the crosslinking density, or the CLD of “primary chains” in the gel polymer. The two latter quantities provide unique information towards a better understanding of the synthetized hydrogel microstructure.

As previously mentioned, swelling data were used to estimate the primary cyclization coefficient, \( \eta_{cp} \). This coefficient is expected to be affected by the dilution of the monomer mixture. The higher the dilution, the higher the probability of intramolecular compared to intermolecular reactions. The primary cyclization coefficient is calculated from equation (2.32) using the results of the three series of experiments (\( w_c = 3-5\% \)). An empirical fitting is then proposed to describe the variation of the primary cyclization coefficient with the monomer concentration, \( w_i \):

\[
\eta_{cp} = \exp(-3.356w_i^2) \tag{2.36}
\]

The final results are presented in Figure 2.6; as already noticed by Tobita,\cite{Tobita} the amount of crosslinker has little effect on the primary cyclization coefficient in this range of concentrations. A significant role of the primary cyclization reaction is expected in the system under examination, as already observed in the literature.\cite{32,33} At low monomer concentration (\( w_i = 3\% \)) the fraction of PDBs involved in primary cyclization reaches 99.5\%; this means that, even though less than 1\% of the potential PDBs is actually available for crosslinking reactions,
complete gelation of the polymer network can be achieved. On the other hand, the primary cyclization coefficient decreases to 91% when the monomer concentration increases up to 16%.

![Figure 2.6 Estimated value of $\eta_{cp}$ as a function of the monomer weight fraction for three different amounts of crosslinker, $w_c$. The line corresponds to the fitting equation $\eta_{cp} = \exp\left(-3.356 \, w_c^2\right)$.](image)

Using the empirical expression for $\eta_{cp}$ introduced above, the comparison between experimental and model predicted swelling ratios (employing equation (2.30)) is obtained (cf. Figure 2.7). The agreement is generally good, particularly at the highest concentrations; discrepancies appear at high dilution, where the model under-predicts the swelling ratios. However, it should be mentioned that the swelling ratios observed experimentally at very low amount of monomer are extremely large and therefore difficult to measure because the gel slices are really soft. This behaviour is even more pronounced when the concentration of crosslinker is also low; therefore, the reliability of these measurements is quite questionable. Figure 2.7 also shows how the swelling ratio decreases when increasing monomer concentration, i.e. stronger gels are obtained with concentrated systems. These results confirm the impact of the system dilution on the
primary cyclization reactions and, in turn, on the properties of the gel. As suggested by the plateau reached at the highest concentrations, the competition between intra- and intermolecular reactions tends to favour the latter and the effect of the dilution becomes less important at high concentration. Thus summarizing, the polymer network structure is not only dependent on the relative concentration of divinyl monomer with respect to that of the monovinyl monomer \((w_c)\) but also on the absolute value of the concentration of the monomer mixture \((w_i)\).
Figure 2.7. Swelling ratio versus monomer weight fraction for different amounts of crosslinker ($w_c$ = (a) 3%, (b) 4% and (c) 5%). Continuous lines represent model prediction; symbols are experimental values. Error bars represent the standard deviation of 8 different samples.
Notably, the $\eta_{cp}$ estimated from our swelling measurements is always comprised between 0.9 and 0.99, in agreement with Okay et al.,\cite{33} whereas Tobita and Hamielec\cite{31} and Naghash and Okay\cite{32} reported the smaller value 0.81, estimated employing titration measurements. This discrepancy can be probably explained reminding that pre-gel soluble polymer was used for the titration in the latter cases, whereas swelling measurements on the gel were performed in this work and in Okay et al.\cite{33} In particular, cyclization reactions are expected to be really significant at high conversion in the gel because of monomer depletion, while the primary cyclization coefficient obtained by titration of the sol polymer PDB is extrapolated at zero conversion. As a matter of fact, Stockmayer\cite{27} was already suggesting not to use the statistical approach (at that time still neglecting cyclization) in the post gelation period because cyclization reactions at high conversion could generate a major difference between sol and gel polymer.

2.5.2. Validation of the model

In order to provide a general model validation as well as check the reliability of the estimated parameter values, different swelling data published by Okay et al.\cite{33} are finally simulated (i.e. predicted) using the estimated parameters. Experimental results are reported at $w_i = 5\%$ and different amounts of divinyl monomer ($w_c = 0.7\% - 15\%$). The $\eta_{cp}$ value of 0.99 estimated from equation (2.36) at this monomer concentration is comparable to the value of 0.95 already proposed by Okay et al.\cite{33} and leads to good predictions, as shown in Figure 2.8.
In Figure 2.8 the prediction obtained with $\eta_{cp} = 0$ is also reported, in order to appreciate that primary cyclization has to be accounted for to obtain correct predictions. Moreover, the predictions employing the value $\eta_{cp} = 0.81$, suggested by Tobita and Hamielec \cite{31} and Naghash and Okay \cite{32}, is also reported: it is confirmed that the suggested value of 0.81 can be employed only in the pre-gel regime, otherwise leading to erroneous predictions of the gel properties. The results obtained by Tobita and Hamielec \cite{31} by Naghash and Okay \cite{32} by Okay et al.\cite{33} and in the present work, indicate that the primary cyclization is most likely a conversion-dependent reaction, with an increased relevance along the reaction coordinate.
2.5.3. Parametric calculations

The parameters provided in the present work can be used to control the hydrogel structure for Am/BAm systems. By properly tuning the total monomer concentration \( w_t \), the efficiency of cyclization will be affected (equation (2.36)), leading to changes both in the crosslinking density structure as well as in the gel conversion. A set of parametric calculations has been performed to clarify the impact of \( \eta_p \) on the gel properties: the results are reported in Figure 2.9 (gel fraction) and Figure 2.10 (crosslinking density).

![Figure 2.9 Gel fraction as a function of conversion for different values of \( w_t \) (numbers indicate weight percentages).](image-url)
As expected, when increasing $w_i$ (from 12% to 30%) the efficiency of primary cyclization is reduced, therefore more PDB are available for crosslinking, resulting in the anticipated gelation shown in Figure 2.9. The same reasoning can explain the trends observed in Figure 2.10: when increasing $w_i$, more PDB are consumed via crosslinking reactions, leading to larger values in the crosslinking densities of both the sol and gel phase.

The impact of changing the total monomer concentrations can be further appreciated when calculating the primary and the elastic crosslinking densities versus conversion (equation (2.10) and (2.21), respectively). Employing the aforementioned range of $w_i$, these quantities are calculated and shown in Figure 2.11.
Once more, by increasing the total monomer concentration, the crosslinking reaction consumes more PDB than the primary cyclization, leading to an increase in the elastic crosslinking density (hence to a stiffer gel) and to a decrease in primary cyclization density. The latter findings not only prove the soundness of the estimated parameters but also indicate that the final network structure can be tuned by changing the total monomer concentration.

2.6. Conclusions

New parameter values for the reactions of crosslinking and intramolecular cyclization have been estimated for the solution copolymerization of Am/BAm, using the probabilistic model proposed by Tobita and Hamielec,\cite{35} an effective tool for the simulation of kinetically controlled copolymerization processes. In particular, an empirical expression as a function of the overall
content of monomer mixture is proposed for the primary cyclization efficiency ($\eta_p$), by fitting model predictions against our own experimental data of swelling for hydrogels produced at three different weight fractions of divinyl monomer (3-5%) and fourteen monomer weight fractions (3-16%). Finally, the general reliability of the estimated parameter values and of the selected modelling approach is proved by comparison with literature data for the same copolymerization system: the average molecular weight between consecutive crosslinks is well predicted using the $\eta_p$ value as estimated through the empirical relationship developed in this work. Finally, parametric simulations showed the impact of primary cyclization on the hydrogel properties.
3. Modeling multiradicals in crosslinking MMA/EGDMA bulk copolymerization

3.1. Introduction

Free radical copolymerization has been studied since the late 40s, where the first works of Flory \[58\] and Stockmayer \[43\] put up solid bases for the understanding of such reacting systems. Since then, several models were proposed,\[59, 60\] and ameliorations performed, e.g. in recognizing the kinetic rate constants dependence upon chain length\[61\] and conversion.\[59, 62\] The most common assumptions adopted when modeling free radical polymerization reactions are the pseudo steady-state assumption (PSSA) and the mono-radical hypothesis. The first assumption implies that the radical chains have such a high reactivity, that they can be considered at steady state with respect to the other species present in the reactive mixture, while the latter one considers that the maximum number of active sites per chain is one. The mathematical and numerical simplifications resulting from these assumptions are indeed of great benefit to limit the computational effort.

While in linear copolymerization the latter assumption usually holds, things might change when crosslinking, or transfer to polymer and termination by combination occur. In these cases, a gel phase arises, changing the reaction environment to such an extent that radicals can accumulate in the reactive mixture and even coexist on the same chain. The first authors to raise

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\[2\] The present chapter has been partially published as: S. Lazzari, G. Storti, “Modeling Multiradicals in Crosslinking MMA/EGDMA Bulk Copolymerization”, Macromolecular Theory and Simulations, 1, 23, (2014)
this problem were Kuchanov and Pis’men,\textsuperscript{[63]} who discussed the role of multiradicals (MRs) and PSSA in the gel formation and concluded that further investigation was required.

Later on, Zhu and Hamielec addressed this problem\textsuperscript{[5]} and solved the non-stationary, multiradical population balance equations for both branching and crosslinking free-radical polymerization, up to the gel point by means of the method of moments. They established a criterion for deciding whether or not taking into account MRs: the critical parameter identified was the ratio of the propagation constant over the termination one, $\frac{k_p}{k_t}$. If the ratio is larger than $10^{-3}$, MRs and non-stationary state should be accounted for, as summarized in equation (3.1):

\[
\frac{k_p}{k_t} \begin{cases} 
< 10^{-3} & \rightarrow \text{monoradical+PSSA} \\
\geq 10^{-3} & \rightarrow \text{multiradical}
\end{cases}
\] (3.1)

After this first paper, several other criteria for specific situations were proposed. For instance, Zhu\textsuperscript{[64]} studied a system involving a peroxide initiator which favors transfer to polymer, leading to significant formation of MRs. Accordingly, a new criterion was proposed for this specific case (polymer modification), stating that monoradicals and PSSA are acceptable if the ratio of radical initiation rate $R_n$ over the product of hydrogen abstraction rate constant $k_{HA}$ by the square of the total concentration of polymerized units $\mu$ is less than $10^{-7}$, as indicated in equation (3.2):

\[
\frac{R_n}{k_{HA} \mu^2} \begin{cases} 
< 10^{-7} & \rightarrow \text{monoradical} \\
\geq 10^{-7} & \rightarrow \text{multiradical}
\end{cases}
\] (3.2)

In another contribution, Zhu and Tobita\textsuperscript{[65]} studied a similar system and calculated the distribution of MRs starting from primary polymer molecules having a Schulz-Zimm distribution. Beyond concluding that the Flory/Stockmayer theory is valid irrespectively of the existence of MRs if the crosslinking is random, they suggest that the amount of MRs becomes significant only
when the weight average degree of polymerization reaches sizes comparable to $1/\phi$, being $\phi$ the probability for a monomer unit to bear an active site. Such probability is defined as the ratio of the radical concentration $R_{\text{tot}}$ over the first order moment of the chain length distribution $\mu$:

$$\phi = \frac{R_{\text{tot}}}{\mu}$$  \hspace{1cm} (3.3)

The aforementioned criteria$^{[5, 64, 65]}$ are claimed of practical utility even though rather arbitrary by the authors themselves, who didn’t justify the selected threshold values in a quantitative way.

More recently, further evidence on the need of considering MRs was reported.$^{[66, 67]}$ In the case of branching systems with and without bimolecular termination, Iedema et al. solved the complete 2-D PBES with a Galerkin finite element method using pseudo-distributions and compared the results with Monte Carlo predictions in the case of CSTR reactors.$^{[66]}$ Quite good agreements were found between the results provided by the two methods; moreover, it was shown that the distribution of the active sites per chain conforms to a binomial distribution at constant chain length. Furthermore, it turned out that the monoradical assumption does not hold even at low values of the ratio $k_p/k_i$ when the ratio between the rate constants of chain transfer to polymer and propagation becomes large enough, namely larger than $5 \times 10^{-3}$. This result indicates that the mechanism of formation of nonlinear chains needs to be accounted for in a general criterion intended to estimate the relevance of multiradicals.

Costa and Dias introduced a very comprehensive model based on the methods of the Generating Functions, which accounts for MRs.$^{[67]}$ Comparing the results of such model in terms of average molecular weight with those obtained by a monoradical model solved through a different numerical method (Numerical Fractionation$^{[68]}$), the authors concluded that
discrepancies between the two sets of simulation results could be imputed to the contribution of MRs.

In the case of living free-radical systems, Hernandez-Ortiz et al.\(^6\) reported a MR model for crosslinking polymerization in the presence of nitroxides; the model was solved using the method of moments in the pre-gel region, while the Flory-Stockmayer theory was applied in the post-gel. Even though good agreements with experimental data were found by the same authors using the monoradical assumption in a previous contribution,\(^7\) the more detailed model was applied because considered more appropriate for nonlinear copolymerization with crosslinking. It was found that the formation of multi-capped polymer chains delays the onset of gelation as it prevents the formation of multiradical chains; however, the actual need of introducing MRs in these polymerization systems remains questionable, as the relative abundance of active chains with respect to dormant chains is known to be quite low in controlled polymerization.

In this frame, the aim of the present work is to discuss the relevance of MRs in crosslinking copolymerization, in an attempt to quantify the error made when neglecting multiple active sites and proposing a procedure to decide upon the actual need of taking into account MRs. To do so, a computationally efficient kinetic model accounting for non-stationary MRs and handling gel formation in batch reactors has been developed. Four-dimensional PBEs, taking into account chain length, bridges, pendant double bonds (PDB) and active sites, have been written and solved by means of the Numerical Fractionation\(^6\) and the method of moments. Model calculations have been carried out with reference to the binary system methyl-methacrylate (MMA)/ethylene-glycol-dimethacrylate (EGDMA), whose parameter values are available in the literature. This system was selected because especially suited to the proposed model; as a matter of fact, its crosslinking behavior is not affected by primary cyclization reactions, a kinetic mechanism not included in our model.
3.2. Model development

As anticipated, multiple properties (or internal coordinates) have been used to characterize the unknown distributions of active ($R$) and dead polymer ($P$) chains. In particular the chains are characterized in terms of chain length $r$, number of bridges $b$, number of PDB $i$ and number of active sites $y$. Notably, the radical species need four indices ($R_{r,b,i,y}$), while the dead polymer chains only 3 ($P_{r,b,i}$). The meaning of all symbols is reported in Appendix B.

The multiradical model has been developed based on a kinetic scheme involving initiation, propagation, crosslinking and bimolecular termination by disproportionation and by combination:

1. Initiation

$$I_2 \xrightarrow{k_2} 2I^*$$  \hspace{1cm} (3.4)

2. Propagation

$$I^* + M_1 \xrightarrow{k_{p1}^*} R_{1,0,0,1}$$  \hspace{1cm} (3.5)

$$I^* + M_2 \xrightarrow{k_{p2}^*} R_{1,0,1,1}$$  \hspace{1cm} (3.6)

$$R_{r,b,i,y} + M_1 \xrightarrow{y^*k_{p1}^*} R_{r+1,b,i,y}$$  \hspace{1cm} (3.7)

$$R_{r,b,i,y} + M_2 \xrightarrow{y^*k_{p2}^*} R_{r+1,b,i+1,y}$$  \hspace{1cm} (3.8)

3. Crosslinking

$$R_{r,b,i,y} + P_{q,a,j} \xrightarrow{y^*k_{p1}^*} R_{r+q,b+a+1,i+j-1,y}$$  \hspace{1cm} (3.9)

$$R_{r,b,i,y} + R_{q,a,j,z} \xrightarrow{y^*k_{p2}^*} R_{r+q,b+a+1,i+j-1,y+z}$$  \hspace{1cm} (3.10)
4. Termination by disproportionation

\[
R_{r,b,i,y} + R_{q,a,j,z} \xrightarrow{y k_m^*} R_{r,b,i,y-1} + R_{q,a,j,z-1} \quad \forall y > 1, z > 1
\]  

\[
R_{r,b,i,y} + R_{q,a,j,1} \xrightarrow{y k_m^*} R_{r,b,i,y-1} + P_{q,a,j} \quad \forall y > 1
\]  

\[
R_{r,b,i,1} + R_{q,a,j,1} \xrightarrow{k_m^*} P_{r,b,j} + P_{q,a,j}
\]

5. Termination by combination

\[
R_{r,b,i,y} + R_{q,a,j,z} \xrightarrow{y k_n^*} R_{r+q,b+a,j,y+z-2} \quad \forall y + z - 2 \geq 1
\]  

\[
R_{r,b,i,1} + R_{q,a,j,1} \xrightarrow{k_n^*} P_{r+q,b+a+j}
\]

All the kinetic constants are assumed chain length independent. Pseudo-kinetic rate constants,\textsuperscript{71} defined in the Appendix (equations (B1)-(B4)) as well as conversion-dependent termination rate constants, also reported in the Appendix (equations (B5)-(B6), derived by Li et al.\textsuperscript{72} for the specific system under examination), have been employed. Given the copolymer nature of the system under examination, the three different types of radicals sketched in Table 3.1 are involved. Notably, radicals of type 1 and 2 are terminal radicals on a mono- and di-vinyl unit, respectively, while radicals of type 3 are pendant radicals on di-vinyl monomer units along a chain.
### Table 3.1 - Radical types

<table>
<thead>
<tr>
<th>Radical type</th>
<th>Sketch</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![Sketch 1]</td>
</tr>
<tr>
<td>2</td>
<td>![Sketch 2]</td>
</tr>
<tr>
<td>3</td>
<td>![Sketch 3]</td>
</tr>
</tbody>
</table>

Assuming isothermal, well-mixed batch reactor, the following population balances can be written for active and dead polymer chains, respectively:

\[
\frac{dR_{r,b,i,j}}{dt} = -k_{p}^{*}M_{1}yR_{r,b,i,j} + k_{p1}^{*}M_{1}yR_{r-1,b,i,j} + k_{p2}^{*}M_{2}yR_{r-1,b,i-1,j} \\
- k_{p3}^{*}R_{r,b,i,j}C_{PDB} + k_{p3}^{*}iR_{r,b,i,j}R_{tot} + k_{p3}^{*} \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} yR_{r-1,b-a-1,i-j+1,y}R_{tot} \\
+ k_{p3}^{*} \sum_{z=1}^{r-1,b-1,i+1} \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} (y-z)R_{r-1,b-a-1,i-j+1,y}yR_{q,a,j}R_{tot} \\
- \left(k_{tc}^{*} + k_{td}^{*}\right)yR_{r,b,i,j}R_{tot} + k_{td}^{*}(y+1)R_{r,b,i,j}R_{tot} \\
+ \frac{1}{2} \sum_{z=1}^{r-1,b,i+1} \sum_{q=1,a=0,j=0}^{r-1,b,i+1} (y-z+2)R_{r-1,b-a-1,i-j+1,y}yR_{tot} + \delta(r=1,b=0,i=0,y=1)k_{p1}^{*}M_{1}I^{*} + \delta(r=1,b=0,i=1,y=1)k_{p2}^{*}M_{2}I^{*}
\]

(3.16)

\[
\frac{dP_{r,b,i}}{dt} = -k_{p}^{*}iP_{r,b,i}R_{tot} + \frac{1}{2}k_{tc}^{*} \sum_{q=1,a=0,j=0}^{r-1,b,i} R_{r-1,b-a-1,i-j+1,y}R_{q,a,i}R_{tot} + k_{td}^{*}R_{r,b,i}R_{tot}
\]

(3.17)

Note that the following abbreviations have been used for the sake of brevity:

\[
\sum_{r=1,b=0,i=0}^{k_{1},k_{2},k_{3}} = \sum_{r=1}^{k_{1}} \sum_{b=0}^{k_{2}} \sum_{i=0}^{k_{3}}
\]

(3.18)
where $C_{PDB}$ represents the overall concentration of PDB on both dead and active chains, while $R_{tot}$ is the overall amount of radicals or active sites present on the chains. Moreover, it is worth mentioning that index $y$ is equal to 1 in the dead polymer balance (3.17), as only monoradicals can generate dead polymer chains upon termination.

### 3.3. Model numerical solution

The direct numerical solution of the population balances reported above with four internal coordinates (chain length, bridges, pendant double bond and active sites) would require a huge computational effort.\textsuperscript{[73]} As an alternative, in this work we focus on the Method of Moments, which reduces the problem solution to the evaluation of a few, selected integral properties. Even though this corresponds to a significant loss of information (the complete distribution is no more directly accessible), the number of equations to be solved is drastically reduced and a reliable reconstruction of the distribution is still feasible in some cases.

The moments are calculated only with respect to chain length, bridges and PDB; on the other hand, as the number of active sites or radicals per chain is the focus of this model, their full distribution is accounted for. In other words, the following moments are introduced on alive and dead chains, respectively:

$$
\lambda_{k,k'i,k''i,y} = \sum_{r=1}^{\infty} \sum_{b=0}^{\infty} \sum_{i=0}^{\infty} \rho^{k} b^{k'} t^{k''} R_{r,b,i,y}
$$
\[ \mu_{k_1k_2k_3} = \sum_{q=1}^{\infty} \sum_{a=0}^{\infty} \sum_{j=0}^{\infty} q^k a^k j^k P_{q,a,j} \]  

(3.22)

where the first three subscripts on the left hand side indicate the order of the moment with respect to the first three coordinates, while the last subscript in the moments of the active chains still explicitly represents the corresponding coordinate (number of active sites). In principle, moments of any desired order could be expressed applying the definitions above, equations (3.21) and (3.22), to the original population balances. However, the method is computationally effective when we limit ourselves to a small number of moments, whose order should not be larger than first or second.

When the moment equations are written, the so-called closure problem is readily found, i.e. the need of moments whose order is higher than the maximum calculated.\cite{74} In the present case, we confine ourselves to the simplest case for bridges and PDB (meaning that zero-th and first order moments with respect to these variables are considered sufficient), while moments up to the second order are considered for the chain length. As expected, higher-order moments (i.e., \( \mu_{002} \) as well as \( \mu_{011}, \mu_{101}, \mu_{010} \)) appear in the equations of the dead polymer; the situation is fully equivalent in the case of active chains. To estimate such quantities the approach previously suggested by Kilizel et al.\cite{19} has been employed. For instance, considering the moment of the dead polymer of \( n \)-th order with respect to chain length, zero-th order with respect to the bridges and \( m \)-th order with respect to PDB, \( \mu_{n0m} \), equation (3.23) can be employed:

\[ \mu_{n0m} = \sum_{q=1}^{\infty} \sum_{a=0}^{\infty} \sum_{j=0}^{\infty} q^n j^m P_{q,a,j} = \omega^m \sum_{q=1}^{\infty} \sum_{a=0}^{\infty} \sum_{j=0}^{\infty} q^{n+m} P_{q,a,j} = \omega^m \mu_{(n+m)00} \]  

(3.23)

where \( P_{q,a,j} \) are the dead polymer chains bearing \( q \) units, \( a \) bridges and \( j \) PDB, and the factor \( \omega \) is defined in equation (3.24):
\[ \alpha = \frac{\mu_{100}}{\mu_{001}} = \frac{\sum \sum \sum j P_{q,a,j}}{\sum \sum \sum q P_{q,a,j}} \]  

(3.24)

The physical background of this approximation is the expected homogeneity of the chain composition (fractional amounts of bridges and PDB with respect to chain length): in other words, the ratio between the total number of bridges or PDB and that of monomer units is quickly reaching a constant value at increasing chain length, as it is the case for the chain composition in linear copolymers. By applying this methodology a third order moment on the chain length, \( \mu_{300} \), comes into play. Therefore, the closure formula reported by Hulburt and Katz,\[74\] based on the assumption that the chain length distribution resembles a modified Gamma distribution, has been applied. Namely, in the case of dead polymer, the third order moment is expressed as:

\[ \mu_{300} = 2 \left( \frac{\mu_{200}}{\mu_{100}} \right)^2 - \frac{\mu_{200} \mu_{100}}{\mu_{000}} \]  

(3.25)

and a fully equivalent approach is applied to active chains. Notably, the employed closure equation might be inaccurate in non-batch situations, where different closure equations should be employed.\[75\]

Even if all closure issues could be handled, another major problem needs to be dealt with: for crosslinking systems like those under examination, the divergence of the moments with respect to chain length whose order is larger than one is known to occur at the gel point,\[75\] limiting the applicability of the moment method to the pre-gel interval. To overcome this difficulty, the Numerical Fractionation\[68\] has been combined with the method of moments, thus bypassing the divergence issues and using the same set of equations throughout the whole simulation, without the need to distinguish between a pre- and a post-gel phase. Notably, the
same higher-order moments encountered in the overall moment equations appear in the fractionated moment equations and the aforementioned strategy to estimate them can be applied.

The fractionated population balances are reported in the following. The same notation used for the entire populations holds for the generations, with the addition of a superscript characterizing the generation number. According to the Numerical Fractionation, the polymer chains of the non-linear sol are split into generations, or classes: linear chains are in the first generation (generation zero), and progressively larger and more crosslinked chains are in higher order generations. The actual distribution of chains among generations is dictated by transfer rules from one generation to another: such rules are specific of each system, depending upon the kinetic scheme. The final balances have been separately written for active (equations (3.26)-(3.28)) and dead chains (equations (3.29)-(3.31)), for the first two generations, 0 and 1, and for the generic generation $k$. Notably, the fractionation has been applied with respect to chain length only, since the complete distribution of the active sites was accounted for whereas non-diverging, first order moments were calculated for bridges and PDB. As a matter of fact, the final equations are not involving higher order moments with respect to these coordinates and there is no need to further fractionate the population balances with respect to these variables.

Focusing therefore on the variable chain length, the selected fractionation rules are quite conventional: transfers of chains among generations are possible only from smaller generations to higher ones and only through two mechanisms, termination by combination and crosslinking (including all the reactions where an active chain reacts with the PDB of a dead or active chain). More in detail, transfer from generation 0 (linear chains) to generation 1 occurs solely via a crosslinking reaction between two chains of generation 0. Transfer from generation 1 to generation 2 takes place when two chains of generation 1 react together via crosslinking or termination by combination. The latter rule applies to all other generations, up to the last
generation, $N_{gen}$: when two chains of generation $N_{gen}$ react via termination by combination or crosslinking, they end up in the gel. Notably, crosslinking or termination by combination reactions between any two generations $s$ and $t$ are allowed, but a transfer to a higher generation occurs only if $s = t$, otherwise the new formed molecule stays in the generation of higher order.

Reminding that a full detail with respect to the active sites per chain was desired, the fractionated population balances of the sol polymer (i.e. for generation index smaller than $N_{gen}$) were written for each value of the number of radicals, from 0 to an arbitrary maximum value $N_{rad}$. Chains formed by crosslinking of active chains with large numbers of active sites, larger than $N_{rad}$, are directly transferred to the last generation, i.e. into the gel. It is useful to iterate that the maximum number of radicals per chain, $N_{rad}$, refers to the active sites of polymer chains in the sol. In the gel phase such limit does not apply, which is reasonable considered the huge size of the gel polymer chains and, therefore, the possible large accumulation of active sites in a single chain.

The fractionated population balances consistent with the aforementioned fractionation rules are reported in the following, along with a few, selected comments.

**Generation 0**

$$
\frac{dR_{r,b,i,y}^0}{dt} = -k_p^*M_yR_{r,b,i,y}^0 + k_{p1}^*M_1yR_{r-1,b,i,y}^0 + k_{p2}^*M_2yR_{r-1,b,i-1,y}^0 - k_{p3}^*yR_{r,b,i,y}^0 C_{PDH} - k_{p4}^*yR_{r,b,i,y}^0 R_{rad} - (k_{i0}^* + k_{i1}^*)yR_{r,b,i,y}^0 R_{rad} + \delta(r = 1, b = 0, i = 1, y = 1)k_{p1}^*M_1I^* + \delta(r = 1, b = 0, i = 1, y = 1)k_{p2}^*M_2I^*
$$

Linear chains only can be present in this generation: hence the index $y$ is actually always equal to 1 in this case. If a crosslinking reaction between two linear chains occurs, the newly formed chain
is immediately transferred to generation 1, thus preventing the presence of multiradical chains in generation 0. Moreover, no termination can produce a radical chain of generation 0: for this to happen, a chain needs to bear at least 2 active sites and, as previously explained, this is not possible for linear chains.

**Generation 1**

\[
\frac{dR_{r,b,i,y}^1}{dt} = -k_p^* M_y R_{r,b,i,y}^1 + k_{p1}^* M_1 y R_{r-1,b,i,y}^1 + k_{p2}^* M_2 y R_{r-1,b,i-1,y}^1 \\
- k_{p3}^* y R_{r,b,i,y}^1 C_{PDB} - k_{p3}^* i R_{r,b,i,y}^1 R_{no} \\
+ k_{p3}^* \left( \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y}^0 j P_{q,a,j}^0 + \sum_{z=1}^{y-1} (y-z) \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y-z}^0 j R_{q,a,j,z}^0 \right) \\
+ k_{p3}^* \left( \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y}^0 j P_{q,a,j}^1 + \sum_{z=1}^{y-1} (y-z) \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y-z}^0 j R_{q,a,j,z}^1 \right) (3.27) \\
+ k_{p3}^* \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y}^1 j P_{q,a,j}^0 + \sum_{z=1}^{y-1} (y-z) \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} R_{r-q,b-a-1,i-j+1,y-z}^1 j R_{q,a,j,z}^0 \\
- \left( k_{ac}^* + k_{ad}^* \right) y R_{r,b,i,y}^1 R_{no} + \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} (y+1) R_{r,b,i,y+1}^1 R_{no} \delta(y < N_{rad}) \\
+ k_{ac}^* \sum_{q=1,a=0,j=0}^{r-1,b-1,i+1} (y-z+2) R_{q,a,j,y-z+2}^1 z R_{r-q,b-a,j,z}^0
\]

In the balance of active chains of the first generation, positive terms appear for termination by disproportionation and combination: they reflect the formation of active chains by termination of multiradical chains and, as already explained above, the constraint about the maximum number of radicals per chain, \( y \leq N_{rad} \), has to be always fulfilled. This means that, when \( y = N_{rad} \), the disproportionation term is zero and the summation index in the combination term ranges from 2 to \( y \).
The same considerations made before for the first generation concerning the terminations hold also for the \( k \)-th generation.

Finally, the following population balances can be written for the generations of dead polymer:

**Generation 0**

\[
\frac{dP^0_{r,b,i,y}}{dt} = -k_{p3}^* y P^0_{r,b,i,y} + \frac{1}{2} k_{ic}^* \sum_{q=1,a=0,j=0}^{r-1,b,i} R^0_{r-q,b-a-i-j,1,y} + k_{ic}^* \sum_{q=1,a=0,j=0}^{r-1,b,i} R^0_{r-q,b-a-i-j,1,y} + k_{id}^* R^0_{r,b,i,y} R_{\text{tot}} \delta(y < N_{\text{rad}}) \\
+ \frac{1}{2} k_{ic}^* \sum_{q=1,a=0,j=0}^{r-1,b,i} \sum_{z=1}^{y+1} \sum_{h=0}^{r-1,b,i} R^0_{r-q,b-a-i-j,1,y-z+z} R^0_{q,a,j,z} 
\]

**Generation 1**

\[
\frac{dP^1_{r,b,i,y}}{dt} = -k_{p3}^* y P^1_{r,b,i,y} + k_{ic}^* \sum_{q=1,a=0,j=0}^{r-1,b,i} R^1_{r-q,b-a-i-j,1,y} + k_{id}^* R^1_{r,b,i,y} R_{\text{tot}} + k_{id}^* R^1_{r,b,i,y} R_{\text{tot}} \delta(y < N_{\text{rad}}) \\
+ \frac{1}{2} k_{ic}^* \sum_{q=1,a=0,j=0}^{r-1,b,i} \sum_{z=1}^{y+1} \sum_{h=0}^{r-1,b,i} R^1_{r-q,b-a-i-j,1,y-z+z} R^1_{q,a,j,z} 
\]
Generation \( k \)

\[
\frac{dP^k_{r,b,i}}{dt} = -k^s_{p,i} P^k_{r,b,i} R^k_{rad} + \frac{1}{2} k^s_{ic} \sum_{q=1,a=0,j=0}^{r-1,b,i} R^{k-1}_{r-q,b-a,i-j} R^{k-1}_{q,a,i,j} + k^s_{id} R^k_{r,b,i} R_{tot} + k^s_{tc} \sum_{q=1,a=0,j=0}^{r-1,b,i} \left( \sum_{h=0}^{k-1} R^h_{q,a,i,j} \right)
\]

(3.31)

As anticipated, the resulting set of \( 2(N_{gen} + 1) \) differential-difference equations (equations (3.26)-(3.31)) has been solved by the method of moments. The corresponding moment equations of each generation are summarized in the Appendix. In particular, the first order moments on bridges (equations (B26)-(B31)) and PDB (equations (B32)-(B37)), and the first three-order moments on the chain length were calculated for both active and dead chains using equations (B8)-(B10),(B17)-(B19) for generation 0, equations (B11)-(B13), (B20)-(B22) for generation 1 and equations (B14)-(B16), (B23)-(B25)) for the generic \( k-th \) generation. In those equations, \( \lambda \) and \( \mu \) represent the moments of active and dead polymer chains, respectively, as already introduced in equations (3.21) and (3.22). Keeping in mind that all values of active sites per chain are accounted for (from 0 to the maximum value \( N_{rad} \)), the previously presented \( 2(N_{gen} + 1) \) differential-difference population balances is reduced to a set of ordinary differential moment equations, \( 5(N_{gen} + 1)N_{rad} \) for the active chains and \( 5(N_{gen} + 1) \) for the dead chains. Including also the material balances of additional species (such as monomer, initiator, overall radicals, etc. reported in the Appendix, equations (B44)-(B52)), the total number of ordinary differential equations, \( N_{eq} \), to be solved is:

\[
N_{eq} = 9 + 5(N_{gen} + 1) + 5(N_{gen} + 1)N_{rad}
\]

(3.32)
quite a small number when compared to the size of the original set of multidimensional population balances. Under typical conditions (typical values of $N_{\text{rad}}$ and $N_{\text{gen}}$), the number of equations is around a few hundreds, whose numerical integration could be achieved in a few minutes of computational time in a Fortran code using the DVODE solver$^{[76]}$ from the Livermore library, on an personal computer running with a 3 GHz CPU.

### 3.4. Results

In order to critically evaluate the predictions of the developed multiradical model, a series of parametric calculations was carried out using model parameter values representative of the bulk copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). As anticipated, this system has been chosen as it is known that the role of PDB-consuming intramolecular reactions (the so-called primary cyclizations) is limited to 3-4% in MMA/EGDMA bulk copolymerization$^{[77]}$ therefore, since this model is not considering explicitly these specific reactions, all the predictions in terms of properties related to PDB and bridges (such as gel fractions and crosslinking densities) are correct. The selected values of all physical and kinetic parameters can be found in Table 3.2 and Table 3.3, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Molecular weight $[g/mmol]$</th>
<th>Density $[g/cm^3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>100.12</td>
<td>0.936</td>
</tr>
<tr>
<td>EGDMA</td>
<td>198.22</td>
<td>1.051</td>
</tr>
<tr>
<td>AIBN</td>
<td>164.21</td>
<td>1.11</td>
</tr>
</tbody>
</table>
### Table 3.3 - MMA/EGDMA parameters

<table>
<thead>
<tr>
<th>Parameter/units</th>
<th>MMA/EGDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2(t = 0)$ wt%*</td>
<td>0.3%</td>
</tr>
<tr>
<td>$M_1(t = 0)$ wt%</td>
<td>99%</td>
</tr>
<tr>
<td>$M_2(t = 0)$ wt%</td>
<td>1%</td>
</tr>
<tr>
<td>$k_d$ [1/s]</td>
<td>$3.43 \times 10^{-5}$</td>
</tr>
<tr>
<td>$f$ [-]</td>
<td>0.59</td>
</tr>
<tr>
<td>$k_{p_{11}}$ [$cm^3/(mol\ s)$]</td>
<td>$4.617 \times 10^5$</td>
</tr>
<tr>
<td>$k_{p_{22}}, k_{p_{32}}$ [$cm^3/(mol\ s)$]</td>
<td>$9.418 \times 10^5$</td>
</tr>
<tr>
<td>$k_{p_{12}}$ [$cm^3/(mol\ s)$]</td>
<td>$6.890 \times 10^5$</td>
</tr>
<tr>
<td>$k_{p_{21}}, k_{p_{31}}$ [$cm^3/(mol\ s)$]</td>
<td>$6.320 \times 10^5$</td>
</tr>
<tr>
<td>$k_{p_{13}}$ [$cm^3/(mol\ s)$]</td>
<td>$2.317 \times 10^5$</td>
</tr>
<tr>
<td>$k_{p_{23}}, k_{p_{33}}$ [$cm^3/(mol\ s)$]</td>
<td>$3.452 \times 10^5$</td>
</tr>
<tr>
<td>$k_{adj}$ [$cm^3/(mol\ s)$]</td>
<td>$1.013 \times 10^{10}$</td>
</tr>
<tr>
<td>$k_{rcij}$ [$cm^3/(mol\ s)$]</td>
<td>$1.054 \times 10^{10}$</td>
</tr>
</tbody>
</table>

* weight % over total monomers

### 3.4.1. Evaluation of best values of $N_{gen}$ and $N_{rad}$

To obtain reliable model predictions, suitable values of the number of generations, $N_{gen}$, and of the maximum number of active sites per chain, $N_{rad}$, have to be chosen. To do so, let us consider a computationally sensitive quantity, i.e. the maximum value of the weight average degree of polymerization of the sol polymer, $DP_w^{MAX}$. This is the chain length reached by the polymer when the gel appears, thus corresponding to the maximum chain length of the sol polymer: right after gel formation, the weight average chain length will decrease due to the
transfer of the largest chains to the gel polymer. The evolution of this quantity with conversion, exhibiting a strong cusp at the gel point, was taken to check the accuracy of the numerical solution. Notably, this same quantity has been used before to evaluate the reliability of the predictions of a set of population balances solved by the method of Numerical Fractionation.\[^{[78]}\]

The values of $DP_{w}^{MAX}$ predicted at different pairs of values of $N_{rad}$ and $N_{gen}$, both varying in the range from 1 to 8, are shown in Figure 3.1 as a function of $N_{rad}$ at constant values of $N_{gen}$. Increasing the number of generations causes an increase of $DP_{w}^{MAX}$ for any value of $N_{rad}$. This is expected, as a larger number of generations means that more high-molecular weight polymer chains are part of the sol. However, such increase is limited and converging to a value of $DP_{w}^{MAX}$ which is larger at larger values of $N_{rad}$. Since the absolute value of the chain length is continuously increasing at increasing number of active sites, we stop the search when large enough values are established, i.e. at $DP_{w}^{MAX}$ of the order of $2 \times 10^5$ repeating units (corresponding to $N_{gen} = 7$ and $N_{rad} = 6$), that is a molecular weight of about $2 \times 10^7$ Da. This value has been arbitrarily selected because representative of the maximum chain length typically measurable by experimental fractionation techniques like size exclusion chromatography in sol polymers; however, different limiting values can be used without affecting the evaluation procedure discussed here.
To further prove that the selected combination $N_{rad} - N_{gen}$ guarantees the convergence of the model predictions, the gel fraction (equation (B53)) has been plotted for $N_{gen} = 7$ and $N_{rad} = 1 - 7$ in Figure 3.2: the overall difference among the various gelation curves can be appreciated only in terms of the steepness of the gelation onset. In particular, the higher the number of active sites is, the steeper the gelation onset. Even looking at the zoomed inset of Figure 3.2, the results of the simulations with $N_{rad}$ equal to 6 and 7 are practically superimposed, thus indicating that model predictions were converging already when considering $N_{rad} = 6$. The same conclusion is drawn when considering the evolution of the weight average degree of polymerization for $N_{gen} = 7$ and $N_{rad} = 1 - 7$, as shown in Figure 3.3. Once more, only minor differences between the simulations performed with 6 and 7 active sites per chain can be appreciated very close to the gel point.
Figure 3.2
Gel fraction calculated with $N_{rad} = 1,2,3,4,5,6,7$ and $N_{gen} = 7$

Figure 3.3
$DP_n$ for $N_{gen} = 7$ and $N_{rad} = 1-7$
To conclude, best values of the model parameters $N_{\text{gen}} - N_{\text{rad}}$ ensuring accurate enough model predictions are readily identified through numerical experiments. In the specific case examined in this section, 7 generations and a maximum of 6 radicals per chain are enough to achieve this accuracy: these values require the numerical solution of less than 300 simultaneous ODEs (cf. equation (3.32)), while about 90 ODEs are needed in the equivalent monoradical model ($N_{\text{gen}} = 7, N_{\text{rad}} = 1$). Therefore, the additional computational effort required to account for the multiradicals is quite limited.

### 3.4.2. Model results and validation

Once selected the numbers of generation and radicals suitable to achieve reliable model predictions, it is worth to analyze the model results and especially the concentrations of the chains with multiple active sites with more detail.

As shown in Figure 3.4, the concentrations of the sol chains with more than one active site become noticeable only close to the conversion corresponding to the gel formation: far from the gel point, their concentrations are 5 to 10 orders of magnitude smaller than that of the monoradicals. On the other hand, their relevance at the gel point is clearly confirming their role into the gelation process.
This contribution is also clear when comparing the results shown in Figure 3.5 and Figure 3.6, where the concentrations of active chains with different number of active sites are again reported for the first and the seventh generation, respectively. While the amount of multiradicals is fully negligible with respect to that of monoradicals in the first generation, their amounts are much closer in higher generations where the largest values are found close to the gel point, as anticipated in Figure 3.4. This seems reasonable, as the higher generations include the longer and more branched polymer chains which are more likely to contain multiple active sites.
Figure 3.5
Multiradicals in generation 1

Figure 3.6
Multiradicals in generation 7
However, all the previous results indicate a minor impact of the multiradicals on the model predictions: this becomes even more clear when considering the crosslinking densities (equations (B57)-(B59)): as shown in Figure 3.7, no difference between the predictions of the mono- and the multiradical model can be appreciated, and the curves provided by the two models perfectly overlap. This finding can be explained considering that the average crosslinking density is a type of “compositional” property: no difference can arise once multiradical sites are accounted for because they simply change the number of chains and the distribution of the active sites among those chains, but not the composition of the chains themselves. For this reason average crosslinking densities and other compositional properties, such as PDB densities, are expected not to be affected by the multiradicals and they won’t be discussed in the subsequent sections. More important, we can also conclude that the impact of the multiradicals for the copolymer system under examination, MMA/EGDMA, is indeed quite small: the use of the standard, monoradical modeling is therefore adequate and there is no real need of the refined multiradical modeling.
Finally, the reliability of the models is proven by the comparison with experimental data. Namely, the prediction of gel fraction vs. conversion is compared to the experimental values reported by Li et al.\cite{72} in Figure 3.8. The agreement between model and experiment is reasonably good and the predictions of the two models, mono- and multiradical, are superimposed. As expected, this comparison does not allow any model discrimination but is intended to confirm the general correctness of the developed equations.
3.4.3. A criterion about multiradicals

At this point, a quantitative criterion to establish \textit{a priori} if and at which operating conditions MRs are relevant in determining the kinetics of crosslinking copolymerization system would be very desirable. Given such criterion, it becomes possible to decide the modeling approach most suited to the specific system under examination.

As mentioned in the Introduction, a criterion of this type was proposed since 1993 by Hamielec and Zhu:\textsuperscript{[5]} no difference between the predictions of mono- and multiradical models was found when the ratio of propagation over termination rate constants, $k_p / k_\text{tr}$, is smaller than $10^{-3}$. Given reliable values of these rate constants, this criterion has indeed the advantage of being very simple; on the other hand it does not include any effect of the crosslinker content as well as of the reaction extent (conversion), two aspects which intuitively should play a role in the multiradical formation. It is worth to mention that Zhu and Hamielec studied the effect of the

Figure 3.8
Gel fraction vs. conversion, comparison between model (continuous line) and experimental data by Li et al. (squares)
ratio $k_p / k_i$, parameterizing the crosslinking reaction: since the identified threshold value of $k_p / k_i$ holds for the different examined values of the crosslinking reaction, their criterion does not include such reaction.

Let us now apply the literature criterion to the system discussed above, the free-radical bulk copolymerization of MMA and EGDMA. It is well known that the Trommsdorff effect plays a role in this system: therefore, the ratio $k_p / k_i$ for this specific system is shown as a function of conversion in Figure 3.9 and compared with the proposed (constant) threshold value. Before 40% of conversion, the ratio has increased to such an extent that the criterion is violated, suggesting that the monoradical assumption loses its validity after this point. On the other hand, the simulations performed previously showed no difference between the mono- and multiradical predictions for the complete range of conversion. This contradictory behavior can be explained by considering that the gel point lies around 10% of conversion with the chosen set of parameters (1% of crosslinker): since MRs play a role only close to the gel point, this happens when the criterion is still fulfilled and hence their influence cannot be relevant. Moreover, we noticed before that the difference between mono- and multiradical modeling is significant only in terms of properties of the sol polymer: since the amount of sol polymer at 40% of conversion is less than 10% (cf. Figure 3.2), the impact of violating the criterion after such conversion can be expected to be practically negligible, as indeed indicated by the model results discussed in the previous section.
This finding indicates that the error made when neglecting MRs might become significant if gelation occurs after violating the Zhu-Hamielec criterion: this situation occurs if the crosslinker content is decreased, and gelation is delayed. To check if this is the case, comparative simulations using the mono- and the multiradical model have been performed: the results are shown in Figure 3.10 as $DP_w$ of the sol polymer at decreasing crosslinker contents. Note that all kinetic parameter values were kept constant in all these simulations, including the dependence of $k_i$ upon conversion, as it has been reported that this termination model is poorly dependent on the crosslinker content.\cite{79} As expected, the predicted values of $DP_{w}^{\text{MAX}}$ are different and they reflect the different type of model used: larger values are evaluated when multiradicals are accounted for. But our main focus here is on the gel point (the conversion of first gel formation), indicated by the peak of such maximum degree of polymerization: while the difference between predicted
gel points is almost negligible at 0.25% of crosslinker content, discrepancies appear at lower crosslinker contents. The difference is quite remarkable at 0.05%, where the gel point predicted by the model accounting for MRs is anticipated of about 5% of conversion with respect to the prediction of the model neglecting them. Therefore, it can be concluded that the criterion by Zhu and Hamielec works well provided its violation takes place before the gel formation, i.e. at low crosslinker contents in the system under examination. In other words, the curve in Figure 3.9 has to be combined with the knowledge of the gel point to be effective for systems exhibiting diffusion limitations. Notably, these considerations are of general validity and extend the validity of the criterion to all polymerization systems undergoing the Trommsdorff effect.\cite{80,81}

On the other hand, we should now ask ourselves what happens at large contents of crosslinker, since intuition suggests that the formation of multiradicals is favored in highly crosslinked polymers. Again, model simulations were carried out accounting and neglecting the presence of...
MRs and the results, once more in terms of $DP^{\text{MAX}}_w$, are shown in Figure 3.11: by progressively increasing the crosslinker content, the predicted values of gel point diverge, being the corresponding conversion smaller when MRs are considered. Such a behavior cannot be foreseen using the criterion by Zhu and Hamielec (in all cases, gel is formed well before crossing the threshold value in Figure 3.9).

![Figure 3.11](image.png)

$DP_w$ at increasing crosslinker contents

In order to better understand the system behavior, let us focus on the probability of formation of multiradicals in the sol polymer, $P_{MR}$, defined in equation (3.33):
where \( C_{PDB} \) and \( C^*_p \) indicate the concentrations of pendant double bonds in the sol polymer on all (active and dead) and active chains, respectively. This probability is defined as the ratio between the rate of crosslinking between any two active chains of the sol and the summation of the rates of all possible reactions that an active chain belonging to the sol can undergo. Of course, large values of \( P_{MR} \) reflect a corresponding relevance of multiradical chains in the sol polymer.

The evolutions of such probability as a function of conversion at different crosslinker contents are shown in Figure 3.12. Larger values of \( P_{MR} \) are found at high and low crosslinker contents, in complete agreement with the results discussed previously (Figure 3.10 and Figure 3.11). While at low contents of crosslinker the same arguments reported above for the literature criterion apply (too large values of \( k_p / k_t \) because of the Trommsdorff effect already present at conversion smaller than the gel point), the further increase of \( P_{MR} \) at large contents of crosslinker is also predicted, simply reflecting increasing values of pendant double bonds (the numerator in equation (3.33) increases). Another interesting feature of this probability is that its peak value correspond the gel point, like the peak of molecular weight of the sol polymer presented above. This is clearly shown in Figure 3.13, where gel fraction and \( P_{MR} \) are reported as a function of conversion at 2.5% of crosslinker content. Therefore, the results in Figure 3.11 are quite informative, since the relevance of the multiradicals as well as the conversion of gel formation are provided in a single curve.
Figure 3.12
$P_{MR}$ as a function of conversion for different crosslinker contents (0.05%-20%)

Figure 3.13
Gel fraction and $P_{MR}$ vs conversion for 2.5% crosslinker
In order to evolve the previous findings into a criterion of model accuracy for the specific system, the error associated with the prediction of the gel point accounting for and neglecting the multiradicals (i.e., the relative difference between the values predicted with and without MRs) has been plotted for different initiator amounts (0.1-0.9 wt%) against crosslinker content in Figure 3.14. Note that the selected range of crosslinker contents (0.01-10 wt%) is representative of the applicative range typical of industrial crosslinked polymers.

![Figure 3.14](image)

**Figure 3.14**
Error on the gel prediction for different initiator concentrations (0.1-0.9 wt%) against crosslinker concentration. Dotted line: 0.1%, Dashed line: 0.3%, Continuous line: 0.6%, dash-dotted line: 0.9%

For all the conditions explored the error exhibits a minimum, reflecting the physics previously elucidated through the probability $P_{MR}$: by increasing the crosslinker content, MRs are more likely formed, whereas by decreasing it, the Trommsdorff effect increases the radical concentration, leading once more to higher $P_{MR}$, which implies a larger error when MRs are
neglected. The interplay of these two trends is affected by the initiator concentration: by changing it, the minima of the error curves are shifted, as can be seen in Figure 3.14. Notably, the plot represents a tool to quantitatively evaluate the relevance of MRs: once the crosslinker content and the initiator concentration are defined, the error is read from the curves in Figure 3.14 and the impact of neglecting MRs is found. It is worth mentioning that the most interesting part of this graph is comprised between 0.01% and 1% of crosslinker, as for higher amounts of di-vinyl monomer, gelation always occurs very early at these conditions, typically below 1% of conversion (data not shown), and it becomes indeed questionable if the estimation of an error is of any use in these cases. The error made for crosslinker contents on the left side of the figure can be quite significant, suggesting that diffusion-limited systems may require MRs for accurate predictions even at very low crosslinker contents. If a 10% error is assumed as maximum threshold, the monoradical assumption holds when the crosslinker content is between 0.1 and 1% for any initiator concentration. Note that not only gel points are wrongly predicted when MRs are neglected, but also average molecular weights, as can be seen in Figure 3.10 for the 0.05% crosslinker case.

3.5. Conclusions

A comprehensive kinetic model of bulk crosslinking copolymerization has been developed. The resulting multidimensional PBEs were numerically solved combining the numerical fractionation with the method of moments, thus reducing the computational effort to the integration of a few hundreds of ordinary differential equations.

In order to analyze the predicted system behavior, selected parametric calculations were carried out with reference to the bulk copolymerization of MMA/EGDMA at 70°C. It is shown
that multiradicals in the sol polymer are (possibly) formed shortly before gelation: in such a case, their contribution has to be accounted for in order to predict the gel point with accuracy. In general, the contribution of MRs can be lumped into a single quantity, the probability of multiradical formation, $P_{MR}$: when evaluated as a function of conversion, such quantity provides quantitative information about the relevance of MRs (through its value) and the onset of gelation (through the position of its peak).

Using the developed model (and its simplified version neglecting MRs), the Zhu-Hamielec criterion proposed to select the most suitable model of crosslinking copolymerization for a given system was tested and improved. In particular, the applicability of this criterion has been extended to the case of systems suffering diffusion limitations, which is invariably the case for industrially relevant polymers. For the specific MMA/EGDMA bulk copolymerization, a master plot has been produced, allowing the quick selection of the adequate model type. It turned out that the monoradical assumption holds in the range 0.1%-1% crosslinker, provided a maximum error of about 10% is accepted.
4. **Bulk Crosslinking copolymerization: comparison of different modeling approaches**

4.1. **Introduction**

Crosslinked copolymers are materials of great interest in a large variety of application fields.\[^6\] Besides a very intensive experimental research,\[^72, 79, 82, 83\] modeling tools have been developed throughout the years, in order to predict product properties and deepen the understanding of such complex systems.\[^2, 5, 17, 22, 84-87\] Notably, the models employed in free-radical bulk crosslinking copolymerization need to deal not only with chain length distribution (CLD), which naturally arises in any type of polymerization, but also with complex molecular architectures, whose detailed structure determines the end use properties. Typically, one of the two monomers present in a crosslinking copolymerization is a divinyl-monomer (or crosslinker) which, once incorporated, leads to the formation of pendant double bonds (PDB) along the chain. Such reactive groups are responsible of the formation of intermolecular linkages by crosslinking, resulting in the formation of polymer networks and extremely large molecular weights. According to the amount of crosslinker present and on the polymerization kinetics, the chains can be interconnected to such an extent they become insoluble and a new phase (usually termed “gel”) is formed.\[^2\] This new phase is typically extremely reactive as it bears a large amount of PDB and progressively takes up the other soluble chains (named “sol”) till the system consists of few, extremely large and highly branched macromolecules. Due to the complex chain

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\[^3\] The present chapter has been partially published as: S. Lazzari, S. Hamzehlou, Y. Reyes, J.R. Leiza, M.R.P.F.N. Costa, R.C.S Dias, G. Storti, “Bulk Crosslinking Copolymerization: comparison of different modeling approaches”, Macromolecular Reaction Engineering, in press
architecture, multiradicals (MR), i.e. chains with multiple active sites can be formed also in the sol polymer, further complicating the theoretical description of the polymerization reaction.\textsuperscript{[5, 63, 88]}

Given the complexity of the polymerization process briefly sketched above, it becomes clear that the choice of suitable modeling approaches is of the utmost importance to ensure reliable predictions. Historically, statistical approaches were the first ones to be introduced by Flory and Stockmayer for network formation in polycondensation systems\textsuperscript{[89, 90]} and were later extended by Tobita towards kinetically controlled free-radical polymerization systems.\textsuperscript{[85]} This statistical/kinetic model, henceforth called Flory/Tobita (FT), has been successfully employed to simulate different systems such as styrene-divinylbenzene\textsuperscript{[45]} and acrylamide/bisacrylamide.\textsuperscript{[91]} It represents an attractive compromise between required computational effort and amount of predicted properties. Even though average properties only can be calculated (such as sol and gel fractions, degrees of polymerization, and crosslinking densities), this modeling approach describes the polymer microstructure remarkably well, accounting for intramolecular cyclizations and “chains history”.\textsuperscript{[85]} Due to its almost negligible computational cost, this model is the ideal tool when parameter estimation is the primary aim.

Kinetic Monte Carlo (KMC) simulations are a powerful methodology to describe polymerizations with complex kinetics, e.g. polymerization of acrylates and crosslinked systems.\textsuperscript{[92-94]} Originally developed by Gillespie,\textsuperscript{[95]} KMC has been applied to predict the kinetics of a large number of chemical processes. Since the method offers a direct approach to the detailed evolution of the sol molecular weight distribution, crosslinking polymerizations have been studied through KMC.\textsuperscript{[20, 96-101]} On the other hand, this type of approach is frequently criticized because of its large demand of computational power, in particular when compared to more traditional deterministic approaches. In the last years, due to a significant increment in available
computational resources, KMC is finding application in revealing the full microstructure of the polymer chains that cannot be obtained by deterministic models without making assumptions that might jeopardize the accuracy of the predictions. Thus, polymerization processes with complex kinetic schemes (e.g. multiple monomers, branching and crosslinking) have become an ideal niche for the application of KMC approaches.\textsuperscript{[21, 99, 102, 103]}

Deterministic polymerization models are typically based on population balance equations (PBE).\textsuperscript{[104]} Such equations characterize each single individual of the population in terms of specific values of each property of interest, the so called internal coordinates. Considering that in crosslinking copolymerization at least two internal coordinates are necessary to accurately describe the process kinetics (i.e., the number of monomer units and of pendant double bonds, PDB) and that such coordinates have to span very large ranges of values, the number of equations to be solved is usually extremely large. Computationally effective solving approaches, like the popular method of moments, besides accessing only average quantities are not feasible as second and higher-order moments diverge when gelation is taking place. This major issue can be handled applying the approach proposed by Teymour and Campbell:\textsuperscript{[84]} they developed the numerical fractionation (NF) technique, which allows the utilization of the method of moments overcoming the divergence issues. Accordingly, the sol polymer is classified into generations related to the chain size, whose moments can be easily calculated, whereas the gel is confined in a further generation for which only non-diverging (0\textsuperscript{th} and 1\textsuperscript{st} order) moments are calculated. Despite the obvious loss of information one deals with when employing NF, it represents a powerful technique to calculate average properties with little computational cost and maintaining a straightforward kinetic approach. This method has been applied in the case of crosslinking copolymerization\textsuperscript{[19, 105]} and, more recently, a multi-radical version of the numerical fractionation (MRNF) has also been proposed.\textsuperscript{[88]} As an alternative, different discretization techniques have
been developed to solve the same balances throughout the years.\cite{106,107} Butte et al.\cite{17} employed the Kumar-Ramkrishna algorithm in a 2-D model, while Wulkow implemented, for 1-D PBE, a very powerful version of the Galerkin algorithm in the commercial software PREDICI.\cite{108} On the other hand, Costa et al. developed a method relying on a stoichiometric-based description of the polymer chains, resulting in a multidimensional PBE. By employing the generating function (GF) method, the PBE is transformed into the Laplace domain and solved employing the method of characteristics, a strategy already validated in previous papers.\cite{109,110} This approach, henceforth referred to as GF model, allows to predict sol and gel average properties (by solving ODE in the Laplace domain), as well as the sol CLD (for which a numerical anti-transform is required). Interestingly, the distinction between sol and gel properties occurs automatically by employing the method of characteristics, as will be detailed in the numerical section. This multidimensional approach (e.g. 5-D or 7-D) gives access to a large number of information, but has the downside of requiring a certain computational effort when treating the resulting system of stiff ODE as well as the numerical anti-transformation.

In this frame, the present work aims to compare the predictions of different modeling approaches with reference to a kinetic scheme typical of bulk crosslinking copolymerization. In order to make the comparison as meaningful as possible, several simplifying assumptions were employed. The comparison is implemented using two different sets of parameter values, corresponding to two specific case studies. The following 4 modeling approaches have been examined: a KMC based on the Gillespie algorithm, the statistical/kinetic approach based on the Flory/Tobita (FT) model and two deterministic PBE-based models, a 4-D PBE solved with the multiradical numerical fractionation (MRNF) and a 7-D PBE solved by means of the generating function (GF) method. This work is organized as follows: after briefly describing the kinetic scheme, the modeling approaches and their corresponding computational efforts, the different
predictions of average properties such as sol and gel fractions, average molecular weights and crosslinking densities, as well as the chain length distributions will be comparatively evaluated.

4.2. The Kinetic Scheme

The kinetic scheme employed for the comparison between the different modeling approaches involves initiation, propagation, crosslinking and termination by combination. Due to the comparative nature of the work, all kinetic constants have been assumed to be conversion and chain-length independent. Moreover, pseudo-kinetic constants have been employed (cf. equations (C1)–(C3) in the Appendix). All the reactions accounted for are sketched below using the following notation: \( R^* \) and \( P \) represent the active and dead chains, whereas the internal coordinates \( n, i \) and \( y \) indicate the numbers of monomer units, of pendant double bonds and of active sites, respectively.

Initiation

\[
I_2 \xrightarrow{k_I} 2I^* \tag{4.1}
\]

Propagation

\[
I^* + M_1 \xrightarrow{k_{I1}} R_{1,0,1} \tag{4.2}
\]

\[
I^* + M_2 \xrightarrow{k_{I2}} R_{1,1,1} \tag{4.3}
\]

\[
R_{r,i,y} + M_1 \xrightarrow{k_{R1}} R_{r+1,i,y} \tag{4.4}
\]

\[
R_{r,i,y} + M_2 \xrightarrow{k_{R2}} R_{r+1,i+1,y} \tag{4.5}
\]
Crosslinking

\[ R_{r,i,y} + P_{q,a,j} \xrightarrow{y^{k_{p3}}} R_{r+q,i+j-1,y} \]  \hspace{1cm} (4.6)

\[ R_{r,i,y} + R_{q,j,z} \xrightarrow{y^{k_{ps}}} R_{r+q,i+j-1,y+z} \]  \hspace{1cm} (4.7)

Termination by combination

\[ R_{r,i,y} + R_{q,j,z} \xrightarrow{y^{k_{ps}} z^{k_{y}}} R_{r+q,i+j,y+z-2} \quad \forall \ y + z - 2 \geq 1 \]  \hspace{1cm} (4.8)

\[ R_{r,i,1} + R_{q,j,1} \xrightarrow{k_{c}} P_{r+q,i+j} \]  \hspace{1cm} (4.9)

Note that all models assume an isothermal, well-mixed batch reactor with constant volume. Moreover, it should be stressed that the FT approach does not take into account multiradicals (MR), which are instead accounted for by KMC, MRNF and GF.

In the next section, details about the different modeling approaches are provided. A brief description of each model, including the calculated properties, the computational/numerical effort required as well as the necessary references for a fully-detailed description, clearly out of the scope of this work, are presented. As an exception, the equations of the GF model are presented as they have never been published in the present form. The necessary kinetic parameters employed in the different case studies are presented in Table 1. Notably, these parameters are arbitrary ones and have been chosen to the sole purpose to keep the comparison as easy and direct as possible.
Table 4.1
Parameter values of Case I and II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case I</th>
<th>Case II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1^0$ [mol L$^{-1}$]</td>
<td>8.50</td>
<td>8.50</td>
</tr>
<tr>
<td>$M_2^0$ [mol L$^{-1}$]</td>
<td>1.36x10$^{-1}$</td>
<td>3.4x10$^{-2}$</td>
</tr>
<tr>
<td>$I_2^0$ [mol L$^{-1}$]</td>
<td>6.55x10$^{-2}$</td>
<td>3.27x10$^{-2}$</td>
</tr>
<tr>
<td>$k_d$ [s$^{-1}$]</td>
<td>4.16x10$^{-3}$</td>
<td>4.16x10$^{-3}$</td>
</tr>
<tr>
<td>$k_i$ [L mol$^{-1}$ s$^{-1}$]</td>
<td>7.61x10$^2$</td>
<td>7.61x10$^2$</td>
</tr>
<tr>
<td>$k_{p11}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p12}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p21}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td>7.61x10$^2$</td>
<td>7.61x10$^2$</td>
</tr>
<tr>
<td>$k_{p22}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p31}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p32}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p13}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{p23}$ [L mol$^{-1}$ s$^{-1}$]</td>
<td>7.61x10$^2$</td>
<td>7.61x10$^2$</td>
</tr>
<tr>
<td>$k_{p33}$ [L mol$^{-1}$ s$^{-1}$]</td>
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<td></td>
</tr>
<tr>
<td>$k_w$ [L mol$^{-1}$ s$^{-1}$]</td>
<td>1.38x10$^6$</td>
<td>1.38x10$^4$</td>
</tr>
</tbody>
</table>

4.3. Modeling Approaches

4.3.1. Kinetic Monte Carlo (KMC)

The full kinetic Monte Carlo (KMC) according to the Gillespie approach was implemented.[95] The KMC model presented here naturally considers the presence of multiradicals, primary and secondary cyclization with no pre-assumptions. It is possible to follow the properties of the polymer also after gelation. A detailed description of this method is provided
in previous papers\textsuperscript{[21, 98]} and hence will not be repeated here. Only the most specific features will be discussed.

This simulation method employs a control volume, $V$: given the initial concentration of the reactants and using the Avogadro's constant, the number of molecules of each reactant is established in order to calculate the rate of each considered reaction. The control volume used in the simulation presented in this work is $V = 2.0 \times 10^{-18} \text{ L}$. It is worth noting that this volume is large enough to obtain statistically meaningful average properties as well as to provide the CLD of the sol.

One important point to highlight is that, contrary to other simulation techniques, in this modelling approach there is no divergence of the average molecular weights at the gel point (that is usually defined as the conversion at which the molecular weight diverges to infinity): as mentioned above, KMC uses a finite number of molecules and, therefore, the molecular weight of the largest cluster (i.e. the gel) remains finite. Even when a large enough control volume is employed, “intensive” properties such as crosslinking or pendant double bond density of the largest clusters have statistical meaning, while “extensive” properties, such as chain length, do not. As a result, the KMC provides the sol distribution only. On the other hand, the aforementioned lack of divergence does not allow identifying the sol/gel transition in a model-independent way, as typically done by deterministic models. In this work, as a model comparison is needed, a maximum degree of polymerization of sol chains has been arbitrarily set to $10^5$ units: longer chains belong to the gel, shorter ones to the sol. Notably, a very similar approach was previously employed in the literature.\textsuperscript{[17, 111]} The choice of this threshold value is critical and its erroneous determination has a strong impact on the predictions of the onset of gelation, i.e. allowing more or less chains to be part of the sol. In the present case such threshold has been identified by comparison with the predictions of a kinetic model. Note that employing a critical
crosslinking density to discern between sol and gel molecules would have been more correct; being though this choice arbitrary as the maximum degree of polymerization, the latter has been chosen here for the sake of simplicity.

It is often mentioned that KMC simulations are time consuming, but it should be kept in mind that intensive numerical calculations are cheap and fast due to the current available computational power and represent an acceptable cost, considering all the information that can be obtained by Monte Carlo simulation. For the specific polymerization simulated in this work, a single simulation of Case I, coded in Fortran under Linux takes about 5 minutes in a PC with 16 cores Intel(R) Xeon(R) CPU E5620 @2.40 GHZ. The code has not been parallelized and only standard optimization options of the compiler were used.

Finally, as already mentioned, large enough control volumes are needed in order to obtain statistically reliable results. Moreover, it is also good practice to calculate the average of different runs obtained by changing the seed number of the random generator, i.e. use different sequences of the (pseudo) random numbers. This way, besides increasing the statistical meaning of the results, the effect of rare events is also checked. In the present work, the results reported are the average of at least 40 runs: this selection strategy guarantees convergence on both average and distributed properties (data not shown). The computation time for those 40 runs is 200 min and 10 min for Case I and Case II, respectively.

4.3.2. Generating Functions (GF)

The GF method has been fully detailed in previous papers \cite{109,110} and will be explained here only in terms of the solution procedure and the main equations/quantities. Two key ideas lie behind the GF method: a description of the polymer chains based on the count of their chemical
groups and the numerical computation of moment generating functions. A polymer chain is described here by means of 7 indices, i.e. \( P(r_1, r_2, r_3, b, x_1, x_2, c) \), accounting for the type of radical sites \( (r_1 - r_3) \), PDB \( (b) \), mono- and di-functional repeating units \( (x_1 \text{ and } x_2) \) and tetra-functional crosslinks \( (c) \). More concisely, the population is referred to as \( P(a) \), where \( a = [r_1, r_2, r_3, b, x_1, x_2, c] \).

The generating function \( G(s) \) of the mole concentration of polymer chains with respect to the group counts is defined in terms of the dummy Laplace variables \( s_j \) as:

\[
G(s) = \sum_{r_1=0}^{\infty} \sum_{r_2=0}^{\infty} \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} \sum_{x_1=0}^{\infty} \sum_{x_2=0}^{\infty} \sum_{c=0}^{\infty} s_1^r s_2^r s_3^r s_b^b s_{X_1}^x s_{X_2}^x s_c^c c_P (r_1, r_2, r_3, b, x_1, x_2, c)
\]

\[
s = [s_1, s_2, s_3, s_b, s_{X_1}, s_{X_2}, s_c]
\]

(4.10)

The mass balance of the polymer species in terms of GF in a batch reactor can be written as:

\[
\frac{\partial G(s,t)}{\partial t} = \left[ k_{p_1} c_M s_1 s_{X_1} + k_{p_0} c_M s_2 s_{X_2} + k_{p_0} (s_3 - s_b) G_b \right] c_{R_1}
\]

\[
+ \left[ k_{p_1} c_M (s_1 s_{X_1} - s_1) + k_{p_2} c_M (s_2 s_{X_2} - s_1) \right] G_1
\]

\[
+ \left[ k_{p_2} c_M (s_2 s_{X_2} - s_2) + k_{p_2} c_M (s_2 s_{X_2} - s_2) \right] G_2
\]

\[
+ \left[ k_{p_3} c_M (s_3 s_{X_3} - s_3) + k_{p_3} c_M (s_3 s_{X_3} - s_3) \right] G_3
\]

\[
+ k_{p_1} (s_1 s_c G_b G_R - c_R s_b G_b - c_b s_1 G_1) + k_{p_2} (s_2 s_c G_b G_R - c_R s_b G_b - c_b s_2 G_2)
\]

\[
+ k_{p_3} (s_3 s_c G_b G_R - c_R s_b G_b - c_b s_3 G_3) + k_i \left[ (G_1 + G_2 + G_3)^2 - 2c_R (s_1 G_1 + s_2 G_2 + s_3 G_3) \right]
\]

(4.11)

By solving the latter equation, the generating function is evaluated from which the full, multidimensional distribution of the sol chains and the corresponding average properties are obtained by numerical inversion. Below, the calculation of the average properties will be first presented, followed by the recovery of the entire distribution.
4.3.2.1. Average properties

Equation (4.12) is solved by the method of characteristics,\textsuperscript{[112, 113]} leading to the set of ODE equations in the Laplace domain reported in the Appendix (equations (C11)-(C25)). To distinguish among sol and gel properties, the time evolution of the Laplace variables $s_j$ (equations (C19)-(C23) in the Appendix) is employed. Notably, the initial conditions of these differential equations, $s_{j0}$, are known and equal to 1 only before the gelation onset ($t < t_g$). In this case, these set of equations reduce to an initial boundary problem. Things change significantly at $t > t_g$: after gelation at least some $s_{j0} < 1$, meaning that a two point boundary value problem (2PBVP) has to be solved, employing a shooting method in order to identify the unknown initial conditions $s_{j0}$. As the resulting numerical problem is highly non-linear, a good enough starting estimation is needed. A heuristic method for choosing the initial mesh and the profiles of the $s_j$ has been described elsewhere.\textsuperscript{[109]} More recently, it has been found (unpublished results) that a more effective approach is developed starting from the approximate solution assuming equal reactivity of the free-radical sites. Due to the extreme stiffness of these ODE systems, only the code TWPBVPL\textsuperscript{[114]} is known to deal effectively with the numerical sensitivity issues found in radical polymerization modeling.\textsuperscript{[109]} Before the gel point, integer positive moments can be computed by solving an IVP (the method of moments) and the gel point can be identified as corresponding to the divergence of the 2\textsuperscript{nd} and higher order moments.

Solving the aforementioned set of equations gives access to the sol properties; for instance, the sol fraction is defined as:

$$w_s = \frac{G_{s1}(1) + G_{s2}(1)}{M_1^0 - M_1 + M_2^0 - M_2}$$

(4.13)
For the average degrees of polymerization, similar formulas are employed (equations (4.14) and (4.15)):

\[
DP_n = \frac{G_{s_1}(1) + G_{s_2}(1)}{G(1)} \tag{4.14}
\]

\[
DP_w = \frac{G_{s_{1,1}}(1) + 2G_{s_{1,2}}(1) + G_{s_{2,2}}(1)}{G_{s_1}(1) + G_{s_2}(1)} \tag{4.15}
\]

Notably, for calculating average sol properties (\(DP_n, DP_w\) or any other average value weighted on a generic internal coordinate of the population), a further set of ordinary differential equation has to be solved (Appendix, equations (C26) - (C47)). It is worth stressing that all these quantities (e.g., \(G_{s_1}, G_{s_2}, \ldots\)) are a function of the aforementioned Laplace variables \(s\) along the characteristic curves defined by solving the set of ODE (C19)-(C25).

### 4.3.2.2. Sol distributions

The sol distributions with respect to the counts of groups can be evaluated by numerical inversion; notably, a 2PBVP has to be solved regardless of gelation taking place or not. In this work, the Gaver-Stehfest method,\[115\] belonging to the wider class of the so-called power algorithms for the inversion of Laplace transforms,\[116\] has been employed. Accordingly, the equation originally derived in the case of Laplace transform \(F(s)\):

\[
f(x) \approx \frac{1}{x} \sum_{n=1}^{N} \omega_n F\left(\frac{a_n}{x}\right) \tag{4.16}
\]

has been extended to the generating function. In contrast to the most general case, both nodes \(a_n\) and weights \(\omega_n\) (\(n = 1 \ldots N\)) are real numbers rather than complex ones. The weights exhibit alternating sign and their values grow very quickly, being larger than \(10^7\) already at \(N = 10\).
Hence, the method is effective only when the values of the transform are known with high enough accuracy and/or multi-precision arithmetic is employed. In order to be able to numerically estimate the inverse for large values of the argument, the scaling approach suggested by Avdis and Whitt\textsuperscript{[116]} has been used; however, this procedure only mitigates the inaccuracy of the calculations and chain length values larger than $3 \times 10^4$ remain practically inaccessible.

The total number of equations of the 2PBVP to be solved for each value of chain length consists therefore of 14 ODE (equations (C11)-(C16), (C19)-(C23) plus an additional dummy equation for the derivative of elapsed time). Moreover, two numerical inversions for each chain length have been performed to check their accuracy ($N = 10$ and $N = 12$). Approximately 30 values of chain length have been used in all cases. For the simulation of Case I and II, these calculations on a 3.2 GHz PC running OpenSuSE Linux 12.2 (64 bits) took about 6 minutes for each distribution.

4.3.3. Multiradical Numerical Fractionation (MRNF)

The multiradical numerical fractionation (MRNF) has been fully detailed in a previous paper\textsuperscript{[88]} and will be therefore only briefly sketched here, without the full description of the employed equations or their derivation. The PBE for active and dead polymer are:
\[
\frac{dR_{r,b,i,v}}{dt} = -k_{p}^{*} y R_{r,b,i,v} + k_{p1}^{*} M_{1} y R_{r-1,b,i,v} + k_{p2}^{*} M_{2} y R_{r-1,b,i-1,v} \\
- k_{p3}^{*} y R_{r,b,i,v} C_{PDB} - k_{p3}^{*} i R_{r,b,i,v} R_{not} + k_{p3}^{*} \sum_{q=1}^{r-1-b-i+1} y R_{r,q,b-a-i+1,v} y i P_{q,a,j} \\
+ k_{p3}^{*} \sum_{z=1}^{y+1} \sum_{a=0}^{r-1-b-i+1} (y-z) R_{r,q,b-a-i+1,v} y z R_{q,a,j} \\
- (k_{a}^{*} + k_{d}^{*}) y R_{r,b,i,v} R_{not} + k_{d}^{*} (y+1) R_{r,b,i,v+1} R_{not} \\
+ \frac{1}{2} \sum_{z=1}^{y+1} \sum_{q=1}^{r-b-i} (y-z+2) R_{r-q,b-a,i+1,v} y z R_{q,a,j} + \\
+ \delta (r=1,b=0,i=0,y=1) k_{p1}^{*} M_{1} I^{*} + \delta (r=1,b=0,i=1,y=1) k_{p2}^{*} M_{2} I^{*}
\]

(4.17)

\[
\frac{dP_{r,b,i}}{dt} = -k_{p}^{*} y P_{r,b,i} R_{not} + \frac{1}{2} k_{p}^{*} \sum_{q=1}^{r-1-b-i} R_{r-q,b-a-i,j} R_{q,a,j} + k_{d}^{*} R_{r,b,i} R_{not}
\]

(4.18)

where \( r \) represents the number of units per chain, \( b \) the number of bridges, \( i \) the PDB, and \( y \) the number of active sites.

The MRNF is based on the very same concept as the classical numerical fractionation (NF), introduced by Teymour and Cambpell\[84\] with the notable difference of accounting for multiradical species, the solving procedure is the one typical of NF, in 4 steps: i) the polymer is divided into an arbitrary number of generations, ii) transfer rules from one generation to the other are defined, iii) PBE for each generation are written, iv) the necessary moments of these PBE are derived and solved, giving access to the desired average properties (sol and gel fractions, sol degrees of polymerization, crosslinking densities). More specifically, transfers of chains among generations are possible only from lower-numbered generations to higher ones and only through two mechanisms, termination by combination and crosslinking. The latter rules apply to all generations up to the last one, \( N_{gen} \): when two chains of generation \( N_{gen} \) react via termination by combination or crosslinking, they end up in an additional generation representing the gel.
Notably, crosslinking or termination by combination reactions between any two generations \( s \) and \( t \) are allowed, but a transfer to a higher generation occurs only if \( s = t \), otherwise the newly formed molecule stays in the generation of higher order. The only exception is generation 0: only crosslinking of two chains belonging to this generation move to the next one.

The fractionated population balances of the sol polymer were written for each value of the number of radicals, from 0 to an arbitrary maximum value \( N_{\text{rad}} \). Chains formed by crosslinking of active chains with large numbers of active sites, larger than \( N_{\text{rad}} \), are directly transferred to the gel generation. Suitable values of the two parameters \( N_{\text{gen}} \) and \( N_{\text{rad}} \) are determined by numerical experiments.\(^{[19, 84, 88]} \)

Employing this numerical method, the total number of ordinary differential equations, \( N_{eq} \), to be solved is:

\[
N_{eq} = 9 + 5(N_{\text{gen}} + 1) + 5(N_{\text{gen}} + 1)N_{\text{rad}}
\]  

(4.19)

quite a small number when compared to the size of the original set of multidimensional population balances. Under typical conditions (typical values of \( N_{\text{gen}} \) and \( N_{\text{rad}} \)), the number of equations is around a few hundreds, whose numerical integration is achieved in a few minutes of computational time in a non-parallelized Fortran code using the DVODE solver,\(^{[76]} \) from the Livermore library, on an 4-core personal computer running with a 3 GHz CPU.

4.3.4. Flory/Tobita (FT)

The Flory/Tobita (FT) model is based on primary chains, defined as the linear chains one would obtain when severing all crosslinkages in a polymer network. By following the birth of the primary chains along the conversion, it is possible to account for the different conditions a chain “experiences” during the reaction, being exposed to more or less crosslinker according to when it
was formed. Notably, the following assumptions are underlying the employment of the present model: (1) monoradical assumption, (2) pseudo-steady-state assumption, (3) PDB on primary chains consumed only by intramolecular reactions, and (4) equal crosslinking density for chains born at the same conversion. The complete set of equations and their derivation are out of the scope of this work as this well-accepted model has been already thoroughly described.\cite{45, 85, 117} In the present section, a very brief explanation of the procedure, the essential equations and the numerical effort required will be given.

Through a quite simple, computationally efficient three step procedure, the FT model provides average properties such as sol and gel fractions, average molecular weights, and crosslinking densities. The necessary calculations are based upon the evaluation of i) the distribution of the primary chains, ii) the crosslinking densities and iii) the sol and gel fractions.\cite{85} This information are readily obtained as primary chains are linear chains, whose distribution is typically analytically known (equation (4.20)):

\[ f_w(n, \theta) = \frac{n\alpha(\theta)}{(1 + \alpha(\theta))^{n+1}}[\gamma(\theta) + 0.5\alpha(\theta)\beta(\theta)(n-1)] \]  

(4.20)

where \( \alpha(\theta) = \beta(\theta) + \gamma(\theta) \), \( \beta(\theta) = \frac{k_{p1}^*M_1 + k_{p2}^*M_2}{k_{it}^*R^*} \), \( \gamma(\theta) = \frac{k_{p1}^*M_1 + k_{p2}^*M_2}{k_{it}^*R^*} \) and \( \theta \) represents the birth conversion of the chains. The total crosslinking density \( \rho(\theta, \psi) \) (of chains born at conversion \( \theta \), estimated at conversion \( \psi \)) is calculated through equations (4.21)-(4.23):

\[ \rho(\theta, \psi) = \rho_i(\theta) + \rho_a(\theta, \psi) \]  

(4.21)

\[ \rho_i(\theta) = \frac{k_{p3}^*(\theta)PDB(\theta)}{k_{p}^*M(\theta)} \]  

(4.22)
\[
\frac{\partial \rho_s(\theta, \psi)}{\partial \psi} = k^\ast_{p3}(\theta)(F_{2}(\theta) - \rho_s(\theta, \psi)) \left( \frac{k^\ast_p M(\theta)}{M^0_1 + M^0_2} \right)(1 - \psi)
\]  

(4.23)

where \( F_2(\theta) = k^\ast_{p2}(\theta)M_2(\theta)/k^\ast_p M \) and \( \overline{k^\ast_p M(\theta)} = k^\ast_{p1}(\theta)M_1(\theta) + k^\ast_{p2}(\theta)M_2(\theta) \). Sol and gel fractions are calculated by finding the zeros of a non-linear function, which reads:

\[
w_s(\theta, \psi) = \sum_{n=1}^{\infty} f_w(n, \theta)(1 - \rho(\theta, \psi)(1 - w_s(\theta, \psi)))^n
\]  

(4.24)

Notably, the zeros of equation (4.24) give access to all other properties (sol and gel crosslinking densities and sol degrees of polymerizations)\(^{[85]}\) and can be found after the time-integration of 5 ODE and one single PDE (equation (4.23)). Discretizing the PDE along the birth conversion coordinate in \( N_\theta \) points, leads the total number of ODE equations to be solved with this model to be:

\[
N_{eq} = 5 + N_\theta
\]  

(4.25)

Notably, 5 ODE account for mono- and divinyl monomer, PDB, bridges and total radicals, whereas \( N_\theta \) is typically around \( 10^2 \) and represents the birth conversions chosen to discretize the PDE. Being this a non-stiff system of few hundreds ODE, the typical computational time in a non-parallelized Fortran code using the DVODE solver,\(^{[76]}\) from the Livermore library, on an 4-core personal computer running with a 3 GHz CPU is less than 1 minute.
4.3.5. Summary

In order to summarize the main features of each model, the typical outputs provided by the different models are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Model</th>
<th>$x_{sol}$, $x_{gel}$</th>
<th>$DP_{n}$, $DP_{w}$</th>
<th>$\rho_{cross}$, $\rho_{gel}$, $\rho_{total}$</th>
<th>MR</th>
<th>CLD (sol)</th>
<th>Sol/gel criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>intrinsic</td>
</tr>
<tr>
<td>MRNF</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>intrinsic</td>
</tr>
<tr>
<td>GF</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>intrinsic</td>
</tr>
<tr>
<td>KMC</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>arbitrary</td>
</tr>
</tbody>
</table>

4.4. Results and discussion

The predictions of the aforementioned approaches were compared employing two case studies and will be presented hereafter. Namely, average properties as well as complete distributions predicted by the different models are comparatively discussed. The parameter values employed for the case studies are reported in Table 4.1. Notably, these values are arbitrary ones, chosen to the sole purpose to keep the comparison among the approaches as simple and direct as possible.

4.4.1. Case I

4.4.1.1. Average properties

In this case, the ratio of $k_p / k_i$ is about $10^{-4}$, and since diffusion limitations are neglected, no multiradicals are expected to be formed.\textsuperscript{[5, 88]} The average properties chosen to compare the model predictions are sol and gel fractions ($x_{sol}$, $x_{gel}$), number and weight average degree of
polymerization of the sol \( (D_P^{sol}, D_P^{gel}) \) and the average crosslinking densities of sol, gel and total polymer chains \( (\rho_{cross}^{sol}, \rho_{cross}^{gel}, \rho_{cross}^{total}) \). The definitions of these quantities can be found in Appendix ((C4)-(C10)).

The predictions of the sol and gel fractions are reported in Figure 4.1, where the predictions of all models are in almost perfect agreement. This is indeed interesting as the various approaches calculate the sol and gel fraction in quite different ways. As anticipated, the KMC model employs a threshold value of chain length to define the gel equal to \(10^5\) units. As already mentioned, the GF approach distinguishes among sol and gel average properties by identification of the bifurcation of the characteristics in the Laplace domain. This approach allows a mathematically exact determination of the gel point by employing few equations ((C19)-(C23)), although their numerical solution is non-trivial. Note that only average properties of the sol polymer are calculated (e.g. through equations like (4.13)-(4.15)), whereas the gel properties are obtained only for non-diverging quantities by difference: as an example, knowing the total number of polymerized units and those belonging to the sol polymer, the first order moment of the gel can be readily calculated as the difference. As for the MRNF, the determination of the gel and sol fraction occurs automatically, once the convergence on the number of generations is reached.\[^{[19, 84, 88, 105]}\] In fact, increasing enough the number of generations (typically up to values from 5 to 7), a convergence on the gel vs. conversion curves is typically found. This might look counterintuitive, as larger molecules become part of the sol, the larger the number of sol generations is. On the other hand, the high reactivity of these large-size chains allow them to “jump” from one generation to the next very quickly: therefore, above the maximum number of generations mentioned above, further generations remain practically empty, with the corresponding huge chains being transported very quickly towards the gel, without affecting the
gel-conversion curve anymore. In the present case study \( N_{\text{gen}} = 7 \) and \( N_{\text{rad}} = 6 \) have been used. This kind of self-consistent evaluation of the gel point is indeed one of the peculiarities of the MRNF as compared to other modeling approaches. Finally, the FT model calculates the gel curve based on statistical arguments, employing equation (4.24). Once the distribution of primary chains and the overall crosslinking density is known, the sol and gel fraction are easily calculated.

![Graph showing sol and gel fraction predictions for Case I. Dashed line: MRNF, dash-dotted line: FT, circles: KMC, continuous line: GF.](image)

Focusing on the average number and weight degrees of polymerization of the sol, reported in Figure 4.2, it can be seen that again the four models lead to very similar predictions. As expected, the \( DP^\text{sol}_n \) and \( DP^\text{sol}_w \) reach a maximum at the gel point, then progressively decrease as all longer chains in the sol polymer are taken up by the gel and only shorter ones remain in the sol. After roughly 60% of conversion very slight differences start to appear in the predictions of both \( DP^\text{sol}_n \) and \( DP^\text{sol}_w \). Notably, at such conversions the sol polymer accounts for less than 5% of the total
polymer mass (Figure 4.1): therefore, this discrepancy has indeed negligible relevance. All models predict short sol chains at the end of the reaction, in the order of few hundreds monomer units. Notably, GF, MRNF, and FT models enable the direct calculation of the $DP_n^{sol}$ and $DP_w^{sol}$ only,\cite{85, 88, 109, 110} whereas the Monte Carlo model provides these quantities according to the aforementioned criterion on the maximum chain length of the sol.

![Figure 4.2](image)

$DP_n$ and $DP_w$ predictions for Case I. Dashed line: MRNF, dash-dotted line: FT, circles: KMC, continuous line: GF.

When comparing the crosslinking densities ($\rho_{cross}^{sol}$, $\rho_{cross}^{gel}$, $\rho_{cross}^{tot}$), once again a very nice agreement is found among the different models, as shown in Figure 4.3. In particular, when all the polymer is in the sol phase (i.e., before gelation, $\rho_{cross}^{tot} = \rho_{cross}^{gel}$), all models predict the very same quantities. The gel phase starts forming at around 9% of conversion (as expected from Figure 4.1), readily exhibiting a larger crosslinking density than that of the total polymer (sol and gel). This well-known behavior\cite{2} is due to the fact that the gel formation is mediated by
propagation through PDB, a reaction promoting the formation of crosslinks among chains. Also
for $\rho_{\text{gel}}^{\text{cross}}$, a perfect agreement between models is found. With increasing conversion $\rho_{\text{tot}}^{\text{gel}}$ tends to
overlap with $\rho_{\text{tot}}^{\text{cross}}$, as progressively more and more polymer chains crosslink and are taken up by
the gel, as already seen in the Figure 4.1. Meanwhile, $\rho_{\text{sol}}^{\text{cross}}$ decreases, as crosslinking reactions
among sol chains become less favorable than sol-gel reactions. After 50% of conversion, a slight
discrepancy in terms of $\rho_{\text{sol}}^{\text{cross}}$ is observed: MRNF and FT tend to predict a larger increase of this
quantity as compared to KMC and GF. The KMC and GF predictions are superimposed: as both
models do not have any underlying assumption they lead to fully comparable predictions. On the
other hand, the overlapping of the MRNF and FT curves is most likely incidental and can be
related to the approximations of the two approaches. The MRNF model employs some closure
rules\cite{19} which become less reliable as soon as chains become shorter (cf. Figure 4.2), whereas the
FT model involves several assumptions, as detailed in paragraph 4.3.4. On the other hand it is
worth mentioning that this discrepancy occurs when the residual sol phase is less than 10%,
meaning that the different models are fully equivalent in terms of overall average quantities.
4.4.1.2. Distributions

As the FT is typically employed to predict average properties solely, and only gives access to total average moments which are known not to be enough to reconstruct distributions,\textsuperscript{[75]} it was decided not to attempt any CLD reconstruction with this model. Therefore, only the distributions predicted by the KMC, GF and MRNF will be compared with one another. Notably, KMC and GF provide the sol distribution, whereas the MRNF approach calculates only the leading moments of the different sol generations, whose distributions are then reconstructed assuming that they conform to a suitable model distribution, specifically the perturbed Gamma distribution. \textsuperscript{[74, 75]} All distributions were calculated at selected values of conversion, namely $\chi$ equal to 5, 9 and 14\%. These values were selected as representative of: i) sol polymer only is present ($\chi = 5\%$), ii) the onset of the gelation ($\chi = 9\%$) and iii) a condition where 50\% of the polymer is sol and 50\% is gel ($\chi = 14\%$). The calculated distributions are
presented as normalized weight distribution, \( f_w(n) = n P_n / \sum_{n=1}^\infty P_n \), as well as the non-normalized \( n f_w(n) \), where \( P_n \) indicates the total concentration of polymer chains with the given degree of polymerization. The latter representation has been selected because it amplifies model discrepancies (due to the second power with respect to the chain length) and it corresponds to the typical representation of the distribution measured by size exclusion chromatography.

As shown in Figure 4.4a, a very good agreement between the two kinetic models, MRNF (dashed line) and GF (continuous line), is seen in terms of \( f_w(n) \) before the gelation onset (Figure 4.4a). The KMC result (circles) exhibits the maximum value at the same chain length as the two other models, although larger chains are formed in more significant amount, as can be best seen when comparing the predictions in terms of \( n f_w(n) \), shown in Figure 4.4b. The predictions of the kinetic GF model are in relatively good agreement with those of the KMC model up to chain lengths of \( 10^4 \); unfortunately, no further predictions are given at larger chain lengths due to the numerical difficulties encountered in the distribution evaluation from its transform. Notably, a shoulder in the distribution is predicted by MRNF in this case: this is indeed an artifact and due to a well-known issue of reconstructing distributions from the generations.\(^{17, 75}\) Nevertheless, considering the simplicity of the method and the negligible computational effort, the agreement with the predictions supplied by the more complex models (KMC and GF) is more than satisfactory in the pre-gel regime.
\( f_w(n) \) and \( n f_w(n) \) predicted at 5% conversion for Case I. Circles: KMC, dashed line: MRNF, continuous line: GF.

On the other hand, significant discrepancies among the CLD predictions start to occur at the gelation onset (\( \chi = 9\% \)), as can be seen in Figure 4.5a and 5b. These discrepancies are again more significant at high molecular weights and especially visible in terms of \( n f_w(n) \), where the role of the longest chains is amplified. As soon as gelation occurs, the distributions predicted by MRNF become quite unreliable, showing multiple, artificial peaks again due to the reconstruction through moments, which becomes especially sensitive to the large polydispersity of the high generations at the gel point.[17] As a matter of fact, also the most realistic distribution (which should be the one predicted by the KMC model) reflects the onset of gelation by developing a bimodal CLD: the smaller peak at larger chain lengths represents the first few % of gel polymer, whereas the larger peak the sol polymer, which is still dominant at \( \chi = 9\% \). Finally, the predictions of the kinetic GF model are again in reasonable agreement with those of KMC model up to chain lengths of \( 10^4 \), above which the numerical issues mentioned above arise again.
Figure 4.5

\( f_w(n) \) and \( n f_w(n) \) predicted at 9% conversion (about 1% gel) employing parameters of case I. Circles: KMC, dashed line: MRNF, continuous line: GF

When the gel and sol phases are present in comparable amount (both at around 50% at \( \chi = 14\% \)), the sol CLD predictions of MRNF and GF models are quite close while that of KMC is slightly underestimated (Figure 4.6a). On the other hand, when considering Figure 4.6b, the second peak at very large chain length provided by KMC should be regarded as a qualitative representation of gel chains, whose size should be practically infinite. Interestingly, such a peak is practically invisible in the \( f_w(n) \) representation, indicating that only very few, extremely large chains are actually constituting the gel phase.
Note that the most demanding case is indeed that corresponding to the onset of the gel formation (Figure 4.5): these specific conditions are therefore ideal to highlight even minor discrepancies among the predictions of the different models. The computational times required for the complete simulation of Case I using the different models are reported in Table 4.3. As expected, a trade-off between computational time and detail of the obtained information can be recognized. The FT and MRNF models are very fast (1 and 2 minutes, respectively) but give direct access to the average properties only, while the CLD is reconstructed given a model distribution. On the other hand, GF and KMC, giving direct access to the sol distribution, require larger computational effort (20 and 200 minutes, respectively). Note that the GF predictions are limited to chains whose length is lower than $n = 3 \times 10^4$. 

Figure 4.6

$f_w(n)$ and $n f_w(n)$ predicted at 14% conversion (about 50% gel) employing parameters of case I. Circles: KMC, dashed line: MRNF, continuous line: GF
### Table 4.3
Computational efforts for case studies I and II (non-parallelized cores)

<table>
<thead>
<tr>
<th>Model</th>
<th>Case I</th>
<th>Case II</th>
<th>Case I</th>
<th>Case II</th>
<th>Cores [-]</th>
<th>GhZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>~1</td>
<td>~2</td>
<td>~300</td>
<td>~1600</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>MRNF</td>
<td>~2</td>
<td>~20</td>
<td>~300</td>
<td>~1600</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>GF</td>
<td>20***</td>
<td>20***</td>
<td>14 × N × Nₚ**</td>
<td>14 × N × Nₚ**</td>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td>KMC*</td>
<td>200</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*The reported computational time is the time to perform the required number of simulations to obtain a meaningful average.

**Nₚ (30) is the number of desired chain lengths at which the distribution is evaluated, N (10 and 12) is the number of terms in the sequence given by equation (4.16), and 14 is the number of ODE involved in the 2PBVP to be solved iteratively.

*** These computational times correspond to the evaluation of the distribution at 3 different conversion values.

### 4.4.2. Case II

The key difference in terms of kinetic parameters in Case II, as compared to Case I, is the value of the termination rate constant, which has been reduced by 2 orders of magnitude. This way, the ratio \( k_p / k_r \) is large enough to establish conditions where multiradicals (MR) play a role.\[5, 88\] The very same quantities in terms of average properties as in Case I will be compared with one another, as well as the CLD for the various models, in order to see how the different approaches deal with MR. Note that the FT model is not considered in this case; in fact, both the monoradical and pseudo-steady-state assumptions (on which the model relies) are violated employing these parameter values.\[5\]

### 4.4.2.1. Average properties

In this case the model predictions cease to overlap with one another, as can be seen in Figures 4.7-4.9. Focusing on the sol and gel curves in Figure 4.7, all predictions are in reasonably good agreement. This simply confirms that all the three models properly account for
multiradicals, as previously mentioned: while GF and MRNF need an extra coordinate in the respective PBE, the KMC model naturally accounts for chains bearing more than one active site. On the other hand, a small discrepancy exists in terms of gel point prediction: KMC shows a faster gelation when compared to both MRNF and GF. The reason for this discrepancy is most likely due to the selected threshold value of chain length between sol and gel polymer (once more equal to $10^5$ units like in Case I): since this value is affected by the model parameter values, such disagreement is not surprising to occur.

![Figure 4.7](image)

Figure 4.7
Sol and gel fraction predictions employing parameters of case II. Dashed line: MRNF, circles: KMC, continuous line: GF

As for the other average properties, degrees of polymerization and crosslinking densities, the three models are in good agreement, as shown in Figure 4.8 and 4.9. This holds all along the reaction, with the exception of slight discrepancies at high conversion already commented in the
previous case study. Overall, it can be said that the three models are equivalent in terms of average properties.
Figure 4.8.
$DP_n$ and $DP_w$ predictions employing parameters of case II. Dashed line: MRNF, circles: KMC, continuous line: GF

Figure 4.9.
Total, sol and gel Crosslinking densities predictions employing parameters of case II. Dashed line: MRNF, circles: KMC, Continuous line: GF
4.4.2.2. Distributions

The comparison of the distributions has been done also in this case for three different conversions, namely $\chi$ equal to 2%, 4% and 8% (Figure 4.10-4.12). Also in this case, the selected values represent: i) a situation where only sol polymer is present ($\chi = 2\%$), ii) the onset of the gelation ($\chi = 4\%$) and iii) a condition where almost the same polymer weight fraction is found in sol and gel ($\chi = 8\%$).

![Figure 4.10](image)

$f_w(n)$ and $n f_w(n)$ predicted at 2% conversion employing parameters of case II. Circles: KMC, dashed line: MRNF, continuous line: GF
A reasonable agreement is found between the GF method (continuous line) and the KMC approach (circles) at all the three values of conversion; this is the case until a chain length of about $3 \times 10^3$, where the numerical issues mentioned above do not allow GF to provide reliable
predictions. Note that similar issues are quite evident also at short chain lengths, around and below 100 units. Once more, these difficulties are due to the selected anti-transformation approach and different methods are under examination to overcome them both at short and long \( n \) values. The sol-gel transition captured by the KMC ending up with a bimodal distribution (Figure 4.12), is only qualitative, as already discussed. Moreover, as expected, the largest discrepancies among the models appear very close to point of gel formation (Figure 4.11), where the peculiar nature of the sol distribution makes the comparison especially meaningful. On the other hand, the MRNF provides reconstructed CLDs with limited accuracy at all conversion values: this is not surprising, given the previously mentioned limitations in terms of reconstruction of the distribution given only its three leading moments. Such limitations appear to be amplified when multi-active chains are involved, despite the detailed description of the distribution of active sites. The computational times for Case II are reported in Table 4.3. Notably, the increase in computational time for the MRNF is due to the increased values of the two parameters \( N_{\text{gen}} \) and \( N_{\text{rad}} \) \( (N_{\text{gen}} = N_{\text{rad}} = 17) \), leading to a larger number of equations to be solved (1600 ODE instead of 300 ODE in Case I). As for the other methods, the GF and KMC require 20 and 10 minutes, respectively. While the GF approach is quite insensitive to the values of the kinetic parameters employed, a significant reduction in the computational time is observed for the KMC (10 minutes in Case II vs. 200 minutes of Case I). This behavior can be imputed to the well-known sensitivity of the sampling time to the specific parameter values.
4.5. Conclusions

A comparison among four different modeling approaches for crosslinking copolymerization (stochastic KMC, statistical/kinetic FT and two kinetic approaches, GF and MRNF) has been carried out in terms of average properties as well as CLD. The comparison involved two case studies differing in the values of the kinetic parameters as well as recipe conditions.

The fully stochastic approach (KMC) gives access to the sol distribution and naturally accounts for several complicating aspects. The simulation time needed to obtain a statistically meaningful prediction is a strong function of the kinetic parameter values and varies significantly, between 10-200 minutes. Average properties are in good agreement with those predicted by the other models provided the chain length threshold discriminating between sol and gel is appropriately chosen, for example by fitting the KMC prediction of gel point to that of a kinetic approach.

The kinetic approach based on generating functions, GF, predicts with full detail the evolution of all sol species during the polymerization. The computational time for one simulation is in the order of 20 minutes. A model-independent criterion is used to establish the gel point, based on the divergence of the 2nd order moment. Notably, the predicted distributions of molecular weight of the sol polymer are in good agreement with those provided by the fully stochastic approach, even though some numerical issues associated with the shortest and the longest chains (below 100 and above $10^4$ units, respectively) are present. Different anti-transformation approaches are currently under examination to solve such problem.

The MRNF kinetic model, based on the engineering-effective method of moments, requires very limited computational effort (with typical parameter values, no more than 5 minutes of
computation time) and its predictions are in good agreement with those of more comprehensive models in terms of average properties. The distribution of the polymer chains between sol and gel is identified in a model-independent way through numerical experiments. On the other hand, the prediction of distributed properties (such as the CLD) represents an intrinsic weakness of the methodology: in fact, the reliability of such distributions is difficult to be judged a priori and it is affected by numerical details like the selected model distribution as well as closure formulas. Similarly to the classical numerical fraction, the present method is best suited to quantify average properties, with minimal computational effort, making it ideal for parameter calculation.

The statistical/kinetic FT model exhibits a remarkably effective compromise in terms of reliability and computational effort provided the (many) underlying assumptions are fulfilled. The distribution between sol and gel is identified through statistical arguments, without any need of arbitrary criteria. The very few equations required still provide predictions which compare very favorably to those of more demanding models.

In conclusion, simpler kinetic models (FT, MRNF) are fast and reliable when focusing on average properties of sol and gel. Therefore, they are particularly suitable for parameter estimation or when limited experimental data are available, a quite frequent situation in crosslinking copolymerization. To directly access detailed polymer properties such as the sol CLD, more complex models (based on deterministic as well as stochastic approaches) require indeed more demanding numerical implementation and larger computational times (GF, KMC).
5. Shear-Stability and Gelation of Inverse Latexes\textsuperscript{4}

5.1. Introduction

Inverse emulsions (IE) are liquid (e.g. water)-in-oil dispersions, while inverse latexes (IL), based on the terminology employed in the literature,\textsuperscript{[118]} are polymer (or water-swollen polymer)-in-oil dispersions. Latex instead typically refers to a polymer-in-water dispersion. Both IE and IL are of utmost importance in a great variety of industrial areas, such as cosmetics,\textsuperscript{[119]} pharmaceuticals\textsuperscript{[120]} and oil industry.\textsuperscript{[121]} Thus, many studies have been devoted to these systems, dealing with their preparation, stabilization and destabilization mechanisms.\textsuperscript{[122-126]}

More than 60 years ago, Koelmans and Overbeek\textsuperscript{[123]} investigated the stability of charge-stabilized emulsions in low polar solvents. They concluded through theoretical analysis that in spite of the low dielectric constant of apolar media, the electrical double layer is very diffuse and the corresponding Debye length is very large. In this case, only a little charge is needed to obtain appreciable surface potentials. On the other hand, this is not enough for ensuring a stable emulsion, as the particles possess a non-zero potential energy even at large distances, which lowers the energy barrier.\textsuperscript{[123, 127]} Moreover, it was shown\textsuperscript{[122, 124]} that as the particle concentration increases, the interaction of the diffuse layers among the particles further reduces the electrostatic stability. In other words, not only high absolute values but also high gradients of surface potentials are needed to ensure effective charge-stabilization. As this becomes difficult in oil,

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Steric stabilization for IE and IL is typically preferred.\textsuperscript{128} Stability of liquid-liquid emulsions is of particular interest in the oil industry.\textsuperscript{129} Undesired water in oil emulsions, stabilized by surface active compounds naturally present in the oil, render the water removal a cumbersome task. To destabilize these emulsions, typically a so-called “demulsifier” is added. The demulsifier is usually of a high HLB\textsuperscript{130} (hydrophilic to lipophilic balance) value, thus rather hydrophilic, which substitutes the more hydrophobic (low HLB) surfactant originally present on the water drop surface, thus lowering the stability of the emulsion.\textsuperscript{131}

An abundant literature can be found also for the IL constituted of water affine polymer particles dispersed in an oil phase, and these studies focus mainly on their preparation\textsuperscript{132-134} and their shelf-life stability.\textsuperscript{135, 136} In his extensive review, Capek\textsuperscript{133} addresses the essential requirement for the IL stability: surfactants with low HLB values should be employed and a strong lyphobe (typically an electrolyte) should be added to the water phase, i.e., inside the particles, in order to prevent Ostwald Ripening, which can occur during polymerization. Armanet et al.\textsuperscript{135} investigated the stability of poly(acrylamide) based water-in-oil IL using the classical acceleration tests, shear measurements and shelf life. It turned out that a mixture of a triblock copolymeric stabilizer combined with two fatty acid ester-type emulsifiers was rather effective for stabilizing the IL, regardless of the blend composition. This result was ascribed to the more “condensed” interfacial film and maximized entropy of mixing. Also the occupied volume fraction was found to influence the IL stability. For example, when the volume fractions are smaller than 55\%, all the prepared IL were found to be unstable. However, few studies can be found in the literature on the shear-induced aggregation of such IL, despite the fact that, due to customers need, these dispersions are usually produced at the verge of stability and can undergo undesired coagulation and gelation by the shearing forces during their processing.
Concerning the shear-induced aggregation, some interesting investigations have been carried out in the literature for different dispersions. Guery et al.\textsuperscript{[137]} investigated the shear stability of non-Brownian particles, consisting of a double emulsion of water droplets dispersed in larger globules of crystallizable oil, dispersed in water. The particles have an average diameter of about 5 \( \mu \text{m} \) and an occupied volume fraction of 10\%. A shear-induced gelation was observed at the shear rate in the range of 80-300 s\(^{-1}\). The key results of this work are: i) showing an exponential decay of the induction time for the gelation with the shear rate; ii) the observed gelation is abrupt, leading to dramatic changes from the liquid-like aqueous dispersion to a solid-like paste. Giermanska-Khan et al.\textsuperscript{[138]} studied the shear-induced gelation of a suspension at high mass fractions (up to 50\%), consisting of large (~50 \( \mu \text{m} \)) solid paraffin oil droplets dispersed in water and stabilized by silica nanoparticles. This work shows the existence of a critical occupied volume fraction, beyond which the gelation time is significantly faster (from hours to almost instantaneous gelation). Moreover, it was observed that the gelled materials resemble elastic solids and cannot be redispersed into primary droplets, due to the occurrence of partial coalescence among the droplets under the shear force.

In the case of polymer-in-water dispersions, \textit{i.e.}, latexes, several studies, both experimental\textsuperscript{[118, 139-143]} and theoretical,\textsuperscript{[144]} can be found in the literature. For latexes that are stabilized by DLVO interactions, shear-induced gelation typically occurs after an induction time. Moreover, Zaccone et al.,\textsuperscript{[144]} by extending Kramer’s theory, derived an Arrhenius-type rate equation\textsuperscript{[144]} accounting for the shear-activated aggregation. The theory is able to explain the typical induction period observed in systems with a repulsive barrier. In particular, based on the derived theory, a characteristic time for shear-induced aggregation can be defined, which has the following scaling,
\[ \tau_{\text{agg}} \propto \exp\left(\frac{U_m - 6\pi \alpha \eta \dot{\gamma} a^3}{k_B T}\right) = \exp\left(\frac{U_m}{k_B T} - 2\alpha Pe\right) \]  

(5.1)

where \( U_m \) is the particles interaction barrier, \( T \) the temperature, \( k_B \) the Boltzmann constant, \( \alpha \) a geometrical parameter, \( a \) the particle or cluster radius, \( \eta \) the system viscosity, \( \dot{\gamma} \) the shear rate, and \( Pe \) the Peclet number, representing the ratio between shear and Brownian aggregation rates (\( Pe = 3\pi \eta \dot{\gamma} a^3 / k_B T \)). Thus, when shear is introduced into the system, the stability is related to the competition between the interaction barrier, \( U_m \), and the shear destabilization contribution, \( Pe \). Once the repulsive barrier is high enough such that the exponential is positive, the characteristic time of aggregation will be large, i.e., the aggregation rate is small. Upon aggregation, \( Pe \) increases significantly, as it scales with the cube of the clusters radius, \( a \). Then, when \( a \) increases to a certain extent, the sign of the exponential becomes negative and the characteristic time of aggregation drops abruptly, leading to the observed “explosive” increase in shear-viscosity, due to the gelation of the latex.

To our knowledge, no investigation has been reported in the literature on the shear-induced aggregation of water-swollen polymeric IL, i.e., water-swollen polymer particles suspended in an oil phase, where the dominant interactions are steric, instead of DLVO. Therefore, the aim of this work is i) to explore the possibility of the shear-induced gelation in the IL and ii) to identify the key parameters that regulate the observed destabilization and gelation phenomena. To do so, we have employed water swollen polyacrylamide-based particles at large particle contents, dispersed in an organic solvent and stabilized by a mixture of steric surfactants. Therefore, under shear, the systems undergo not only the shear-induced aggregation, but also coalescence (due to the softness of the particles) and thixotropy (due to the crowding of the particles).
5.2. Materials and Methods

5.2.1. The IL systems

The IL systems were supplied by an industrial partner, prepared using a mini-emulsion polymerization technique at 313 K. The continuous phase is paraffin oil consisting of a mixture of hydrocarbons, while the dispersed particles are composed of a mixture of water and copoly(acrylamide and 2-dimethylamino-ethyl acrylate, methyl chloride quaternary salt) (henceforth referred to as the charged co-monomer). A non-ionic emulsifier, namely, sorbitan mono oleic acid ester, with an HLB value of 4.3, henceforth called E₁, was employed to stabilize the particles.

IL systems with different characteristics were prepared, and the details are reported in Table 5.1. The \( \eta_{PR} \) value shown in Table 5.1 is an indication of the relative viscosity of the particles (scaled on the lowest viscosity of the systems prepared).
<table>
<thead>
<tr>
<th>IL code</th>
<th>Polymer % in particle wt</th>
<th>Co-monomer % [mol]</th>
<th>( E_1 % \text{wt} )</th>
<th>( \eta_{PR} )</th>
<th>d [nm]</th>
<th>PDI [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>55.0</td>
<td>15</td>
<td>2.3</td>
<td>2.04</td>
<td>703±70</td>
<td>0.302±0.238</td>
</tr>
<tr>
<td>138</td>
<td>55.0</td>
<td>15</td>
<td>2.3</td>
<td>1.49</td>
<td>705±25</td>
<td>0.42±0.295</td>
</tr>
<tr>
<td>142</td>
<td>55.0</td>
<td>15</td>
<td>2.3</td>
<td>1.28</td>
<td>687±75</td>
<td>0.178±0.09</td>
</tr>
<tr>
<td>235</td>
<td>51.6</td>
<td>10</td>
<td>2.3</td>
<td>1.41</td>
<td>584±15</td>
<td>0.244±0.155</td>
</tr>
<tr>
<td>238</td>
<td>55.5</td>
<td>20</td>
<td>2.3</td>
<td>1.43</td>
<td>615±15</td>
<td>0.134±0.071</td>
</tr>
<tr>
<td>240</td>
<td>59.4</td>
<td>30</td>
<td>2.3</td>
<td>1.39</td>
<td>615±5</td>
<td>0.221±0.036</td>
</tr>
<tr>
<td>241</td>
<td>62.1</td>
<td>40</td>
<td>2.3</td>
<td>1.42</td>
<td>621±7</td>
<td>0.181±0.046</td>
</tr>
<tr>
<td>0032</td>
<td>54.6</td>
<td>15</td>
<td>2.7</td>
<td>1.88</td>
<td>670±28</td>
<td>0.193±0.092</td>
</tr>
<tr>
<td>0034</td>
<td>54.6</td>
<td>15</td>
<td>2.7</td>
<td>1.00</td>
<td>730±22</td>
<td>0.234±0.102</td>
</tr>
<tr>
<td>0047</td>
<td>44.8</td>
<td>15</td>
<td>2.5</td>
<td>1.90</td>
<td>619±42</td>
<td>0.33±0.099</td>
</tr>
<tr>
<td>0049</td>
<td>48.1</td>
<td>15</td>
<td>2.6</td>
<td>1.88</td>
<td>678±32</td>
<td>0.21±0.029</td>
</tr>
<tr>
<td>0050</td>
<td>51.4</td>
<td>15</td>
<td>2.6</td>
<td>1.88</td>
<td>687±11</td>
<td>0.21±0.051</td>
</tr>
<tr>
<td>0075</td>
<td>52.1</td>
<td>10</td>
<td>2.7</td>
<td>1.44</td>
<td>608±3</td>
<td>0.10±0.035</td>
</tr>
<tr>
<td>0076</td>
<td>55.0</td>
<td>20</td>
<td>2.6</td>
<td>1.45</td>
<td>623±5</td>
<td>0.232±0.079</td>
</tr>
<tr>
<td>0077</td>
<td>55.1</td>
<td>30</td>
<td>2.7</td>
<td>1.47</td>
<td>639±6</td>
<td>0.34±0.13</td>
</tr>
<tr>
<td>0078</td>
<td>55.1</td>
<td>40</td>
<td>2.7</td>
<td>1.43</td>
<td>697±14</td>
<td>0.29±0.027</td>
</tr>
</tbody>
</table>

It should be mentioned that the particles of all the investigated IL systems are rather soft, and they can coalesce if they aggregate. In fact, if we dilute the IL in pure paraffin oil, due to desorption of the surfactants from the particle surface, the particles are destabilized, leading to aggregation. What we obtained after the dilution is phase separation, with the paraffin oil phase on the top and the water-polymer phase on the bottom. In the water-polymer phase, no identity of the original particles can be found, indicating full coalescence among the particles.
5.2.2. The rheometer shear experiments

An ARES rheometer (Rheometric Scientific) was employed for the shear-induced gelation of IL, equipped with a cooling bath and a temperature controller, to maintain the sample at constant temperature while shearing.

Preliminary analysis employing standard geometries, such as cone-plate, plate-plate and Couette flow, revealed a substantially high stability of the IL systems, as no gelation was observed when a shear rate up to 2000 s\(^{-1}\) was employed (data not shown). Then, further increase in the shear rate was attempted by reducing the gap in the case of the plate-plate geometry, however an excessive wall slipping was observed (data not shown). Therefore, a specially-designed, gridded stator geometry was used for all the experiments. This stator was placed inside a rotating cup in order to avoid fluid losses. The cup diameter was 34 mm, while the stator had a diameter of 30 mm, and hence the side gap was 2 mm. The rheometer shear experiments were carried out in a temperature range of 298-328 K, at a fixed rotational speed of 50 rad/s (unless otherwise stated), with a bottom gap of 0.15 mm between stator and cup. Since the side gap is 2 mm, the dominant shear rate is generated in the bottom gap.

Since the employed geometry is non-standard, we performed a CFD (Computational Fluid Dynamics) study in order to evaluate the real shear rate that the IL systems undergo. The details of the CFD study are presented in the Electronic Supplementary Information (ESI). It was found that the overall average shear rate is only 581 s\(^{-1}\), while the maximum shear rate lies around 5600 s\(^{-1}\). Since no gelation occurred at a shear rate of 2000 s\(^{-1}\) for standard geometries, as discussed above, this means that the gelation phenomena observed in the following is dominated by the maximum shear rate, rather than the average one.
For each shear experiment, 1.5 ml IL was dropwise added in the rheometer cup, and then, when the right bottom gap (0.15 mm) was set by lowering the stator, the steady shear test started at the desired rotational speed. When a demulsifier was used, it was dropwise added to the IL under gentle magnetic stirring (250 rpm) for 10 minutes to ensure sample homogeneity, followed by the steady shear test. When the experiments were performed at a temperature different from room temperature, the IL were pre-heated in an oven for 10 minutes to the desired temperature.

5.2.3. Dynamic Light Scattering

The particle size in the IL systems was measured by dynamic light scattering (DLS) at 298 K using a Zetasizer Nano instrument (Malvern, UK). To perform the experiment, the IL were diluted to a desired particle volume fraction by paraffin oil which contained a certain amount of \( E_1 \). The addition of \( E_1 \) to the paraffin oil for the IL dilution was necessary in order to avoid desorption of the originally adsorbed \( E_1 \) on the particles surface, and their consequent destabilization (aggregation). On the other hand, adding an excessive quantity of \( E_1 \) would form a large amount of micelles in the solution, which would generate depletion forces among the IL particles, leading again to particle destabilization.\[^{[143]}\] To define the correct concentration of \( E_1 \) in paraffin oil, we have diluted the IL systems 235 and 238 in Table 5.1 to the \( E_1 \)/paraffin oil solutions at different \( E_1 \) concentrations and measured the corresponding IL particle diameters. The results are shown in Fig. 1. It is seen that in both cases, the particle diameter is a strong function of the \( E_1 \) concentration, in a non-monotonic way. At very low \( E_1 \) concentrations, the diameter decreases as the \( E_1 \) concentration increases. This confirms the above argument that the added \( E_1 \) progressively avoids desorption of the originally-adsorbed \( E_1 \) on the particle surface, thus, avoiding particle destabilization. At the \( E_1 \) concentration around 2.5%wt, the diameter
reaches the minimum. Then, further increase in the E\textsubscript{1} concentration leads to increase in the particle diameter. This can be attributed to the above-mentioned depletion effect of the formed micelles, reducing particle stability. Therefore, from the results in Figure 5.1, the correct E\textsubscript{1} concentration in paraffin oil is 2.5\%wt, where the effects of both the surfactant desorption and depletion reach the minimum. This value has then been used for dilution of all the IL systems.

![Graph showing diameter of particles vs. E\textsubscript{1} concentration](image)

**Figure 5.1**
IL systems 235 (full squares) and 238 (empty squares) with different \% of E\textsubscript{1} (w/w). The added E\textsubscript{1} progressively avoids desorption of the originally adsorbed E\textsubscript{1}, avoiding destabilization. After reaching a minimum in size, a further increase in the E\textsubscript{1} concentration leads to an increase of the size due to depletion induced destabilization.

The particle volume fraction for the DLS measurements was chosen at 0.06\%. Using this somewhat high particle concentration was constrained by the signal of the E\textsubscript{1} micelles present in paraffin oil. The initial size of the micelles is typically small and cannot influence the measurement of the bigger particles. However, since small amount of water was present in the original E\textsubscript{1}, the micelles are water-swollen and undergo Ostwald ripening\textsuperscript{[145]} as shown in the ESI (Figure S3), leading to the average size of the micelles increasing with time, disturbing the characterization of the IL particles.
Employing the aforementioned procedure, the diameter of the particles in all the IL systems considered was analyzed by DLS, and the results are reported in Table 5.1. Note that for some IL systems, the particle diameter measured by DLS was compared with that from image analysis of cryo-SEM pictures, and the agreement was very good. This confirms the validity of the adopted dilution procedure for the DLS experiments.

As can be seen from Table 5.1, the polydispersity index (PDI) is somewhat large in all cases. This arises because of the employed inverse mini-emulsion polymerization technique, which typically leads to relatively high polydispersity of the particle size. The particle volume fraction in all the IL systems is substantially large and equals approximately 0.60. Thus, it will not be surprising later on when we observe thixotropic behavior under shear.

5.2.4. Cryo SEM

Samples for cryo-SEM were vitrified at about -160°C employing the high-pressure freezing machine from BAL-TEC HPM 100. After freeze-fracturing, the particles were coated with tungsten (2 nm, at 45° angle initially, then further 2 nm continuously spread from 45° to 90°). Images were recorded on a Gemini 1530 FEG scanning electron microscope (Zeiss, Oberkochen, Germany) equipped with a cold stage. The cryo-SEM analysis had to be performed without dilution, because, as illustrated in Fig. 1, to avoid E1 desorption from the particle surface and depletion destabilization, one has to use a well-defined E1 concentration for diluting each IL. Slight difference in the E1 concentration for dilution would lead to unpredictable effect on the particle/cluster stability, coalescence state, particle rearrangement within clusters, etc.
5.3. Results and Discussion

5.3.1. Phenomena occurring along the shearing history

The typical profile of the shear viscosity ($\eta$) as a function of time ($t$) is shown in Figure 5.2. It corresponds to the IL system, 0075 in Table 5.1, at a fixed temperature, $T=318$ K, and shear rate, $\dot{\gamma}=5600$ s$^{-1}$. It is seen from Figure 5.2 that the $\eta$ value initially decreases slowly with time, and when reaching a minimum, it increases quite abruptly.

![Viscosity profile of IL system 0075 sheared at 5600 s$^{-1}$ at 318 K. The viscosity initially decreases due to thixotropy, reaches a minimum and grows abruptly due to aggregation, which leads to gelation.](image)

Let us first consider the initial $\eta$ decrease region, i.e., the shear thinning phenomenon. As mentioned above, since the IL systems are very crowded and the particles are repulsive, the position of the particles before shearing reaches a certain equilibrium (energy minimum). Thus, when a shear is imposed to the system, such a structure is progressively broken, leading to the typical thixotropy of non-Newtonian fluids. To further support that thixotropy can explain the shear thinning phenomenon, we have performed a fitting for the shear thinning data of 9 different IL systems, using the following expressions, which are typically used to describe thixotropic
behaviors in emulsions: \[146\]

\[
\frac{d\lambda}{dt} = (-k_1 \dot{\gamma}\lambda + k_2 \dot{\gamma}^{0.5} (1 - \lambda) + k_3 (1 - \lambda))
\]

Equation (5.2) describes the variation of the structural parameter, \( \lambda \), which progressively decreases with time, depending on the shear rate, \( \dot{\gamma} \). The three constants, \( k_1 \), \( k_2 \) and \( k_3 \), are structural parameters that account for the breaking down of the IL “structure”. In particular, \( k_1 \) represents the kinetic constant for breaking the structure by shear, and \( k_2 \) and \( k_3 \) account for building-up the structure by shear and Brownian motion, respectively.\[146\] It follows from eqn (5.3) that the IL viscosity \( \eta \) decreases with time. The three structure parameters, \( k_1 \), \( k_2 \) and \( k_3 \) of our IL systems have been obtained by fitting the measured \( \eta \) profiles, and their values are \( k_1 = 7.66 \times 10^{-9} \), \( k_2 = 3.48 \times 10^{-7} \text{s}^{-1/2} \) and \( k_3 = 5.24 \times 10^{-9} \text{s}^{-1} \), at the shear rate, \( \dot{\gamma} = 5600 \text{s}^{-1} \).

After reaching the local minimum, the abrupt increase in \( \eta \) in Figure 5.2 is very similar to the phenomenon observed during the steady shear tests of aqueous dispersions of polymer particles mentioned above.\[118, 142\] For those experiments, since the particle volume fractions were much lower (<25%), the thixotropic behavior discussed above was not observed, but the abrupt increase in \( \eta \) after reaching certain time did occur, which was related to the shear-activated
aggregation, leading to formation of fractal clusters that occupy the entire available space and eventually to gelation. Thus, the abrupt increase in $\eta$ in Figure 5.2 can also be explained by the gelation of the particles. It should be mentioned that eqn (5.1) was derived for particles kinetically stabilized by the DLVO interactions, where $U_m$ is the interaction barrier. In the present IL systems, the particles are stabilized by the steric repulsion generated by the adsorbed $E_1$ molecules on the surface. In this latter case, it is hard to assess if such a $U_m$ does exist. To explain the occurrence of the aggregation, we may consider that under the intense shear force, as two particles are approaching, they feel from each other more and more the steric repulsion. When the received repulsion force becomes larger than the anchoring force of the $E_1$ molecules on the surface, relocation of the $E_1$ molecules might take place, leading to drastic drop in the repulsion, as if an interaction barrier ($U_m$) has been overcome, and eventually to aggregation between the two particles (by the van der Waals force).

![Figure 5.3](image.png)

**Figure 5.3**
Thixotropic behavior of IL 240: viscosity profile modeled with equation (2) fits experimental data

On the other hand, the particles of all our IL systems are made of water swollen polymer, being
relatively soft, and, when they aggregate, the particles can contact directly due to the relocation of the $E_1$ surfactants, resulting in progressive coalescence, similarly to what happens in rubbery colloids.\footnote{147} Notably, if full coalescence occurs among the aggregated particles, the occupied volume by all the particles would not change with time, and then no gelation occurs. Therefore, having indeed observed the abrupt increase in $\eta$ in Figure 5.2 if coalescence occurs, it can only be a partial coalescence.

To understand what indeed happens during the steady shear tests, we have made cryo-SEM pictures for the IL system, 0075, sheared at different times at $T=318$ K and $\dot{\gamma}=5600$ s$^{-1}$. Figure 5.4 shows the cryo-SEM pictures at time, $t_0=0$ (i.e., the original IL), $t_1=5400$ s and $t_2 \approx 10800$ s. It is worth noticing from Figure 5.2, that $t_1$ is located in the shear thinning region, while $t_2$ is located in the region where $\eta$ is abruptly increasing. As can be seen in Figure 5.4, for the original IL (i.e., at $t_0=0$) all the particles, though somewhat polydisperse, are spherical and homogeneously distributed. After shearing for $t=t_1$, the shear-induced aggregation does occur, as evidenced by the partially coalesced small clusters in the magnification in the right bottom corner of Figure 5.4. In this case, the particles (and clusters) are still rather homogeneously distributed in the system. After shearing for $t=t_2$, the state of the IL system changes substantially. Now we can observe not only larger clusters but also segregation of the clusters from the disperse medium, leading to inhomogeneous distribution of the clusters (particles) in the system. In fact, at $t=t_2$, taking a representative sample becomes difficult, and the given cryo-SEM picture corresponds to the less viscous part of the system.
We believe that the results in Figure 5.4 clearly indicate simultaneous occurrence of both aggregation/gelation and coalescence during the shear test. Moreover, the observed partial coalescence of the clusters at $t = t_1$ might suggest occurrence of full coalescence for a longer time if they do not further aggregate with another cluster/particle. Thus, essentially, the results imply that there is competition between aggregation and coalescence. This competition is governed by the characteristic times of aggregation and coalescence, $\tau_{aggr}$ and $\tau_{coal}$, respectively. The former is given by eqn (5.1), while the latter can be defined as\textsuperscript{[148]}

$$\tau_{coal} \propto \frac{a\eta_p}{\sigma_p}$$ (5.4)
where $\eta_p$ and $\sigma_p$ are viscosity and surface tension of the particles, respectively. Note that the $\tau_{\text{coal}}$ expression given by eqn (5.4) has been used extensively in the literature,\textsuperscript{[149-151]} and in this work, it is solely used in the following to identify key quantities (e.g. the particle viscosity) affecting the characteristic time of coalescence, instead of using it to quantify the coalescence time. Initially, when two primary particles aggregate, they may quickly coalesce to form a new spherical particle before aggregating with another particle, and this corresponds to $\tau_{\text{aggr}} > \tau_{\text{coal}}$.

Since $\tau_{\text{coal}}$ increases and $\tau_{\text{aggr}}$ decreases as the particle (cluster) radius, $a$, increases, when $a$ increases to a certain (critical) value, $a_{\text{crit}}$, it may occur that $\tau_{\text{coal}} > \tau_{\text{aggr}}$. In this case, the clusters may coalesce only partially before aggregating with another particle (cluster), as in the situation at $t=t_1$ in Figure 5.4. More dramatically, when partial or no coalescence occurs, the structure of the clusters becomes very open, typical of fractal objects, as shown in the magnification at $t=t_2$ in Figure 5.4. Such open structure of fractal objects leads to substantial increase in the $\eta$ and $a$ values in eqns (5.1) and (5.4). The consequence is that, due to the exponential form of $\tau_{\text{aggr}}$ in eqn (5.1), the aggregation rate becomes extremely large, resulting in the gelation, as observed in the systems of non-coalescing particles.\textsuperscript{[118, 142]}

From the above analysis, although the shear-induced gelation phenomenon observed in the IL systems is rather similar to that in the latexes of non-coalescing particles, there is a clear difference in the gelation mechanism. For the latter, it is purely related to the fractal growth of the clusters, governed only by eqn (5.1). For the IL systems, it is related to the competition between coalescence and aggregation. Only when the aggregation rate becomes faster than the coalescence rate, the gelation phenomenon becomes possible.
5.3.2. Main parameters affecting gelation

To identify the main parameters affecting the IL stability and gelation, we have carried out the shear-induced gelation in the rheometer at various experimental conditions for the IL systems listed in Table 5.1. In particular, steady shear experiments were performed by changing temperature, shear rate, molecular weight and content of polymer in the particles, charge density on the polymer chains, and surfactant composition on the particle surfaces. The latter two factors change the total interaction potential of the particles. The subsequent subsections illustrate and discuss the results of these parametric studies.

5.3.2.1. Temperature

Figure 5.5 shows the results of the steady shear tests for IL 0032 in Table 5.1 at $\dot{\gamma} = 5600$ s$^{-1}$ for different temperatures. It is seen that this IL system does not gel at $T = 298$ K in the analyzed time frame. Then, from $T = 303$ K on, the shear-induced gelation does occur, and in particular it occurs at an earlier time as the temperature increases. In other words, since the occurrence of gelation is due to competition between aggregation and coalescence, the results in Figure 5.5 show that increasing temperature favors the aggregation rather than coalescence.
IL system 0032 sheared at 5600 s$^{-1}$ at different temperatures. Higher temperature favors aggregation over coalescence: gelation occurs earlier. The viscosity profile in the shear thinning regime becomes steeper as the $T$ increases.

From eqns (5.1) and (5.4), temperature, except for its direct presence in eqn (5.1), affects $\tau_{\text{aggr}}$ and $\tau_{\text{coal}}$ mainly through $U_m$, $\eta$ and $\eta_p$. In particular, the solubility of the surfactant, $E_1$, in paraffin oil, increases as temperature increases. Accordingly, the amount of adsorbed surfactants on the particle surface decreases, leading to reduction in the total interaction potential, i.e., in $U_m$. This, together with $T$ itself, would decrease substantially the $\tau_{\text{aggr}}$ value (or increase the aggregation rate), due to the exponential dependence in eqn (5.1), thus resulting in the occurrence of the gelation at an earlier time.

On the other hand, since the IL and particle viscosities, $\eta$ and $\eta_p$ in eqns (5.1) and (5.4), respectively, decrease as temperature increases, the corresponding $\tau_{\text{aggr}}$ and $\tau_{\text{coal}}$ would decrease with temperature as well, thus leading to increase in both aggregation and coalescence rates.
However, if we note that $\tau_{coal}$ depends only linearly on $\eta_p$, while $\tau_{aggr}$ exponentially on $\eta$, then it is evident that the viscosity effect is larger for $\tau_{aggr}$ than for $\tau_{coal}$, i.e., again, the viscosity effect favors aggregation. Therefore, the variations of both total interaction potential and viscosity explain why the gelation time ($t_{gel}$) decreases as the temperature increases in Figure 5.5.

In addition, in Figure 5.5 it can be seen that the slope of the shear-thinning region before the gelation becomes steeper as the temperature increases. This confirms the aforementioned thixotropic behavior of our IL systems, because upon temperature increase the microstructure is broken more easily.

### 5.3.2.2. Shear rate

From eqn (5.1), the aggregation characteristic time, $\tau_{aggr}$, decreases as the shear rate, $\dot{\gamma}$, increases, while the effect of $\dot{\gamma}$ on the coalescence characteristic time, $\tau_{coal}$, is not evident. Thus, it is expected that the higher the shear rate, the quicker the gelation. Such a conclusion is confirmed by the results in Figure 5.6, where is shown the gelation behavior of the IL system, 235, at 298 K at $\dot{\gamma} = 5100 \text{ s}^{-1}$, $5600 \text{ s}^{-1}$ and $6100 \text{ s}^{-1}$, respectively. As can be seen, the $t_{gel}$ decreases as the shear rate increases.
Figure 5.6
IL system 235 sheared at 298 K at different shear rates. Aggregation rate is higher as shear rate increases (eqn (1)), therefore gelation occurs at earlier times. The viscosity profile in the shear thinning regime becomes steeper as the shear rate increases.

It is worth noting that the slope of the shear-thinning region increases as the shear rate increases, indicating that the thixotropic microstructure is broken easier as the mechanical energy increases. On the other hand, the difference in the minimum shear viscosity among the three cases is insignificant, when compared to those induced by varying temperature in Figure 5.5, indicating that temperature plays a more important role than shear in breaking down the IL microstructure.

5.3.2.3. Polymer composition of the particles

As mentioned earlier, the IL particles are mixtures of water and hydrophilic polymers. The polymer composition, such as polymer content and molecular weight, can change the particle viscosity, $\eta_p$ in eqn (5.4), thus affecting the coalescence process, while it doesn’t directly affect the aggregation rate (compare to eqn (5.1)). However, there is an effect on the gelation rate, as $\eta_p$
modifies the interplay between aggregation and coalescence.

By varying the monomer content in the mini-emulsion during polymerization, one can change the polymer content in the particles. The IL systems, 0050, 0049 and 0047 in Table 5.1, were produced at the monomer content (with respect to the water phase) of 51.4%, 48.1% and 44.8%, respectively. In Figure 5.7 are compared the results of the steady shear tests of these IL at $T=313$ K and $\dot{\gamma} = 5600$ s$^{-1}$. It can be seen that in the applied time frame, shear-induced gelation occurs only for 0050 with the highest monomer (polymer) content. This clearly indicates that at high polymer content in the particles, the high particle viscosity decreases the coalescence rate, affecting the competition between aggregation and coalescence by favoring aggregation, leading to gelation. At lower polymer content, vice versa, we do not observe the gelation in the given time frame. Similar results have also been obtained for the same IL systems at $T=318$ K (data not shown).

![Figure 5.7](image)

**Figure 5.7**

IL systems 0050, 0049 and 0047 sheared at 5600 s$^{-1}$ and 313 K having different monomer contents. The higher the monomer content, the higher is the particles viscosity, thus decreasing the extent of coalescence, and hence speeding up the aggregation and the resulting gelation.
The molecular weight of the polymers in the particles can also be changed during the preparation of the IL by varying the recipe (e.g., initiator concentration, chain transfer, etc.). In this work, the polymer molecular weight for each IL in Table 5.1 is represented by the $\eta_{PR}$ value. For the three IL systems, 128, 138 and 142 in Table 5.1, the only difference is their $\eta_{PR}$ values. Figure 5.8 reports the shear-induced $t_{gel}$ for the three IL systems as a function of $\eta_{PR}$ at two temperatures, $T$=308 K and $T$=318 K, respectively, and a fixed shear rate, $\dot{\gamma}$=5600 s$^{-1}$. Note that, the $t_{gel}$ is computed as the intersection of the slopes of two straight lines: one interpolated from the initial viscosity decrease and the other from the final viscosity increase.

Apart from the expected results that for a given IL the $t_{gel}$ decreases as the temperature increases, at each temperature the $t_{gel}$ decreases as the $\eta_{PR}$ value increases: the increased particle viscosity leads to a reduction in the coalescence rate, thus favoring aggregation.

Note that we have also performed the steady shear tests for the three IL systems, 128, 138 and 142, at $T$=298 K, but no gelation has been observed for all systems (data not shown). This result is expected from the discussion in paragraph 5.3.2.1, due to more adsorbed surfactants, $E_1$, on the particle surface at lower temperatures, which leads to larger $U_m$ values in eqn (5.1).
IL systems 128, 138, 142 sheared at 5600 s\(^{-1}\) and 308 K (squares) or 318 K (circles). IL systems gel quicker, the higher their \( \eta_{PR} \) \( \eta_{PR,128} = 2.04 \), \( \eta_{PR,138} = 1.49 \), \( \eta_{PR,142} = 1.28 \): the increased particles viscosity decreases the extent of coalescence, and hence speeds up the aggregation and the resulting gelation.

**5.3.2.4. Interaction Potential**

The interaction potential, \( U_m \) in eqn (5.1), between the particles of the IL systems consists of three main contributions, the attractive van der Waals force (a function of the particle size and the Hamaker constant of the system), the repulsive steric interaction (due to the adsorbed surfactants), and the repulsive electrostatic or Coulomb interaction (due to the charges present in the particles due to the charged co-monomers). Among the three, since the differences in the size and main composition of the particles are small for all the IL systems, the effect of the variations in the van der Waals force on the shear-induced gelation should be small and cannot be well quantified experimentally. Thus, our focus is on the steric and Coulomb interactions.

To modify the steric potential, we have added small amounts of a surfactant (henceforth called \( E_2 \)) during the steady shear tests. The emulsifier, \( E_2 \), an alkyl-polyethylene glycol ether, is a branched non-ionic emulsifier, with a hydrophobic part consisting of a C10-alcohol and a
hydrophilic part characterized by 6 repeating units of ethylene oxide. Since $E_2$ has a much larger HLB value (~11) than $E_1$ (~4), $E_2$ is likely to replace $E_1$ from the particles surface, reducing the stability due to the higher HLB value. Typical examples of the $E_2$ effect on the shear-induced $t_{gel}$ are shown in Figure 5.9, where the $t_{gel}$ is plotted as a function of the $E_2$ weight percentage added into the IL, 0034, operated at $T$=298 K. It is seen that the $t_{gel}$ decreases monotonically and drastically as the $E_2$ concentration in the IL increases. This confirms that $E_2$ does replace $E_1$ from the particle surface, reducing the steric repulsion. In fact, surfactants of large HLB values like $E_2$ are typically employed as “demulsifiers” in practice to destabilize w/o emulsions to separate water from the crude oil.\cite{129, 131, 152}

![Figure 5.9](image_url)

**Figure 5.9**

IL system 0034, sheared at $5600\, s^{-1}$ and 298 K with different $E_2\, \% (w/w)$. The gelation time decreases monotonically upon $E_2$ increase, as the latter substitutes $E_1$ from the particle surface, lowering the particles stability due to its shorter chains.

In the previous section, we have investigated the effect of the polymer molecular weight (represented as $\eta_{PR}$) on the $t_{gel}$ using three IL systems, 128, 138 and 142, and confirmed that the
$t_{gel}$ decreases as $\eta_{PR}$ increases. Now, we have added 3% E$_2$ to the same three IL systems and measured the gelation time as a function of temperature as reported in Figure 5.10. It is seen that at each given temperature, the same trend has been obtained, i.e., the $t_{gel}$ decreases as the $\eta_{PR}$ value increases. Moreover, it is worth noting that as the temperature increases in Figure 5.10 the differences among the $t_{gel}$ of the three systems progressively diminishes, eventually reaching zero. This further confirms that at high temperature substantial desorption of the surfactants from the particle surface is the dominant factor destabilizing the particles.

![Figure 5.10](image)

IL systems 128 (squares), 138 (circles) and 142 (triangles) sheared at 5600 s$^{-1}$ and different temperatures all with 3% of E$_2$. The gelation time decreases as the $\eta_{PR}$ value increases ($\eta_{PR,128} = 2.04$, $\eta_{PR,138} = 1.49$, $\eta_{PR,142} = 1.28$).

The difference among the gelation time of the 3 systems progressively diminishes.

It is worth mentioning that the effect of adding 3% E$_2$ on the IL stability is larger than that of increasing temperature by 10 K, as clearly demonstrated in Figure 5.11, where IL 128 with 3% E$_2$ gels at 298 K earlier than it does at 308 K with 0% E$_2$. The same conclusion is obtained if one compares the shear viscosity curve at 308 K with 3% E$_2$ to that at 318 K with 0% E$_2$. 

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For our IL systems, as for w/o emulsions, charging on the particle surface on the side of the oil phase is almost unfeasible. However, if chargeable groups are present inside the particle (the water phase), they may dissociate to form charges, which may generate repulsion (electrostatic or Coulomb) interaction between the particles, affecting their stability. To explore the presence of such interactions, we have prepared four IL systems, 0075, 0076, 0077 and 0078, as shown in Table 5.1, which are very similar (particularly in the $\eta_{PR}$ values), except for the amount of the chargeable co-monomers added during the polymerization, 10%, 20%, 30% and 40%, respectively. For these systems, we have performed the steady shear tests at $\dot{\gamma} = 5600$ s$^{-1}$ and $T=318$ K, and the results are shown in Figure 5.12. It turns out that the gelation phenomenon was detectable only for the IL systems, 0075 and 0076, with 10% and 20% co-monomers, while for 0077 and 0078 with 30% and 40% co-monomers, it is out of the investigated time frame. The same trend was found also at 313 K (data not shown), as well as for another set of IL, 235, 238, 240 and 241, at 298 K (data not shown). Thus, the chargeable co-monomer does play a role in stabilizing the particles, which may signify the presence of the electrostatic or Coulomb interactions.
IL system 128 sheared at 5600 s\(^{-1}\) and different temperatures with 3% wt and 0% E\(_2\). The addition of 3% wt E\(_2\) has a larger destabilization effect than an increase in temperature of 10 K.

IL systems 0075, 0076, 0077 and 0078 having 10, 20, 30 and 40% charged co-monomer amounts, respectively. The higher the charge, the more stable the IL.

To further evidence the presence of such electrostatic or Coulomb interactions, we have measured the zeta-potential of the above applied IL systems. To this aim, we have used a ZEN.
1002 dip cell (Malvern, UK), specially designed for oil systems, in the Zetasizer Nano. The original IL systems were diluted for the zeta-potential measurements by the paraffin oil with 2.5% E₁ to avoid desorption of E₁ from the particle surface, as discussed in Section 5.2.4. The measured values of the zeta-potential for the IL systems, 0075, 0076, 0077 and 0078, are reported in Figure 5.13. Indeed, the zeta-potential increases as the co-monomer content inside the particles increases, and the positive values of the zeta-potential are also consistent with the positive charges given by the co-monomers. On the other hand, it should be pointed out that, as mentioned in the Introduction, for highly crowded IL the effect of charges on the particle stability is small, because of small gradients of surface potentials. It is more likely that the charges inside the particles may increase the hydrophilicity of the particles such that the hydrophilic groups of E₁ can anchor more tightly to the particle surface, thus increasing the amount of E₁ on the particle surface, resulting in a higher stability.

![Figure 5.13](image)

Figure 5.13
Zeta potential of IL systems 0075, 0076, 0077 and 0078, having 10, 20, 30 and 40% charged co-monomer amounts, respectively. The higher the amount of charged co-monomer, the higher the zeta potential.
5.3.3. **Comparison with experimental studies in the literature**

As mentioned in the introduction, several studies on the shear-induced gelation of different particle suspensions have been carried out in the literature.\cite{137, 138, 142} In the work of Guery et al.\cite{137}, an exponential decay of the gel time with respect to the shear rate was found, which was then found also by Zaccone et al.\cite{142} Again, the very same exponential decay has been observed in the present IL systems, as reported in the ESI (Figure S4). Despite the three types of the systems being quite different (in terms of type and size of particles, type of dispersants, stabilizers, range of the applied shear rates), the observed gelation time decays exponentially with the shear rate, confirming the general validity of the shear-induced gelation theory proposed by Zaccone et al.\cite{144}

In the work of Giermanska-Khan et al.,\cite{138} they did not perform the experiments at different shear rates, and we cannot verify if the above exponential decay occurs. However, they reported, among the other results, also a time-evolution of the shear viscosity at a fixed shear rate (Fig. 7 in the original paper), which can then be compared to those measured in the present work. As mentioned in the Introduction, their systems consist of large (~50 μm) solid paraffin oil droplets dispersed in water, stabilized by silica nanoparticles. In their case, the measured viscosity profile can be divided into three distinct stages. I) In the initial stage, similar to our cases, the viscosity also decreases slowly with time, but they attributed it to partial deflocculation of the solid paraffin droplets, instead of thixotropy; II) then, at a certain time, the viscosity starts to increase slowly and progressively; III) finally the viscosity increases abruptly, reflecting the occurrence of gelation, as what happened in our IL systems. It is seen that Stages I and II are different from ours, and in fact, we do not have Stage II. They ascribed Stage II to progressive formation of shear-induced droplet clusters. Then, based on their picture of the droplet clusters that exhibit only slight coalescence due to the hindrance of the silica nanoparticles present on the
surface, the $Pe$ value of the clusters would increases extremely fast with time, leading to abrupt gelation, if the above eqn (5.1) can be applied, instead of slow increase in the viscosity. Thus, Stage II might be related to a different, unknown phenomenon. In fact, in the studies of both Zaccone et al.\cite{142} and Guery et al.,\cite{137} only the abrupt increase in the viscosity was observed, without the occurrence of Stage II. In the latter two cases, even no thixotropy was observed, most probably due to their low particle volume fractions (20% and 10%, respectively). Thus, the occurrence of Stage II in the work of Gierimanska-Khan et al. suggests a rather different mechanism in terms of shear-induced gelation. It could be ascribed to the specific stabilization mediated by the silica nanoparticles, while all the other systems studied by Zaccone et al., Guery et al. and us are stabilized by surfactants. However, it is still an open question how the presence of the silica nanoparticles on the droplet surface affects so dramatically the gelation behavior.

5.4. Concluding Remarks

In this work we have investigated, through steady shear experiments in a rheometer, shear-stability of sterically stabilized, highly concentrated inverse latexes (IL), constituted of water-swollen polyacrylamide particles dispersed in paraffin oil.

It is found that in general at a fixed shear rate, the shear viscosity of the IL systems first decreases with time (i.e., shear-thinning) and then, when reaching a local minimum, increases explosively. Since the initial particle volume fractions of all the IL studied in this work reach about 60%, it is not surprising to have observed the shear-thinning phenomenon, typical of thixotropy of crowded non-Newtonian fluids.

To understand the explosive increase in the shear viscosity after the minimum, we have performed cryo-SEM experiments along the shear history, from which we found that there is
competition between coalescence and aggregation. Since the coalescence rate decreases while the aggregation rate increases as the cluster size increases, after the cluster size reaches a certain (critical) value, aggregation becomes the dominant event. In this case only partial or even no coalescence between the clusters (particles) occurs, thus accelerating the growth of the cluster size. When one considers the known fact that the aggregation rate scales exponentially with the third power of the cluster size, it is the partial or no coalescence that results in an explosive shear-induced aggregation and eventually in fractal gelation, as typically observed for non-coalescing colloidal systems. In fact, no-coalescing fractal clusters have been indeed observed from the cryo-SEM pictures.

Through the above shear-induced gelation, we have investigated the main parameters affecting the shear-stability of the IL systems, such as temperature, shear rate, polymer content and molecular weight inside the particles, steric co-surfactants, chargeable co-monomer content inside the particles, etc. The effects of all these parameters on the shear-induced gelation can be well interpreted by considering their role in altering the competition between coalescence and aggregation kinetics.
6. Shear-stability of inverse latexes during their polymerization process\textsuperscript{5}

6.1. Introduction

Polyelectrolytes are of great importance in various areas, such as water treatment, mineral processing and paper making.\textsuperscript{153} A typical preparation method of polyelectrolytes preparation is via inverse emulsion or inverse mini-emulsion polymerization.\textsuperscript{154} In this way, since the produced polymer is solubilized in the water-in-oil droplets, such dispersions are here referred to as inverse latexes (ILs).\textsuperscript{155} Owing to the presence of mechanical agitation and high particle volume fractions, the shear-stability of the ILs is very crucial both during and after the polymerization.\textsuperscript{155, 156} Insufficient shear stability would cause particle aggregation during the polymerization, leading to the formation of fractal clusters, eventually resulting in full percolation (gelation) within the reactor vessel.\textsuperscript{7}

Previous studies highlighted the key parameters affecting shear stability of latexes and ILs after polymerization.\textsuperscript{10, 137, 155} It was found that in the case of ILs where the particles are very soft, besides the aggregation (affected by shear rate, colloidal interactions and temperature),\textsuperscript{10, 137} also inter-particle coalescence plays an important role.\textsuperscript{155} This is because coalescence after aggregation can lead to the formation of compact clusters (perfect spheres in the limit), which decrease their occupied volume fraction, thus avoiding (or delaying) gelation. It follows that any quantities (e.g., polymer content within the IL particles, the polymer molecular weight, etc.) that

\textsuperscript{5} The present chapter has been partially submitted as: S. Lazzari, B. Jaquet, W. Hua, M. Morbidelli, "Shear Stability of Inverse Latexes during Their Polymerization Process", Langmuir
vary the coalescence rate can affect the shear stability of the ILs.\textsuperscript{[155]} While a relative clarity exists concerning the shear-stability of such ILs after polymerization, little is known regarding their shear stability during their formation, i.e. during the polymerization process in inverse emulsion.

This work aims to shed light on the key phenomena regulating the shear-stability of ILs during polymerization. To do so, we take samples at different monomer conversion stages along the inverse mini-emulsion polymerization of several IL systems (based on acrylamide and 2-dimethylamino-ethyl acrylate, methyl chloride quaternary salt), and their shear stability is studied by means of a rheometer. It will be seen that the shear stability of the ILs during the polymerization process varies substantially and non-monotonically with the monomer conversion, reflecting the influence of the amphiphilic nature of the polyelectrolytes, the particle viscosity and the particle volume fraction.

### 6.2. Methods

The IL samples, supplied by an industrial partner, were prepared by mini-emulsion polymerization at \( T = 40^\circ\text{C} \). The particles, composed of a mixture of water and 2 monomers, acrylamide and 2-dimethylamino-ethyl acrylate, methyl chloride quaternary salt, are suspended in a paraffin oil consisting of a mixture of hydrocarbons and stabilized by the non-ionic emulsifier, sorbitan mono oleic acid ester. The recipes and characteristics of the various ILs used in this work are summarized in Table 6.1.
**Table 6.1**

Characteristics of the ILs used in this work

<table>
<thead>
<tr>
<th>IL number</th>
<th>Polymer in particle $w_p$ [% wt]</th>
<th>Comonomer [% mol]</th>
<th>$\phi$ [%]</th>
<th>$E$ [% wt]</th>
<th>$d$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01</td>
<td>55</td>
<td>15</td>
<td>61</td>
<td>2.7</td>
<td>594±132</td>
</tr>
<tr>
<td>S02</td>
<td>50</td>
<td>15</td>
<td>61</td>
<td>2.7</td>
<td>571±145</td>
</tr>
<tr>
<td>S03</td>
<td>55</td>
<td>15</td>
<td>55</td>
<td>2.7</td>
<td>615±150</td>
</tr>
<tr>
<td>S04</td>
<td>52.5</td>
<td>15</td>
<td>61</td>
<td>2.7</td>
<td>588±177</td>
</tr>
<tr>
<td>S05</td>
<td>52.5</td>
<td>15</td>
<td>58</td>
<td>2.7</td>
<td>563±134</td>
</tr>
<tr>
<td>S06</td>
<td>52.5</td>
<td>15</td>
<td>55</td>
<td>2.7</td>
<td>528±243</td>
</tr>
</tbody>
</table>

During the polymerization, samples were taken at different times and immediately quenched by exposure to air (i.e., by spraying the reactive mixture into a glass bottle). The acrylamide conversion, $x$, was then measured as follows: the samples were sprayed into a glass vial containing isopropanol; the polymer precipitates while the residual acrylamide dissolves in isopropanol and is measured via HPLC. After two weeks the quenched samples were measured again: no change in the conversion profiles was observed proving the successful quenching of the reaction (data not shown). The shear-stability of the IL samples at different conversions was then assessed by means of an ARES rheometer (Rheometric Scientific) equipped with a rotating cup and gridded stator, which has been fully described and characterized in our previous work.\[155\]

The rheometer was equipped with a water bath for the temperature control (set either at $T = 40^\circ$C or $50^\circ$C). After pre-heating at the desired temperature, 1.5 ml of each sample were dropwise added into the rheometer cup, a bottom gap of 0.15 mm was selected, and the steady shear experiment was started at 5600 s$^{-1}$.

Dynamic Light Scattering (DLS) was employed to characterize the size of the polymer particles. It was employed only to analyze samples with full monomer conversion, by diluting the
samples in a 2.5% emulsifier rich paraffin oil solution, to prevent particle destabilization, as discussed elsewhere.\[155\]

6.3. Results and Discussion

Let us first consider the three IL systems, S01, S02 and S03 in Table 6.1, which have been prepared using the same amount of surfactant and the same molar ratio of cationic co-monomer/non-charged monomer. They differ only in the particle volume fraction ($\phi$) and the polymer content in the particles ($w_p$), as described in Table 6.1. The typical time-evolutions of the shear viscosity, $\eta_E$, at the steady shear, $\dot{\gamma} = 5600$ s$^{-1}$, in the case of S03 at different acrylamide conversions, $x$, are shown in Figure 6.1a). Except for some intermediate situations, the evolutions can be divided into two distinct types: those exhibiting an abrupt increase in $\eta_E$ after a certain shearing time, and those exhibiting a monotonic decrease in $\eta_E$ until reaching a plateau. As already shown in previous works,\[10, 137, 155\] the former corresponds to the occurrence of the shear-induced gelation due to the fractal growth of the clusters, while the latter indicates that the IL system is stable at the given shear rate. When gelation occurs, the gelation time ($t_{gel}$) is identified as the intersection of two straight lines: one extrapolated from the initial viscosity profile and the other from the final viscosity increase.\[155\]
Figure 6.1. a) Time evolutions of the shear viscosity ($\eta_s$) of IL S03 at different acrylamide conversions ($x$) at $T=40$ $^\circ$C. b) The gelation time, $t_{gel}$, of the ILs under shear at $T=40$ $^\circ$C as a function of $x$ for S01 (filled squares), S02 (triangles) and S03 (open squares). c) The same as b) but for S04 (filled circles), S05 (diamonds) and S06 (open circles). d) The same as b) but for S02 (triangles) and S03 (open squares) at $T=50$ $^\circ$C.

Similar data (not reported) were obtained also for the IL systems S01 and S02. The corresponding $t_{gel}$ values are shown in Figure 6.1b) as a function of the acrylamide conversion, $x$. As a general observation, the $t_{gel}$ vs $x$ curve in Figure 6.1b) for system S03 is located above the S02 one, which in turn is above the one of S01. When comparing S01 with S02 in Table 6.1, it is seen that the only difference is a 10% higher polymer content in the particles ($w_p$). This
leads to the \( t_{\text{gel}} \) vs \( x \) curve of S01 in Figure 6.1b) being below that of S02, i.e., the shear stability is significantly lower for S01 than for S02 during polymerization. This can be explained by recalling that for such soft particles under shear, there is competition between coalescence and aggregation. Note that the glass transition temperature of acrylamide and its copolymers drops by more than 130°C upon addition of few 10% (w/w) of water, allowing thus coalescence to occur in our conditions \( (w_p \approx 50\%) \). The larger \( w_p \) value for S01 signifies that the particles are more rigid, thus with a lower coalescence rate, leading to formation of less compact clusters; it follows that less time is needed for percolation (i.e., gelation) to occur. Thus, \( w_p \) is an important parameter in controlling the shear stability of ILs. Let us now compare S01 with S03 in Table 6.1. Their difference is only a 10% lower particle volume fraction \( (\phi) \) for S03, and this leads to a \( t_{\text{gel}} \) vs \( x \) curve for S03 in Figure 6.1b) which is even above the S02 one. This means that \( \phi \) plays a more important role in the shear stability of ILs than \( w_p \) does. The strong effect of \( \phi \) on the shear stability has also been evidenced in Figure 6.1c), where the \( t_{\text{gel}} \) values as a function of \( x \) are reported for the systems, S04, S05 and S06 in Table 6.1, which differ only for the \( \phi \) values. Again, the position of the \( t_{\text{gel}} \) vs \( x \) curve moves upwards as \( \phi \) decreases. The substantial impact of \( \phi \) on the shear stability arises mostly because the aggregation is a second-order process with respect to the particle concentration, thus very sensitive to the changes in \( \phi \).

It is particularly worth noting the shape of the \( t_{\text{gel}} \) vs \( x \) curves in Figure 6.1b) and 6.1c). For S01 and S04, \( t_{\text{gel}} \) does not change significantly in \( x \in [0, 40\%] \) and then decreases monotonically with \( x \). For S02, S03, S05 and S06, instead, \( t_{\text{gel}} \) increases initially and when \( x >40\% \) it decreases with \( x \). For S03, S05 and S06, however, the \( t_{\text{gel}} \) value starts to increase again at the final stage of the conversion. In fact, as shown in Figure 6.1a), for S03 at \( x \approx 97\% \) and
100%, no gelation was detected in the given investigation time. Similar behavior occurs also for S06 when \( x > 80\% \).

It is easy to explain the common behavior for all the systems in the region, \( x > 40\% \), where \( t_{\text{gel}} \) decreases with \( x \), i.e., the stability of the ILs decreases as the monomer conversion increases. This, based on the above discussion, can be ascribed to the increase in the particle hardness along the polymerization, which reduces the coalescence rate, leading to formation of less compact clusters, thus reducing the time for gelation to occur.

It is somewhat surprising to observe that the \( t_{\text{gel}} \) value increases with \( x \) at the initial stage of the polymerization for S02 and S03 in Figure 6.1b), and for S05 and S06 in Figure 6.1c). It is to be noticed that the same behavior is exhibited in the shearing experiments performed for S02 and S03 at the same shear rate, \( \dot{\gamma} = 5600 \, \text{s}^{-1} \), but at a higher temperature, \( T = 50 \, ^\circ\text{C} \). The corresponding \( t_{\text{gel}} \) vs \( x \) curves are shown in Figure 6.1d). It is seen that the shape of the \( t_{\text{gel}} \) vs \( x \) curves at \( T = 50 \, ^\circ\text{C} \) is very similar to that at \( T = 40 \, ^\circ\text{C} \), except that for a given \( x \) value the \( t_{\text{gel}} \) value is significantly smaller for \( T = 50 \, ^\circ\text{C} \) than for \( T = 40 \, ^\circ\text{C} \). The lower shear stability at \( T = 50 \, ^\circ\text{C} \) results from the reduction in the adsorption of the surfactant on the particle surface, thus in the repulsive interaction potential, as already observed previously for these systems.\(^{155}\)

The above initial increase in the shear stability could be related to the amphiphilic nature of the produced polyelectrolyte chains within the particles.\(^{158}\) Notably, the present charged co-monomer leads to the presence of fixed charges along the polymer chain. While the carbon backbone of the chain defines the hydrophobic nature of the polymer, the charges confer the chain a strong hydrophilicity. Before the polymerization starts, the water/monomer droplets are stabilized by the steric surfactant from the oil phase (Figure 6.2a)). As soon as the first chains are formed, they might start migrating towards the oil/water interface to decrease further the
interfacial tension of the suspended phase. In doing so, the hydrophilic, charged portion of the chains remains in the water phase, and the hydrophobic one is located at the interface (Figure 6.2b), as if a “second surfactant” adsorbs on the particle surface from the aqueous phase. Such a “second surfactant” may improve the particle stability due to several factors. First, the adsorbed hydrophobic portion of the chain increases the steric stability of the particles. Second, the presence of charges close to the hydrophilic heads of surfactant $E$ increase their anchoring stability, thus reducing their mobility. Since the surfactant molecules have to be relocated before allowing the particles to come close enough for their aggregation, the improved anchoring force can certainly hinder such relocation, thus reducing the aggregation tendency (increasing the gelation time). When the shear stability increases to reach a local maximum around $x = 40\%$ (Figure 6.1b and 6.1c), it starts to decrease. This may indicate that the particle surface is saturated by the initially adsorbed surfactant and the “second surfactant,” and such improvement in the shear stability stops. Now, the competition between aggregation and coalescence becomes the dominant phenomenon, as discussed above.
To further deepen this point, different ILs stabilized by a poly-isobutyl amino-functionalized (PIBA) stabilizer were sheared (at both 40°C and 50°C). The PIBA-stabilized samples did not undergo gelation (data not shown), proving the surface activity of polyelectrolytes chains.

The above explanation not only elucidates the initial increase in the shear stability observed for S02, S03, S05 and S06, but also clarifies and supports our previous results,[155] where it was found that increasing the charged/uncharged monomer ratio improves significantly the shear stability of the particles. This observation can in fact be well explained by the role of such a “second surfactant.”

It should be mentioned that for the systems, S01 and S04 at the initial stage of the polymerization, the $t_{gel}$ value keeps almost constant until $x \approx 40\%$. This is most likely because of their high particle concentration and polymer content in particles, such that the aggregation becomes immediately the dominant phenomenon right from the beginning of the polymerization. However, the “second surfactant” role of the formed polymer discussed above still exists;
otherwise the $t_{gel}$ value would decrease monotonically starting from the beginning of the polymerization and not only after conversion has reached about 40%.

There is one phenomenon that remains still unexplained, i.e., for S03, S05 and S06 the shear stability starts to increase at the final stage of the conversion. From Table 6.1, their particle volume fraction, $\phi$, is among the lowest, which might be responsible for this phenomenon, but the mechanism remains unclear, although it is known that $\phi$ is a critical parameter for aggregation, leading to deviations from the classical theory when high-concentrated systems are studied.[11, 12]

### 6.4. Conclusions

The shear-stability of inverse latexes (ILs) has been investigated at different monomer conversions during their corresponding polymerization process using a rheometer. The ILs are dispersions of soft, sterically-stabilized particles (made of acrylamide-based polyelectrolyte in water phase) in paraffin oil.

Three stages of the particle shear stability are identified during the polymerization: (i) an initial increase ($x \approx 0\text{--}40\%$), (ii) followed by a decrease ($x \approx 40\text{--}80\%$) and (iii) then a final increase at the last stage of the polymerization ($x \approx 80\text{--}100\%$). Stage (i) has been explained by the amphiphilic nature of the polyelectrolyte chains, which migrate towards the particle surface, at the beginning of the polymerization, increasing both the steric stability and the surfactant anchoring strength. Stage (ii) has been ascribed to a decrease in the particle coalescence rate (caused by the increased particle hardness with the ongoing polymerization), leading to the formation of more open clusters and thus speeding up the gelation. As for Stage (iii), instead,
only a dependency on the particle volume fraction was assessed. It is concluded that the key parameters affecting the shear stability of ILs during polymerization are the particle volume fraction, the polymer content in particles and the amphiphilic nature of the formed polyelectrolyte chains.
7. Population Balance Modeling of Aggregation and Coalescence in Colloidal Systems

7.1. Introduction

Colloidal systems are typically defined as kinetically stable,\cite{159} meaning that the dispersed phase will eventually separate from the continuous one in which it is suspended. Two phenomena accomplishing such destabilization are aggregation and coalescence of the primary particles originally present in the suspension. It is known that pure aggregation leads to clusters of fractal nature,\cite{160} whereas pure coalescence (e.g. of bubbles or liquid droplets) typically leads to spherical clusters.\cite{161,162} Simultaneous aggregation and coalescence are identified in several systems of practical interest, such as aerosols, soft polymer colloids, liquid-liquid dispersions.\cite{155,162-164} Moreover, in heterogeneous reactions such as suspension, emulsion or mini-emulsion free-radical polymerization, coalescence and aggregation play an important role, affecting the reactor operability as well as the final properties of the produced latex at significant extent.\cite{165} In special processes, such as reactive gelation,\cite{9} this destabilization of polymer latexes is controlled in order to determine the final material properties. In all cases, the concurrent occurrence of coalescence and aggregation leads namely to a continuous reshaping of the aggregate, driven towards a fractal cluster or a spherical one, according to the relative importance of the two interplaying phenomena.

\footnote{The present chapter has been partially published as: I. Kryven, S. Lazzari, G. Storti, “Population Balance modeling of Aggregation and Coalescence in Colloidal Systems”, Macromolecular Theory and Simulations, 3, 23, (2014)}
Modeling approaches aimed to describe the dynamic evolution of the particle size distribution (PSD) in destabilized colloidal systems can be subdivided into two main classes: Monte Carlo (MC) models and deterministic models based on population balance equations (PBEs). MC models allow enucleating physical laws and understanding specific mechanistic aspects,\cite{149, 166, 167} while they fail in describing the full evolution of a real system due to their high computational costs. Deterministic models, on the other hand, are typically based on population balance equations and allow accounting for the evolution of the PSD in time. As a downside, they are mean-field approaches, hence not working in all conditions, e.g. in crowded systems or close to the percolation limit.\cite{11, 12}

When modeling systems of industrial interest where the knowledge of the complete PSD is needed, the natural choice is to employ PBE. In order to account for the evolution of the particle size distribution (PSD) at least two internal coordinates are necessary: the first internal coordinate accounts for the cluster mass (affected by aggregation), whereas the second one for its shape (affected by coalescence). The second internal coordinate gives information on the shape of the cluster and is therefore essential, as the spatial organization of a cluster strongly affects its reactivity.\cite{168} Typically, for aggregating-coalescing systems, cluster mass (\(x\)) (or volume \(v\)) and cluster area (\(a\)) are employed.\cite{150, 169}

To mathematically describe the aggregation-coalescence process, an aggregation kernel is needed. Well-accepted kernels for aggregation in the literature are the diffusion-limited-cluster aggregation (DLCA) kernel and the reaction-limited-cluster-aggregation (RLCA), just to mention some of the most popular ones.\cite{168} These kernels depend on cluster mass and fractal dimension (\(d_f\)), therefore the choice of \(x\) and \(d_f\) as internal coordinates is the most convenient. An additional advantage of using these internal coordinates, is that further mechanisms (besides
aggregation and coalescence) can be accounted for with minor effort. Restructuring and breakage for instance modify the fractal dimension of the clusters, but not their area. Hence they could be easily introduced in a 2-D PBE with $x$ and $d_f$ as internal coordinates (and with appropriate kinetic laws describing the rate of $d_f$ variation), but not as easily using $x$ and $a$. Finally, it should be mentioned that detailed solutions of 2-D PBE having $x$ and $a$ as internal coordinates have already been proposed.\cite{164,169} Using $d_f$ instead of $a$ represents a more challenging task, as the internal coordinates are not simply additive as in the case of $x$ and $a$. Kostoglou et al. \cite{170,171} solved these equations in the case of aggregation and restructuring with MC stating that the numerical integration is “really a formidable task”.

In this frame, the aim of this work is to provide the solution of the 2-D PBE employing cluster mass and fractal dimension as internal coordinates. The model is solved by employing a discretization method based on Gaussian basis functions (GBF), already employed and validated elsewhere.\cite{172} This specific method was selected because especially effective in dealing with convolution integrals, which typically occur in coalescing-aggregating systems. The presented model is able to capture the physics of such systems, as shown by parametric simulations performed employing two kernels, the DLCA and the RLCA one, and different rates of coalescence.

### 7.2. The model

As mentioned in the introduction, two internal coordinates were chosen to describe the unknown distribution of clusters of primary particles. In particular, the clusters are defined by their cluster mass $x$ and fractal dimension $y$. Notably, both internal coordinates have been
assumed to be continuous. This is clearly an approximation, especially at low cluster masses; nonetheless, the error introduced this way becomes negligible after few aggregation steps and has been considered acceptable. The first index represents the number of particles per cluster, with boundaries \([1, \infty)\), whereas the fractal dimension has boundaries \([1,3]\) and accounts for the cluster spatial occupancy.

Let us define the cluster density function \(f(x, y, t)\) such that \(f(x, y, t)dx\,dy\) represents the concentration of clusters consisting of \(x\) to \(x+dx\) primary particles and having fractal dimension from \(y\) to \(y+dy\) at time \(t\). Only two phenomena are considered to affect this density function, aggregation and coalescence: accordingly, the evolution of \(f(x, y, t)\) in time is described by the following 2-D PBE:

\[
\frac{\partial f(x, y, t)}{\partial t} + \frac{\partial}{\partial y}(f(x, y, t)v(x, y)) = \\
- f(x, y, t) \int_{1}^{y_{M}} \int_{1}^{y_{M}} \beta(x, x_{1}, y, y_{1}) f(x_{1}, y_{1}, t) d y_{1} d x_{1} \\
+ \frac{1}{2} \int_{1}^{y_{m}} \int_{1}^{y_{M}} \int_{1}^{y_{M}} \beta(x, x_{1}, y_{1}, y_{2}) f(x_{1}, y_{1}, t) f(x_{2}, y_{2}, t) \mu d y_{1} d y_{2} d x_{1} d x_{2} \\
\mu = \delta(x - g_{1}(x_{1}, x_{2})) \delta(y - g_{2}(x_{1}, x_{2}, y_{1}, y_{2}))
\]

where \(y_{m}\) is the minimum fractal dimension (the value established in the case of pure aggregation, hence defined through the aggregation regime), whereas \(y_{M}\) is the maximum fractal dimension, corresponding to full coalescence \((y_{M} = 3)\).

The influence of coalescence on the PBE can be appreciated in term \(T_{A}\), which accounts for the variation of the cluster population due to the rate of variation in time of its fractal
dimension, \( v(x, y) \). In other words, term \( T_A \) is a Liouville term, as already detailed by Koch and Friedlander.\[150]\) Term \( T_B \), in equation (7.1), accounts for the disappearance of \( x \)-sized clusters with fractal dimension \( y \) aggregating with clusters of any other size and fractal dimension. The formation of \( x \)-sized clusters with fractal dimension \( y \) (term \( T_C \)) on the other hand, is obtained by aggregation of two clusters satisfying the constitutive laws defined in equation (7.2).

Before solving the 2-D PBE, one needs to choose an aggregation kernel (present in terms \( T_B \) and \( T_C \)), to define the constitutive laws \( g_1 \) and \( g_2 \)[170] (term \( T_C \)) and to introduce an equation describing the time-variation of the fractal dimension, \( v(x, y) \) (occurring in term \( T_A \)).

Concerning the aggregation kernel, \( \beta(x_1, x_2, y_1, y_2) \), both the DLCA (equation (7.3)) and the RLCA (equation (7.4)) will be employed:

\[
\beta(x_1, x_2, y_1, y_2) = \frac{2 k_B T}{3 \eta} \left( x_1^{1/y_1} + x_2^{1/y_2} \right) \left( x_1^{-1/y_1} + x_2^{-1/y_2} \right) \quad (7.3)
\]

\[
\beta(x_1, x_2, y_1, y_2) = \frac{2 k_B T}{3 \eta} \frac{(x_1 x_2)^\gamma}{W} \left( x_1^{1/y_1} + x_2^{1/y_2} \right) \left( x_1^{-1/y_1} + x_2^{-1/y_2} \right) \quad (7.4)
\]

where \( k_B \) is the Boltzmann constant, \( T \) the temperature, \( W \) the Fuchs stability ratio, \( \eta \) the continuous phase viscosity and \( \gamma \) the exponent of the product kernel, usually considered a fitting parameter. Note that for the RLCA kernel the formulation suggested by Family et al.[173] has been selected, but any other one (e.g. Odriozola et al.[174] or Ball et al.[175]) could have been chosen with no impact on the numerical aspects, as detailed in the subsequent section.

The aim of the constitutive laws \( g_1 \) and \( g_2 \) in term \( T_C \) is to select among all possible cluster combinations only those actually forming a cluster of the desired size \( x \) and fractal dimension \( y \). They are defined as:
The first constitutive law (equation (7.5)) is simply an additive law, indicating that if a cluster of size \( x \) is sought, the cluster masses of the combining clusters \( x_1 \) and \( x_2 \) added up have to give \( x \).

As the fractal dimension is not an additive property, a more complex constitutive law (\( g_2 \), equation (7.6)) was employed, as suggested in previous works.\(^{170, 171}\) In particular, the fractal dimension of a cluster formed by aggregation of two clusters having different fractal dimensions, is a function of their cluster masses (\( x_1 \) and \( x_2 \)) and their fractal dimensions (\( y_1 \) and \( y_2 \)) as well as of the aggregation regime, which defines the minimum fractal dimension, \( y_m \). For the DLCA case, \( y_m = 1.8 \), while for RLCA, \( y_m = 2.1 \), as these are representative fractal dimensions for these regimes.\(^{160}\) Note that, when \( y_1 = y_2 = y_m \) the constitutive law is always satisfied, as \( g_2 \) becomes always equal to \( y_m \) (cf. equation (7.6)).

Finally, let us discuss the rate of coalescence \( v(x, y) \), i.e. the time-variation of the fractal dimension appearing in term \( T_A \) of equation (7.1). In this frame the fractal dimension is changing due to coalescence only, as in the limit of pure aggregation no variation in fractal dimension occurs, once the aggregation regime is defined. Therefore, the required function needs to be in the form of a relaxation law, i.e. a growing function approaching an asymptotic value, as coalescence is a process in which the primary particles constituting a cluster inter-diffuse in one another and eventually turn into a single, compact sphere, reaching thus the maximum fractal dimension of 3. The oversimplified equation (7.7) fulfills the aforementioned criterion:
\[ v(x, y) = \frac{1}{\tau_c(x)} (y_M - y) \]  

(7.7)

As long as the fractal dimension is smaller than its maximum value, equation (7.7) predicts an increase of fractal dimension until this maximum value is reached and the process ends. Notably, the rate with which this coalescence process occurs, \( v(x, y) \), is inversely proportional to the characteristic time of coalescence \( \tau_c \). The characteristic time of coalescence was defined by Frenkel\[148]\ and can be generalized for \( x \)-sized clusters as in equation (7.8):\[150]\n
\[ \tau_c(x) = x^{1/3} \frac{r_i \eta_\rho}{\sigma_p} = x^{1/3} \tau_c(1) \]  

(7.8)

where \( x \) represents the mass of the cluster considered, \( r_i \) the radius of a primary particle, \( \eta_\rho \) its viscosity and \( \sigma_p \) its interfacial surface tension. Kinetic laws of coalescence similar to equation (7.7) have already been reported in the literature.\[171, 176\] Notably, if in the colloidal system under investigation a polymerization reaction is occurring (e.g. suspension or emulsion polymerization), the characteristic time of coalescence becomes conversion-dependent and further contributions should be added to equation (7.8).

### 7.3. Numerical solution

The numerical solution of the aforementioned 2-D PBE has been pursued by a previously proposed discretization technique based on Gaussian basis functions (GBF).\[172\] Before discussing the discretization procedure, whose full details are reported in the Appendix, some manipulations of Equation (7.1) are required.
7.3.1. Modified Equations

Employing the notation for coalescence speed $v(x,y)$ as defined by equation (7.7), term $I_A$ (in equation (7.1)) reads:

$$I_A = \frac{1}{\tau_c(1)} x^{-1/3} \left( \frac{\partial f(x,y,t)}{\partial y} (y_{\tau} - y) - f(x,y,t) \right)$$  \hspace{1cm} (7.9)$$

From the last expression it becomes clear that a boundary condition is necessary to guarantee the solution uniqueness. Thus we enrich the formulation (7.1) with the boundary condition,

$$\frac{\partial f}{\partial y} \bigg|_{y=y_m} = 0$$  \hspace{1cm} (7.10)$$

that forbids flux of particles beyond the aggregation regime $y_m$. The aggregation kernel, which defines the reactivity rate for a pair of particles $(x_1, y_1)$ and $(x_2, y_2)$, can be represented as a sum of separable kernels. In case of DLCA the kernel has the form:

$$\beta(x_1, x_2, y_1, y_2) = \frac{2 k_B T}{3 \eta} \left( x_1^{\ell_{y_1}} + x_2^{\ell_{y_2}} \right) \left( x_1^{\ell_{y_1}} + y_{\tau} x_2^{\ell_{y_2}} \right) =$$

$$\frac{2 k_B T}{3 \eta} \left( 2 + \beta_1(x_1, y_1) \beta_2(x_2, y_2) + \beta_1(x_1, y_1) \beta_1(x_2, y_2) \right)$$  \hspace{1cm} (7.11)$$

where:

$$\beta_1(x, y) = x^{\ell_{y}}$$

$$\beta_2(x, y) = x^{-\ell_{y}}$$  \hspace{1cm} (7.12)$$

In the RLCA case, an analogous separation is made:

$$\beta(x_1, x_2, y_1, y_2) = \frac{2 k_B T}{3 \eta} \frac{1}{W} \left( x_1 x_2 \right)^{\ell_{y_1}} \left( x_1^{\ell_{y_1}} + x_2^{\ell_{y_2}} \right) \left( x_1^{\ell_{y_1}} + x_2^{\ell_{y_2}} \right) =$$

$$\frac{2 k_B T}{3 \eta} \frac{1}{W} \left( 2 \beta'_0(x_1) \beta'_0(x_2) + \beta_1(x_1, y_1) \beta_2(x_2, y_2) + \beta_2(x_1, y_1) \beta_1(x_2, y_2) \right)$$  \hspace{1cm} (7.13)$$

where:
\[ \beta_0'(x) = x^\gamma \]
\[ \beta_1'(x, y) = x^{\mu_y^y} \]
\[ \beta_2'(x, y) = x^{-\mu_y^y} \]  

The integration with respect to four variables \( x_1, x_2, y_1, y_2 \) that appears in \( \mathcal{I}_c \) (equation (7.1)) can be expressed in terms of a double integral, significantly reducing the computational effort required.\(^{[171]}\) By substituting \( x_2 = x - x_1 \) (compare to condition (7.5)), it is possible to eliminate one integral dimension. A similar, though more elaborated substitution allows a further simplification. In particular, the merging law \( g_2(x_1, x_2, y_1, y_2) \), defining all possible combinations of pairs \( (x_1, y_1) \) and \( (x_2, y_2) \) that aggregate to form a particle \( (x, y) \), is reformulated by narrowing the integration domain in \( \mathcal{I}_c \) to all points that satisfy the following constraint:

\[ \frac{y_n \ln(x_1 + x_2)}{\ln(x_1^{y_n/y_1} + x_2^{y_n/y_2})} - y = 0 \]  

Equation (7.15) is the direct application of the constitutive law (equation (7.6)), imposing the constraint of final fractal dimension after aggregation equal to \( y \).

The integration with respect to \( y_1, y_2 \) in term \( \mathcal{I}_c \) is viewed as a single layer integral, and can be reformulated as a line integral on the collection of parametric lines:\(^{[177]}\)

\[ L_{x_1, x_2, y}(h) = (y_1(h), y_2(h)), \quad h \in [0, 1] \]  

that solve equation (7.15) for each given set of values \( \{x_1, x_2, y\} \). To recover all points from \( L \), equation (7.15) can be solved numerically for every requested set \( \{x_1, x_2, y\} \), or an analytical expression for \( (y_1(h), y_2(h)) \) can be used. In the latter case, an analytical form can be worked out from equation (7.15) as follows:
\[ y_1 = g_2^{-1}(x_1, x_2, y_1, y) = \frac{y_m \ln x_1}{\ln((x_1 + x_2)^{\nu_n/h} - x_1^{\nu_n/h})} \]
\[ y_2 = g_2^{-1}(x_1, x_2, y_1, y) = \frac{y_m \ln x_2}{\ln((x_1 + x_2)^{\nu_n/h} - x_2^{\nu_n/h})} \] (7.17)

Now, the integration lines (7.16) can be parameterized as:
\[
\begin{align*}
  y_2(x_1, x_2, h, y) &= g_1^{-1}(x_1, x_2, h(b - a) + a, y) \\
  y_1(x_1, x_2, h, y) &= h(b(x_1, x_2, y) - a(x_1, x_2, y)) + a(x_1, x_2, y)
\end{align*}
\]  \( h \in [0, 1] \) (7.18)

Here \( a(x_1, x_2, y) \) and \( b(x_1, x_2, y) \) set bounds on \( y_1(x_1, x_2, h, y) \), that is:
\[ y_m \leq a(x_1, x_2, y) \leq y_1(x_1, x_2, h, y) \leq b(x_1, x_2, y) \leq y_M \] (7.19)

By substituting the marginal values \( y_m, y_M \) into relations (7.18), one obtains the expressions for the bounds \( a \) and \( b \). Indeed, assuming \( 1 < x_1 \leq x_2 \), we have:
\[
\begin{align*}
  a(x_1, x_2, y) &= \begin{cases} 
    g_1^{-1}(x_1, x_2, y_M, y), & g_2^{-1}(x_1, x_2, y_M, y) > y_M \\
    y_m, & g_2^{-1}(x_1, x_2, y_M, y) \leq y_M 
  \end{cases} \\
  b(x_1, x_2, y) &= y_M
\end{align*}
\] (7.20)

As for the case \( x_1 > x_2 > 1 \), one should note that the symmetry \( g(x_1, x_2, y_1, y_2) = g(x_2, x_1, y_2, y_1) \) enables us to use the collection of lines discussed earlier, equations (7.18) and (7.20).

The ideas described above result in a reduction of the integral dimensionality: only two dimensions are left instead of four present in the initial formulation; explicitly:
\[
\iiint_{1}^{\infty} \int_{y_m}^{y_M} \int_{y_m}^{y_M} \int_{1}^{\infty} \beta(x_1, x_2, y_1, y_2) f(x_1, y_1, t) f(x_2, y_2, t) \mu d y_1 d y_2 d x_1 d x_2 = \\
\iiint_{1}^{\infty} \int_{y_m}^{y_M} \int_{y_m}^{y_M} \int_{1}^{\infty} \beta(x_1, x-x_1, y_1, y_2) f(x_1, y_1, t) f(x-x_1, y_2, t) \delta(g(x_1, x-x_1, y_1, y_2) - y) d y_1 d y_2 d x_1 = \\
\iiint_{1}^{\infty} \int_{y_m}^{y_M} \int_{y_m}^{y_M} \int_{1}^{\infty} \beta(x_1, x-x_1, y_1(x_1, x-x_1, h, y), y_2(x_1, x-x_1, h, y)) f(x_1, y_1(x_1, x-x_1, h, y), t) \times \\
f(x-x_1, y_2(x_1, x-x_1, h, y), t) J(x_1, x-x_1, h, y) d h d x_1
\] (7.21)
where

\[ J(x_1, x_2, h, y) = \left( \frac{\partial y_1^2}{\partial h}(x_1, x_2, h, y) + \frac{\partial y_2^2}{\partial h}(x_1, x_2, h, y) \right)^{1/2} \times \]

\[ \left( \frac{\partial g_2^2}{\partial y_1} \left( y_1(x_1, x_2, h, y), y_2(x_1, x_2, h, y) \right) + \frac{\partial g_2^2}{\partial y_2} \left( y_1(x_1, x_2, h, y), y_2(x_1, x_2, h, y) \right) \right)^{-1/2} \]

Due to technical aspects related to the numerical implementation, it is convenient to separate the balance of the primary particles from the overall distribution \( f(x,y,t) \). Therefore, a specific differential equation for the primary particles, \( s(t) \), is written:

\[
\frac{ds(t)}{dt} = -s(t) \left( \frac{8 k_B T}{3 \eta} s(t) + \int \int \beta(x,1,y,y_M) f(x,y,t) dxdy \right)
\]  (7.22)

Here, term \( E \) denotes the total concentration of non-primary particles that can react with a primary one. On another hand, the contribution of primary particles to the overall balance (7.1) emerges as the following additional term:

\[
\mathcal{I}_D = 4s(t)^3 \delta(x-2, y-y_{min})
\]

\[ + \frac{1}{2} s(t) \beta(1,x-1,m,y) f(x-1, g^{-1}_2(1,x-1,m,y), t) \]

\[ - s(t) \beta(1,x-1,m,y) f(x,y,t) \]  (7.23)

Finally, the complete equation set ready for discretization reads as:
\[
\frac{\partial f(x, y, t)}{\partial t} = - \frac{1}{\tau_c(1)} x^{-1/3} \left( \frac{\partial f(x, y, t)}{\partial y} (y_M - y) - f(x, y, t) \right)
\]
\[
- f(x, y, t) \int_2^{y_M} \int \beta(x, x_1, y, y_1) f(x_1, y_1, t) \, dy_1 \, dx_1
\]
\[
+ s(t)^2 \delta(x - 2, y - y_m) - s(t) \beta(1, x - 1, m, y) f(x, y, t)
\]
\[
+ \frac{1}{2} s(t) \beta(1, x - 1, m, y) f(x - 1, g_m^{-1}(1, x - 1, m, y), t)
\]
\[
+ \frac{1}{2} \int_{t_{m}} \beta(x_1, x - x_1, y_1, y_2(x_1, x - x_1, h, y_2(x_1, x - x_1, h, y), f(x_1, y_1(x_1, x - x_1, h, y), t)) \times f(x - x_1, y(x_1, x - x_1, h, y), t) J(x_1, x - x_1, h, y) \, dh \, dx_1
\]
\[
\frac{ds(t)}{dt} = - s(t) \left( \frac{8 k_n T}{3 \eta} s(t) + \int_2^{y_M} \int \beta(x, 1, y, y_M) f(x, y, t) \, dx \, dy \right)
\]

(7.24)

Term \(A\) accounts for cluster coalescence, term \(B\) for the loss of \(x\)-sized clusters having fractal dimension \(y\) due to aggregation with any other cluster larger than singlets, whereas term \(C\) for the formation by aggregation of two smaller ones. Term \(D\) has the same meaning as terms \(B\) and \(C\), but it accounts for the formation/disappearance of \(x\)-sized clusters with fractal dimension \(y\) due to interactions with primary particles. This latter term is necessary as the balance on primary particles (term \(E\)) has been treated separately for numerical reasons, as previously mentioned.
7.3.2. Discretization

According to the chosen discretization technique based on GBF, the distribution \( f(x, y, t) \) is approximated by the distribution \( \hat{f}(x, y, t) \) that is defined as the following linear combination:

\[
\hat{f}(x, y, t) = \sum_{i=1}^{N} \alpha_i(t) \phi_i(x, y)
\]  

(7.25)

where the two-dimensional basis functions \( \phi_i(x, y) \) are 2-D Gaussian distributions:

\[
\phi_i(x, y) = \exp\left(-\frac{(x-x_i)^2}{\sigma_{x,i}}\right) \exp\left(-\frac{(y-y_i)^2}{\sigma_{y,i}}\right)
\]  

(7.26)

The main advantage of employing GBF for the discretization lies in the convenient properties Gaussian functions have. As already discussed in a previous work, the convolution of two Gaussians is once more a Gaussian, whose mean and standard deviation can be calculated starting from the means and standard deviations of the Gaussians to be convolved.\(^{[172]}\) Exploiting this property, the cumbersome convolution present in equation (7.24) can be dealt with in a relatively simple way. Notably, in the present case the weighted convolution involves non-integer weights due to the DLCA and RLCA kernels employed. Nevertheless, with some linear transformations it is always possible to reduce the problem to that of a non-weighted convolution, as mentioned already in Kryven and Iedema.\(^{[172]}\) Therefore, the implementation of different kernels becomes straightforward and proves once more the versatility of GBF. A further advantage of using GBF is the possibility to re-write the discretized balance in a quite compact vector form, as detailed in the next paragraph.

The time dependent expansion coefficients \( \alpha_i(t) \), organized as the column vector \( \mathbf{\alpha}(t) \), are obtained from the following system of non-linear differential equations:
\[
\begin{aligned}
\frac{d \alpha(t)}{dt} &= \hat{I}_A \alpha(t) + \hat{I}_B \alpha(t) + \hat{I}_C \alpha(t) + \hat{I}_D \alpha(t) \\
\frac{d s(t)}{dt} &= -s(t) \left( 4s(t) + \hat{I}_E \alpha(t) \right)
\end{aligned}
\] 

(7.27)

where \(I_A, \ldots, I_E\), defined in Appendix 1, represent approximations of the corresponding terms in the equation system (7.24). Time integration of Equation (7.27) with the initial condition:

\[
s(0) = M
\]

(7.28)
yields an approximation of the unknown two dimensional density distribution \(f(x,y,t)\). Note that the primary particle conversion is readily obtained as:

\[
\chi(t) = \frac{M - s(t)}{M}
\]

(7.29)

The success of the discretization approach is strongly dependent on the selected values of basis function centers, \(x_i, y_i\), and on their parameters, \(\sigma_{x,i}, \sigma_{y,j}\). While the geometric grid has been widely used to discretize the classical aggregation problem,\(^{[178]}\) a strategy for the fractal dimension is less obvious, as it depends on the interplay of the coalescence and aggregation rates. Therefore, the ratio of the two process rates, \(p(x,y)\) (defined in equation (7.30)), is introduced and employed to identify a proper grid:

\[
p(x,y) = \frac{v_{\text{COAL}}(x,y)}{v_{\text{AGG}}(x,y)}
\]

(7.30)

where

\[
v_{\text{AGG}}(x,y) = \frac{8 k_b T \mu}{3 \eta} \frac{P(x,x)}{W} \\
v_{\text{COAL}}(x,y) = \tau_c^{-1}(1)x^{-\nu/3}(3 - y)
\]

with \(\left\{ \begin{array}{l}
W = 10^9 \text{ and } P(x,x) = 10^0 \\
W = 10^5 \text{ and } P(x,x) = x^{2.4}
\end{array} \right. \)

for DLCA and RLCA, respectively.

\[
v_{\text{AGG}}(x,y) = \frac{8 k_b T \mu}{3 \eta} \frac{P(x,x)}{W} \\
v_{\text{COAL}}(x,y) = \tau_c^{-1}(1)x^{-\nu/3}(3 - y)
\]

with \(\left\{ \begin{array}{l}
\tau_c^{-1}(1) = 10^{-4} \text{ s} \\
\tau_c^{-1}(1) = 10^4 \text{ s}
\end{array} \right. \)

for DLCA and RLCA, respectively.
For sake of simplicity, the aggregation rate $v_{AGG}$ has been estimated assuming aggregation between equally-sized clusters, which in the DLCA regime results in a size-independent rate, whereas in the RLCA case it is proportional to $x^{2\lambda}$. Despite this limitation, the evaluation of $p(x,y)$ allows one to understand which is the dominant mechanism, aggregation or coalescence. This is shown in Figure 7.1, where the plane cluster size vs. fractal dimension is divided in different domains characterized by the value of $p(x,y)$. Such values span through several orders of magnitude in both the DLCA and RLCA cases when using the selected set of parameter values (Table 7.1). This indicates that the interplay of the two mechanisms dramatically changes with size and fractal dimension of the cluster considered. Therefore, to reduce numerical instabilities, we require the distance between two adjacent basis function centers $(y_a, y_b)$ to be proportional to $p(x,y)^{-1}$, i.e.:

$$y_a - y_b \propto p(x,y)^{-1}$$ (7.31)
On the other hand, the connectivity parameters $\sigma_x, \sigma_y$ are chosen as a function of the distance between adjustment basis centers, as suggested previously. Finally, assuming the system of basis functions is given, the time independent components of the discretized equation (7.27) are computed only once and before the ODE integration. This principle allows major economy of computational time and is of great use especially when repeating the simulation for different parameter sets (e.g. for parameter estimation).

The cpu-time spent to build constant matrices from Appendix 1 was 13 hours, whereas integration times were in the order of 20-30 min running a Matlab v7.14 script on a personal computer with a 2.8 GHz processor. Considerable reductions in process times can be achieved by employing low-level programming languages (e.g. Fortran or C++ code) instead. In particular, after varying the number of GBF between 500 and 1000, a satisfactorily convergence of the solution was found employing 881 two-dimensional basis functions for the discretization, i.e. 881 ODE have been solved for all the results reported.

7.4. Results

Implementing the aforementioned discretization technique, a series of parametric simulations could be carried out to explore the dynamic behavior of the 2-D distribution under different conditions. The set of parameter values employed in the simulations is detailed in Table 7.1.
Table 7.1
Parameter values employed for the simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>$k_B$</td>
<td>1.38x10^{-23}</td>
<td>J/K</td>
</tr>
<tr>
<td>$\tau_c(1)$</td>
<td>$10^{-1}, 10^0$ (DLCA), $10^4, 10^5$ (RLCA)</td>
<td>s</td>
</tr>
<tr>
<td>$r_i$</td>
<td>50x10^{-9}</td>
<td>m</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>8.9x10^{-4}</td>
<td>Pa s</td>
</tr>
<tr>
<td>$M$</td>
<td>$10^{17}$</td>
<td># m^{-3}</td>
</tr>
<tr>
<td>$N_m$</td>
<td>1.8 (DLCA)</td>
<td></td>
</tr>
<tr>
<td>$N_M$</td>
<td>2.1 (RLCA)</td>
<td></td>
</tr>
<tr>
<td>$W$</td>
<td>$10^0$ (DLCA)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^5$ (RLCA)</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.0 (DLCA)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 (RLCA)</td>
<td></td>
</tr>
</tbody>
</table>

The values employed refer to water as a continuous phase as this is a typical solvent employed for colloidal particles in a great deal of application. $W = 10^5$ has been chosen as typical value of the Fuchs stability ratio in the RLCA case; in fact, similar values have already been reported in the literature for water-based systems. The choice of the characteristic times of coalescence will be discussed in the next sections.

Notably, given the primary particle radius of 50 nm and their concentration of $10^{17}$ #/m$^{-3}$, the system has an occupied volume fraction of $5.2 \times 10^{-5}$ hence, the aggregation-coalescence process is studied in fairly diluted conditions, where the mean-field approximation underlying the PBE approach has practically no impact. First the results employing the DLCA kernel are
discussed; afterwards the RLCA case is dealt with and a comparison between the two conditions is attempted.

7.4.1. DLCA kernel

When employing the DLCA kernel for the simulation, it is assumed that every collision between clusters leads to the formation of a larger cluster, having size equal to the sum of the two colliding aggregates. In particular it should be noted that the DLCA kernel favors the aggregation of large-small clusters, whereas equally sized clusters react with one another with the same rate, disregardful of their size, as can be easily seen from equation (7.3). The shape of the distribution employing the DLCA kernel can be appreciated in Figure 7.2

![Figure 7.2](image-url)

Three-dimensional representation of the density distribution \( f(x, y, t_{end}) \) where \( t_{end} = 9.29 \times 10^{-1}s \), i.e. at a primary particle conversion \( \chi = 0.87 \) and coalescence \( \tau_c(1) = 10^{-1}s \). DLCA kernel was considered
Figure 7.2 shows the distribution for the DLCA regime at a primary particle conversion $\chi = 0.87$ using a characteristic time of coalescence $\tau_c(t) = 10^{-1} s$. The distribution develops towards two asymptotic directions, one at low and one at high clusters masses. In other words, the clusters exhibit a distribution of fractal dimensions which ranges from 1.8 to 2.5 approximately. Notably, 1.8 represents the minimum fractal dimension which can be obtained in the present case due to the DLCA aggregation regime. A fractal dimension of 2.5 instead could be theoretically overcome if enough time for a higher extent of coalescence was given. Notably, smaller clusters exhibit much broader distribution of fractal dimensions than larger ones. Actually, starting from a certain cluster size ($x$ about 50), the fractal dimension distribution narrows significantly and reaches values of about 1.9. This reflects the physics of the system: clusters have a rate of coalescence which is inversely proportional to the characteristic time of coalescence (equation (7.8)), hence their rate of coalescence reads $v(x, y) \propto x^{-1/3}$, $x$ being the cluster mass. The latter relationship indicates that coalescence progressively slows down with increasing cluster mass.

The aforementioned reasoning indicates clearly the necessity of employing a time-dependent fractal dimension in an aggregating-coalescing colloidal system, as this would otherwise lead to a wrong kernel estimation, eventually resulting in incorrect predictions. In fact, in such a system the shape of the distribution is dependent on the ratio of coalescence and aggregation extents. These two quantities are dependent from one another: coalescence can occur only after aggregation takes place, whereas cluster aggregation depends on the cluster diffusivity and size, quantities which are both dependent on the fractal dimension and hence on the coalescence extent.

To get insights on the role of coalescence in the different stages of the aggregation process, simulations were performed employing two different characteristic times of coalescence,
namely a) $\tau_c(1) = 10^0 s$ and b) $\tau_c(1) = 10^{-1} s$. The results are shown in Figure 7.3 where the cluster size is plotted against primary particle conversion (defined as in equation (7.29)) and fractal dimension, whereas the greyscale (color on line) reflects the cluster concentration. The coalescence rate affects the distribution shape in time: in the case of slower coalescence (case a), the clusters fractal dimension does not increase significantly upon primary particle conversion, ranging between 1.8 and 2.4. This happens only after 90% of the primary particle aggregated, indicating that several aggregation steps had to occur, before coalescence could affect significantly the fractal dimension of the clusters. Moreover, only smaller clusters reach such fractal dimensions, whereas larger clusters maintain a fractal dimension very close to 2. On the other hand, when coalescence is faster (case b) the fractal dimension range of the clusters is much broader, from 1.8 to 3.0, a broadness reached already before 90% conversion of primary particles. Once again, it’s rather the small clusters which exhibit such fractal dimension, although the larger clusters have in this case an average fractal dimension of about 2.2, significantly larger when compared to the case a).
Time evolution of the density distributions, obtained for different coalescence times, a: $\tau_c(1) = 10^6 s$, b: $\tau_c(1) = 10^{-1} s$

To further elucidate the role of coalescence during the aggregation process, the contour lines of the 2-D distribution have been plotted in Figure 7.4 at two different conversions ($\chi = 0.87$, $\chi = 0.99$) and coalescence times ($\tau_c(1) = 10^6 s$, $\tau_c(1) = 10^{-1} s$) in a concentration range from $10^{10} - 10^{17} \# / m^3$. Comparing the lines at conversion $\chi = 0.87$ at two different coalescence rates (panels a and c), it is clear that when coalescence is faster (panel a) the fractal dimension distribution is broader and spans between 2 and 2.6 (compared to the much smaller range 1.8-2.1 for slower coalescence at the same conversion, panel c). This difference results in a higher reactivity of the more open clusters, which leads to a slightly larger maximum cluster size. The main difference between these clusters though, lies in their spatial organization as fractal dimensions of 1.8 indicate very open clusters, while 2.6 quite compact ones. The same result holds when comparing the two distributions at almost complete primary particle conversion,
When $\chi = 0.999$, when coalescence is faster (panel b) fractal dimensions are broader (values range from 2 to 3), whereas for slower coalescence (panel d) the fractal dimensions are confined between 1.9 and 2.6. Clearly both ranges are extended when compared to the case at $\chi = 0.87$, as more time for coalescence to restructure the cluster passed. Once more, clusters with a smaller fractal dimension, hence obtained with slower coalescence, tend to react faster and produce slightly larger cluster size ($x = 850$ vs. 750 considering the last contour line).

![Figure 7.4](image)

**Figure 7.4**
Contour lines of the two-dimensional density distribution $f(x, y, t)$ at primary particle conversion $\chi = 0.87$ (a,c) and $\chi = 0.999$ (b,d) employing two values for the characteristic time of coalescence $\tau_c(1) = 10^{-1}\text{s}$ (a,b) and $\tau_c(1) = 10^0\text{s}$ (c,d)

All previous results prove that coalescence plays a significant role in DLCA aggregation and it has to be accounted for to ensure accurate model predictions. On the other hand it is worth to remember that DLCA aggregation occurs in quite small time frames, as its characteristic time, $\tau_{DLCA AGGR} \approx W / (M_0 \beta_{11})$, is less than $10^0\text{s}$ in the present system. Therefore, coalescence has to be
quite fast to actually affect the cluster mass distribution while aggregation occurs: this was the reason for the choice of the specific values $\tau_c(1) = 10^{-1}\,s$ and $\tau_c(1) = 10^0\,s$.

### 7.4.2. RLCA kernel

Another interesting kernel to be employed to appreciate the competition between aggregation and coalescence is the RLCA kernel (equation (7.4)), as it represents the aggregation rates of a typical colloidal system in the presence of stabilizers (emulsifiers, block-copolymers). In the parametric studies carried out in this frame, $W = 10^5$ and characteristic times of coalescence of $10^4\,s$ and $10^5\,s$ have been used. Notably, the minimum fractal dimension considered in this case is 2.1, whereas in the DLCA case it was 1.8, being these two values typically accepted in the literature as representative of the respective aggregation regimes.$^{[160]}$ To ensure a fair comparison between simulations employing such different kernels, a constant value of the ratio of the aggregation rate to coalescence rate has been chosen. In other words, to keep the ratio $p(x,y)$ (equation (7.30)) constant, the ratio $W/\tau_{c,1}$ was adjusted in the RLCA cases to be equal to the DLCA ones. In this case $\tau_{AGGR}^{RLCA} \approx W/(\beta_1 M) \approx 8 \times 10^4\,s$, and the chosen coalescence characteristic times were $\tau_c(1) = 10^4\,s$ and $\tau_c(1) = 10^5\,s$, whereas $\tau_{AGGR}^{DLCA} \approx W/(\beta_1 M) \approx 8 \times 10^4\,s$ and the coalescence characteristic times were $\tau_c(1) = 10^{-1}\,s$ and $\tau_c(1) = 10^0\,s$, respectively.

Notably, this broad range of characteristic times can be obtained by tuning parameters such as polymer particle composition, temperature and particles diameter.$^{[155, 162]}$

A typical 2-D distribution at $\chi = 0.87$ for the RLCA kernel can be seen in Figure 7.5. As in the case of the DLCA kernel (Figure 7.2), the distribution surface develops towards two main,
asymptotic directions: smaller clusters tend to have a wide fractal dimension distribution, whereas larger cluster \((x > 50)\) a narrower one, with average value around 2.2. The physics underlying this different behavior is clearly the same: smaller cluster tend to coalesce faster than larger ones. In the RLCA case under examination, the maximum cluster sizes reached are quite larger when compared to the DLCA case at the same conversion (Figure 7.2).

This is due to the fact that large-large cluster interaction is favored in RLCA (due to the \(x_1x_2\)' proportionality in the kernel, equation (7.4)), which leads to the formation of larger cluster at constant primary particle conversion.

![3D representation of the density distribution](image)

**Figure 7.5**

Three-dimensional representation of the density distribution \(f(x, y, t_{end})\) where \(t_{end} = 9.95 \times 10^4 \text{s}\), i.e. at a primary particle conversion \(\chi = 0.87\) and coalescence \(\tau_{c,1} = 10^3 \text{s}\) using the RLCA kernel

When comparing the contour lines in the RLCA case at two different primary particle conversions, \(\chi = 0.70\) and \(\chi = 0.87\), and two different coalescence times, \(\tau_c(1) = 10^4 \text{s}\) and
\( \tau_c(1) = 10^5 s \), as shown in Figure 7.6, it is confirmed that a faster coalescence implies a slower aggregation rate. This can be best seen when comparing panel \( b \) and \( d \) (comparing hence the contour lines at the same conversion \( \chi = 0.87 \) for \( \tau_c(1) = 10^4 s \) and \( \tau_c(1) = 10^5 s \), respectively. In the case of slower coalescence (panel \( d \)), clusters made of up to 1000 primary particles are found, whereas the maximum sized aggregates in panel \( b \), are of about 250. With the RLCA aggregation kernel this difference becomes more evident than in the DLCA case (panel \( b \) and \( d \) of Figure 7.5), where the difference between the maximum sized clusters was smaller, once again due to the specific kernel type. Moreover, the faster the coalescence, the wider the distribution of fractal dimensions (panels \( a \) and \( b \)): \( d_f \) reaches values up to 2.6, whereas with a slower coalescence, fractal dimension values smaller than 2.3 are found (panels \( c \) and \( d \)). Note that the particle concentrations range between \( 10^{10} - 10^{17} \) \#/m\(^3\).

![Figure 7.6](image)
Contour lines of the two-dimensional density distribution \( f(x,y,t) \) obtained for RLCA at primary particle conversions \( \chi = 0.7 \) (a,c) and \( \chi = 0.87 \) (b,d) employing two values for the characteristic time of coalescence, \( \tau_c(1) = 10^4s \) (a,b) and \( \tau_c(1) = 10^5s \) (c,d).

Finally, some interesting conclusions can be drawn when comparing the DLCA and RLCA fractal dimension distributions as a function of conversion and different \( \tau_c(1) \) (Figure 7.7). It turns out that both aggregation regimes lead to a bimodality when coalescence is fast enough (compare panels a and c of Figure 7.7). On the other hand, such bimodality is not observed when coalescence is slow (panels b and d) and only a drift from the starting fractal dimension to a slightly larger one is observed. In the cases where coalescence is fast enough, the bimodality arises as both smaller and larger clusters partially coalesce to different extents. The corresponding rate is namely inversely proportional to the coalescence characteristic time (equation (7.8)), resulting in \( v(x,y) \propto x^{-1/3} \). On the other hand, when coalescence is slower, a more uniform, almost monomodal distribution is found as neither smaller nor larger clusters coalesce at an extent large enough to affect the fractal dimension.
7.5. Conclusions

In the present work, the 2-D population balance for stagnant aggregating-coalescing colloidal systems has been solved employing cluster mass and fractal dimension as internal coordinates. In particular, DLCA and RLCA kernels have been used, even though any other type of kernel could have been considered without affecting the solution strategy. The Gaussian basis functions method has been employed for discretization and revealed its power in dealing with convolutions.

It was confirmed that coalescence significantly influences the shape and the aggregation rate of clusters, by affecting their fractal dimension. This is valid especially for smaller sized cluster, rather than for larger sized ones, on which coalescence has a smaller impact. As a matter
of fact this distinction between smaller and larger clusters leads to the presence of two asymptotic behaviors in terms of cluster masses: smaller cluster will exhibit a larger fractal dimension distribution (up to values of 3), whereas larger clusters maintain the fractal dimension characteristic of the operating aggregation regime (1.8 for DLCA and 2.1 for RLCA). The latter considerations, already accepted in the literature, can be thus quantitatively described by the present model.

This 2-D formulation, having cluster mass and fractal dimension as internal coordinates, allows not only to account for coalescence, but in general for any other phenomena affecting the fractal dimension of the aggregating clusters, such as breakage or restructuring. Notably, a proper modification of equation (7.7), describing the time variation of the fractal dimension, suffices to account for such phenomena as well as for polymerization. Therefore, this same modeling and the corresponding solution can be easily extended to include other important phenomena occurring in colloidal systems with and without reactions and could become a valuable tool to elucidate their complex interplay.

The present 2-D formulation allows accounting for aggregation processes involving any type of fractal dimension changing mechanism, such as coalescence, restructuring or breakage, provided a relaxation law to describe the fractal dimension time-variation is known. Notably, applying this model to heterogeneous polymerization systems represents an interesting possibility, allowing to elucidate the complex interplay of occurring phenomena.
8. Concluding remarks and outlook

In the present thesis, chemical and physical gels have been dealt with, in an attempt to clarify their formation and properties.

In the first part of the thesis, statistical and kinetic modelling approaches have been developed to deepen the understanding of the formation of two industrially relevant network systems: acrylamide/N’N’-methylenebisacrylamide and methyl methacrylate/ethylene glycol dimethacrylate. To further clarify advantages and disadvantages of the employed modelling approaches, a comparison thereof has been performed with a kinetic Monte Carlo model and another deterministic model, based on the Generating Function approach.

In the second part of the thesis, the shear-stability of an industrial Inverse Latex, viz. a polymer particle suspension in oil, has been deepened during as well as after their polymerization process by means of a rheometer. It turned out that their gelation is mediated by the interplay of aggregation and coalescence. Finally, a deterministic model accounting for these phenomena has been developed.

The main results of this work are summarized in the following.

Cyclization

While studying the solution crosslinking copolymerization of acrylamide/N’N’-methylenebisacrylamide, the competition between the cyclization and crosslinking reactions was deepened. It turned out that the less monomer is employed in the polymerization, the more cyclization (a mono-molecular reaction) is gaining importance when compared to crosslinking.
As a net result, the gels produced this way are softer and less crosslinked. By employing a literature model developed by Flory and Tobita, it was possible to estimate the necessary parameters to simulate such a system and appreciate the role of cyclization on the swelling capacity and crosslinking density. An empirical relationship has been proposed to account for the increasingly important role of cyclization at lower monomer concentrations.

**Multiradicals**

By solving a multidimensional population balance equation model, the role of multiradicals in the bulk crosslinking system methyl methacrylate/ethylene glycol dimethacrylate was assessed. In particular, a literature criterion to decide upon the necessity of accounting for multiradicals was revised and extended. It turned out that such criterion, suggesting to use a multiradical model when \( k_p / k_t > 10^{-3} \) (propagation over termination rate constant), is not sufficient to decide upon the presence/absence of multiradicals. As in crosslinking systems the termination rate is often conversion dependent (with \( k_t \) decreasing along the conversion due to the viscosity increase), the criterion might be violated after a given conversion. In those cases, the decision to account for multiradicals is dependent on when the gelation is taking place: if it is occurring before the violation of the criterion multiradicals can be neglected, whereas when the system gels while \( k_p / k_t > 10^{-3} \), multiradicals ought to be accounted for. Knowing that the gel point (i.e. the conversion at which gelation occurs) is affected by the amount of initiator and crosslinker content, multiradicals become important according to the recipes employed. Interestingly, low crosslinker contents lead the system to gel at high conversion, hence when the criterion is typically violated: therefore, multiradicals play a role even at low crosslinker contents due to viscosity increase, causing the termination rate to decrease significantly (Trommsdorff effect).
Model choice for bulk crosslinking copolymerization

While comparing the predictions of four different modelling approaches their strength and weaknesses have been identified along with their most suitable application field. In particular, a statistical/kinetic (FT) model, a kinetic model solved with the numerical fractionation (MRNF), a stochastic/kinetic Monte Carlo (KMC) and a kinetic model based on generating functions (GF) have been compared. Interestingly, despite the many simplifying assumptions, the predictions of the simpler models (FT and MRNF) are in very good accordance in terms of average properties with those of more complex models (KMC and GF). Considering the experimental complexity of the modelled systems and the resulting limited accessibility of experimental data (which are usually confined to average properties), the utilization of the FT and MRNF approaches is recommended as they require very small computational time and numerical effort as compared to the more complex models KMC and GF. In the case multiradicals need to be accounted for, MRNF should be employed instead of FT as the latter cannot account for multiple active sites. The Kinetic Monte Carlo model revealed in this analysis one important intrinsic weakness, namely its inability to predict in a model-independent way the sol/gel transition. The GF model instead encounters severe numerical problems while reconstructing the sol distribution, even with state of the art numerical inversion techniques.

Shear-Stability of Inverse latexes

The shear-stability of inverse latexes, consisting of polyelectrolyte water-swollen particles suspended in an oil phase was studied by means of a rheometer both during as well as after their polymerization. The viscosity profile in time, followed through the rheometric analysis, allowed to identifying the key phenomena occurring. In particular, the system viscosity undergoes at least three phenomena: thixotropy, aggregation and coalescence. Thixotropy explains the viscosity
decrease observed at the beginning of the rheometric analysis, as the microstructure of the system is broken down due to the introduced mechanical energy (i.e. the shear) and the particles can rearrange more freely as compared to their stagnant condition. Aggregation clearly occurs as eventually gelation takes place, hence aggregation proceeded to such an extent that a cluster of the rheometer vessel size is formed. Gelation results in a rapid and abrupt increase in the system’s viscosity; the shear-aggregation rate has been proven to be a strong function of the employed shear rate and the particles repulsive barrier, as already indicated in the literature. Coalescence instead occurs due to the particles softness (induced by the presence of water which lowers significantly the polymers glass transition temperature). Coalescence, if fast enough compared to aggregation, delays the gelation as it compacts the aggregating clusters. This fact is of significant importance for industrial applications: by reducing of a few percentages the polymer amount in the water/polymer particles, significantly larger stabilities are achieved.

The stability of the inverse latexes during their polymerization, turned out to be non-monotonous; in particular, three trends could be identified: an initial increase in stability (ascribed to the stabilizing effect of the first polyelectrolyte chains produced), a decrease (due to the increased viscosity and decreased coalescence rate of the particles) and a final increase which yet needs to be explained. The key parameters regulating the stability during the polymerization are the polymer content in the particles and the concentration of the particles. Further experiments are needed to fully unravel the understanding of these complex systems during their polymerization. The main result of this study allowed appreciating the significant improvement in stability which is obtained by changing the particle occupied volume fraction by few % points.
Deterministic modeling of aggregating/coalescing systems

In an attempt to provide a framework for the modelling of inverse latexes, which undergo simultaneous aggregation and coalescence, a 2-dimensional population balance equation (PBE) model has been solved. In particular, the internal coordinates chosen, cluster mass and fractal dimension, are directly related to the kinetics of the occurring phenomena. The numerical solution of such a PBE represents a novelty, as usually the equations are considered to be too complex to employ a deterministic approach. The discretization technique chosen is based on the utilization of Gaussian Basis functions, which ensure a relatively easy treatment of the convolution terms (appearing in the PBE) which typically represent the most cumbersome part in numerical discretization techniques. The model was successfully tested in two conditions, diffusion-limited and reaction-limited cluster aggregation, correctly describing the interplay between aggregation and coalescence on the cluster mass and fractal dimension distributions.
Appendix A

The most typical free-radical polymerization kinetic scheme involving initiator decomposition, propagation, and bimolecular terminations both by combination and disproportionation is complemented by additional reactions peculiar for monovinyl/divinyl copolymerizations. Notably crosslinking reactions and two different types of cyclization are accounted for. The final kinetic scheme is shown in Table 2.3. The meaning of all symbols is reported in the Nomenclature. All the rate constants are assumed to be conversion-independent, except for the termination rate constants. This model involves three types of monomers and three types of radicals as sketched in Table 2.2. The mass balances for each monomer species, when considering well mixed, isothermal batch reactor are derived in equations (A1) to (A3):

\[
\frac{dM_1}{d\psi} = -\frac{k^*_{p_1} M_1}{k^*_{p_1} M_1 + k^*_{p_2} M_2} \left( M_1^0 + M_2^0 \right) \tag{A1}
\]

\[
\frac{dM_2}{d\psi} = -\frac{k^*_{p_2} M_2}{k^*_{p_1} M_1 + k^*_{p_2} M_2} \left( M_1^0 + M_2^0 \right) \tag{A2}
\]

\[
\frac{dD_\alpha}{d\psi} = \frac{\left( 1 - \eta_{p} \right) k^*_{p_2} M_2}{k^*_{p_1} M_1 + k^*_{p_2} M_2} - \frac{(1 + \alpha_{\text{cyc}}) k^*_{p_1} D_\alpha}{k^*_{p_1} M_1 + k^*_{p_2} M_2} \left( M_1^0 + M_2^0 \right) \tag{A3}
\]

To get rid of the total concentration of radicals the equations are written with respect to monomer conversion \( \psi = \frac{M_1^0 + M_2^0 - M_1 - M_2}{M_1^0 + M_2^0} \). The time derivative of the conversion is given by equation (A4):

\[
\frac{d\psi}{dt} = \frac{(k^*_{p_1} M_1 + k^*_{p_2} M_2) R_{\text{tot}}}{(M_1^0 + M_2^0)} \tag{A4}
\]
where $R_{tot}^* = \sqrt{\frac{2 \beta k_d I_2}{k_i^*}}$ is the total concentration of radicals and $I_2 = I_2^0 e^{-k_d t}$ the concentration of initiator.

The so-called pseudo-kinetic approach is used;\cite{181} accordingly the kinetic parameters propagation ($k_{pi}^*$) and termination ($k_{ti}^*$) are expressed as effective rate constants, defined as:

**Propagation**

$$k_{pi}^* = k_{pi} \phi_1 + k_{pi2} \phi_2 + k_{pi3} \phi_3$$  \hspace{1cm} (A5)

$$k_{p2}^* = k_{p2i} \phi_1 + k_{p22} \phi_2 + k_{p23} \phi_3$$  \hspace{1cm} (A6)

$$k_{p3}^* = k_{p3i} \phi_1 + k_{p32} \phi_2 + k_{p33} \phi_3$$  \hspace{1cm} (A7)

**Termination**

$$k_{ti}^* = k_{t1i} \phi_1^2 + k_{t2i} \phi_2^2 + k_{t3i} \phi_3^2 + 2k_{t12} \phi_1 \phi_2 + 2k_{t13} \phi_1 \phi_3 + 2k_{t23} \phi_2 \phi_3$$  \hspace{1cm} (A8)

$$k_{t}^* = k_{tc}^* + k_{td}^*$$  \hspace{1cm} (A9)

The pseudo-kinetic parameters are composition-dependent and require the computation of the radical mole fractions, $\phi_i$. The fraction of each radical is computed assuming quasi-steady-state (QSS) for all the active species. This assumption has to be seen with particular caution since Okay\cite{182} reported a stability of several month for radicals in the gel phase. However, due to the difficulty to properly quantify their reduced reactivity in gel, it has been used in the present case as well.\cite{28,35} The radical fractions are calculated solving the following system:
\[
\left[ k_{p_1} M_2 + k_{p_2} D_3 \right] \phi_1 + \left[ n_p k_{p_2} M_2 + \alpha_c k_{p_3} D_3 \right] \phi_2 + \left[ k_{p_1} M_1 \right] \phi_3 = 0
\]

\[
\left[ k_{p_1} M_2 \right] \phi_1 - \left[ n_p k_{p_2} M_2 + \alpha_c k_{p_3} D_3 \right] \phi_2 + \left[ k_{p_2} M_2 \right] \phi_3 = 0
\]

\[
\phi_1 + \phi_2 + \phi_3 = 1
\]

(A10)

Where \( n_{cp} \) and \( \alpha_{cs} \) are the coefficients of primary and secondary cyclization respectively.

Nomenclature

\[
\begin{align*}
A & \quad \text{Kinetic parameter} \\
B & \quad \text{Kinetic parameter} \\
C_\eta & \quad \text{Viscosity coefficient in the termination kinetic constant} \\
C_{RD} & \quad \text{Propagational growth in the termination kinetic constant} \\
d_p & \quad \text{Polymer density} \quad \text{g cm}^{-3} \\
d_w & \quad \text{Water density} \quad \text{g cm}^{-3} \\
D_3 & \quad \text{Pendant double bonds concentration} \quad \text{mol L}^{-1} \\
f & \quad \text{Initiator efficiency} \\
f_n & \quad \text{Primary molecules number CLD} \\
f_w & \quad \text{Primary molecules weight CLD} \\
f_{w, sol}, f_{w, gel} & \quad \text{Primary molecules weight CLD of the sol/gel} \\
f_w^c & \quad \text{Primary molecules weight CLD between crosslinks} \\
G_k & \quad \text{Kinetic parameters} \\
I_0^1, I_2 & \quad \text{Initial/present initiator concentration} \quad \text{mol L}^{-1} \\
k_d & \quad \text{Initiator dissociation rate constant} \quad \text{s}^{-1} \\
k_{p_i} & \quad \text{Propagation rate constant of type } i \text{ radical with the monomer of type } j \quad \text{L mol}^{-1} \text{s}^{-1} \\
k_i^* & \quad \text{Pseudo-homogeneous propagation rate constant of the monomer } i \quad \text{L mol}^{-1} \text{s}^{-1} \\
k_f & \quad \text{Termination rate constant} \\
k_{c, c_d} & \quad \text{Combination/Disproportionation rate constant} \quad \text{L mol}^{-1} \text{s}^{-1} \\
k_{c, D}^0 & \quad \text{Purely diffusion controlled termination rate constant} \quad \text{L mol}^{-1} \text{s}^{-1} \\
k_i^* & \quad \text{Pseudo-homogeneous termination rate constant} \quad \text{L mol}^{-1} \text{s}^{-1}
\end{align*}
\]
\( m_{\text{polymer}} \) \text{g} \quad \text{Mass of the slice of gel after immersion in water}

\( m_{\text{dry}} \) \text{g} \quad \text{Mass of the dried slice of polymer}

\( M_1^0, M_2^0 \) \text{mol L}^{-1} \quad \text{Initial concentration of monomers 1 and 2}

\( M_1, M_2 \) \text{mol L}^{-1} \quad \text{Concentration of monomers 1 and 2}

\( M_n^0 \) \text{g mol}^{-1} \quad \text{Molecular weight of the repeated unit}

\( M_n \) \text{g mol}^{-1} \quad \text{Average molecular weight between consecutive crosslinks}

\( n \) \text{--} \quad \text{Number of unit in the polymer chain}

\( P_{m,n} \) \text{mol L}^{-1} \quad \text{Concentration of dead chains of length} \ m \ \text{and} \ n \ \text{divinyl monomers}

\( q \) \text{--} \quad \text{Swelling ratio (w/w)}

\( R_{i,m,n} \) \text{mol L}^{-1} \quad \text{Concentration of growing chains of length} \ m \ \text{and} \ n \ \text{divinyl monomers}

\( R_{\text{tot}} \) \text{mol L}^{-1} \quad \text{Total concentration of radicals}

\( r_{ij} \) \text{--} \quad \text{Reactivity ratios}

\( T \) \text{--} \quad \text{Kinetic parameter}

\( \nu_m^0 \) \text{m}^{3} \text{mol}^{-1} \quad \text{Molar volume of the solvent}

\( w_g, w_s \) \text{--} \quad \text{Instantaneous weight fraction of gel/sol}

\( w_g, w_s \) \text{--} \quad \text{Cumulative weight fraction of gel/sol}

\( w_c \) \text{--} \quad \text{Initial weight fraction of crosslinker}

\( w_t \) \text{--} \quad \text{Initial weight fraction of monomers}

\( x_1, x_2 \) \text{--} \quad \text{Molar fraction of monomer types 1 and 2}

\( X \) \text{--} \quad \text{Divinyl to monovinyl monomer molar ratio}

\textbf{Greek letters}

\( \alpha \) \text{--} \quad \text{Kinetic ratio}

\( \alpha_{cs} \) \text{--} \quad \text{Secondary cyclization coefficient}

\( \beta \) \text{--} \quad \text{Kinetic ratio}

\( \Gamma_1 \) \text{--} \quad \text{Kinetic parameter}

\( \eta_{cp} \) \text{--} \quad \text{Primary cyclization coefficient}

\( \theta \) \text{--} \quad \text{Birth conversion}

\( \mu_{k}, \mu_{c} \) \text{--} \quad \text{Instantaneous and Cumulative \( k^{th} \) order moment of the CLD between consecutives crosslinks}

\( \mu_k \) \text{--} \quad \text{\( k^{th} \) order moment of the primary polymer CLD}

\( \rho, \bar{\rho} \) \text{--} \quad \text{Instantaneous and Cumulative total crosslinking density}

\( \rho_a, \rho_i \) \text{--} \quad \text{Additional and Instantaneous crosslinking density}

\( \rho^f, \bar{\rho}^f \) \text{--} \quad \text{Instantaneous and Cumulative total crosslinking density with respect to the number of units}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{cp}$</td>
<td>Primary cyclization density</td>
</tr>
<tr>
<td>$\rho_{cs,a}, \rho_{cs,i}$</td>
<td>Additional and Instantaneous secondary cyclization density</td>
</tr>
<tr>
<td>$\rho_{el}, \bar{\rho}_{el}$</td>
<td>Instantaneous/Cumulative elastic crosslinking density</td>
</tr>
<tr>
<td>$\rho_{el}, \bar{\rho}_{el}$</td>
<td>Instantaneous/Cumulative elastic crosslinking density with respect to the number of units</td>
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<tr>
<td>$\tau$</td>
<td>Kinetic ratio</td>
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<tr>
<td>$\phi_i$</td>
<td>Fraction of radical of type $i$</td>
</tr>
<tr>
<td>$\phi_p$</td>
<td>Volume fraction of polymer</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Flory-Huggins interaction parameter</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Present conversion</td>
</tr>
</tbody>
</table>
Appendix B

Pseudo kinetic constants employed

\[ k_{p1}^* = k_{p11}^* \phi_1 + k_{p21}^* \phi_2 + k_{p31}^* \phi_3 \]  
\[ k_{p2}^* = k_{p12}^* \phi_1 + k_{p22}^* \phi_2 + k_{p32}^* \phi_3 \]  
\[ k_{p3}^* = k_{p13}^* \phi_1 + k_{p23}^* \phi_2 + k_{p33}^* \phi_3 \]  
\[ k_p^* M^* = k_{p1}^* M_1 + k_{p2}^* M_2 \]  

Conversion dependent termination constants

\[ k_{ic}^* = k_{ic0} \exp(-3.27 \chi + 9.67 \chi^2 - 56 \chi^3) \]  
\[ k_{id}^* = k_{id0} \exp(-3.27 \chi + 9.67 \chi^2 - 56 \chi^3) \]  
\[ \chi(t) = \frac{M_1(t = 0) + M_2(t = 0) - M_1(t) - M_2(t)}{M_1(t = 0) + M_2(t = 0)} \]  

Moments with respect to chain length

Linear Radical chains

\[ \frac{d\lambda_{100,y}^0}{dt} = \delta(y = 1) \left( k_{p1}^* M_1 I^* + k_{p2}^* M_2 I^* \right) \]  
\[ - y \lambda_{100,y}^0 \left[ k_{p3}^* C_{PDB} + (k_{ic}^* + k_{id}^*) R_{tot} \right] - k_{p3}^* R_{tot} \lambda_{1001,y}^0 \]  
\[ \frac{d\lambda_{100,y}^0}{dt} = \delta(y = 1) \left( k_{p1}^* M_1 I^* + k_{p2}^* M_2 I^* \right) + k_p^* M y \lambda_{100,y}^0 \]  
\[ - y \lambda_{100,y}^0 \left[ k_{p3}^* C_{PDB} + (k_{ic}^* + k_{id}^*) R_{tot} \right] - k_{p3}^* R_{tot} \lambda_{1001,y}^0 \]
\[ \frac{d\lambda^0_{200,y}}{dt} = \delta(y = 1) \left( k_{p1}^* M_{11} + k_{p2}^* M_{2} \right) + k_{p1}^* M_{0} \left( 2\lambda^0_{100,y} + \lambda^0_{000,y} \right) \]
\[ - y \lambda^0_{200,y} \left[ k_{p3}^* C_{PDB} + (k_{t}^* + k_{id}^*) R_{tot} \right] - k_{p3}^* R_{tot} \lambda^0_{201,y} \]  \hspace{1cm} (B10)

Branched Radical chains (generation 1)

\[ \frac{d\lambda^1_{000,y}}{dt} = - y \lambda^1_{000,y} \left[ k_{p3}^* C_{PDB} + (k_{t}^* + k_{id}^*) R_{tot} \right] - k_{p3}^* \lambda^1_{001,y} R_{tot} \]
\[ + k_{p3}^* \left( 2 \lambda^0_{000,y} \mu_{001}^0 + \lambda^0_{000,y} \mu_{001}^1 + \lambda^1_{000,y} \mu_{001}^0 \right) \]
\[ + k_{p3}^* \sum_{z=1}^{y-1} \left( 2 \lambda^0_{000,z} \lambda^1_{001,y-z} + \lambda^0_{000,z} \lambda^1_{001,y-z} + \lambda^1_{000,z} \lambda^0_{001,y-z} \right) \]
\[ + k_{id}^* R_{tot} \left( y + 1 \right) \lambda^1_{000,y+1} \delta(y < N_{rad}) \]
\[ + k_{p3}^* \sum_{z=1}^{y-1} \left( y - z + 2 \right) \lambda^1_{000,y-z+2} z \lambda^0_{000,z} \]  \hspace{1cm} (B11)

\[ \frac{d\lambda^1_{100,y}}{dt} = - y \lambda^1_{100,y} \left[ k_{p3}^* C_{PDB} + (k_{t}^* + k_{id}^*) R_{tot} \right] + k_{p3}^* M_{0} \lambda^1_{100,y} - k_{p3}^* \lambda^1_{101,y} R_{tot} \]
\[ + k_{p3}^* \left( \lambda^0_{100,y} \mu_{011}^0 + \lambda^0_{100,y} \mu_{012}^0 + \lambda^0_{000,y} \mu_{001}^1 \right) \]
\[ + k_{p3}^* \sum_{z=1}^{y-1} \left( \lambda^0_{100,z} \lambda^1_{010,y-z} + \lambda^0_{100,z} \lambda^1_{010,y-z} + \lambda^1_{100,z} \lambda^0_{010,y-z} \right) \]
\[ + k_{id}^* R_{tot} \left( y + 1 \right) \lambda^1_{100,y+1} \delta(y < N_{rad}) \]
\[ + k_{p3}^* \sum_{z=1}^{y-1} \left( y - z + 2 \right) \lambda^1_{100,y-z+2} z \lambda^0_{100,z} \]  \hspace{1cm} (B12)
\[
\frac{d\lambda_{200,y}^1}{dt} = -y\lambda_{200,y}^1 \left[ k_{p3}^* C_{PDB} + (k_{ic}^* + k_{id}^*) R_{tot} \right] + k_{p3}^* M y \left[ +2\lambda_{100,y}^1 + \lambda_{000,y}^1 \right] \\
+ k_{p3}^* y \left( \lambda_{000,y,201}^0 + 2\lambda_{100,y,101}^0 + \lambda_{200,y,001}^0 \right) \\
+ k_{p3}^* y \sum_{z=1}^{y-1} \left( \lambda_{000,z,201,y-z}^0 + 2\lambda_{100,z,101,y-z}^0 + \lambda_{200,z,001,y-z}^0 \right) \\
+ k_{id}^* R_{tot} (y + 1) \lambda_{200,y+1}^1 \delta(y < N_{rad}) - k_{p3}^* \lambda_{201,y}^1 R_{tot} \\
+ k_{ic}^* \sum_{z=1}^{y+1} \left[ (y - z + 2) \lambda_{200,y-z+2}^0 + 2(y - z + 2) \lambda_{100,y-z+2}^1 \lambda_{100,y}^0 \right] \\
\] (B13)

Branched radical Chains (generation k)

\[
\frac{d\lambda_{000,y}^k}{dt} = -y\lambda_{000,y}^k \left[ k_{p3}^* C_{PDB} + (k_{ic}^* + k_{id}^*) R_{tot} \right] - k_{p3}^* \lambda_{000,y}^k R_{tot} \\
+ k_{p3}^* y \lambda_{000,y}^k \sum_{h=0}^{k-1} \lambda_{000,y}^h + k_{p3}^* \lambda_{000,y}^k \sum_{h=0}^{k-1} \lambda_{000,y}^h + k_{p3}^* y \lambda_{000,y}^k \lambda_{000,y}^k \\
+ k_{p3}^* \sum_{z=1}^{y-1} \left( z\lambda_{000,z}^k \sum_{h=0}^{k-1} \lambda_{001,y-z}^h + \lambda_{001,y-z}^k \sum_{h=0}^{k-1} \lambda_{000,z}^h + 0.5z\lambda_{000,z}^{k-1} \lambda_{001,y-z}^{k-1} \right) \\
+ k_{id}^* R_{tot} (y + 1) \lambda_{000,y+1}^k \delta(y < N_{rad}) \\
+ k_{ic}^* \sum_{z=1}^{y+1} \left[ (y - z + 2) \lambda_{000,y-z+2}^k \sum_{h=0}^{k-1} \lambda_{000,z}^h \right] \\
+ \frac{1}{2} k_{ic}^* \sum_{y=1}^{y+1} (y - z + 2) \lambda_{000,y-z+2}^{k-1} \lambda_{000,y}^k \\
\] (B14)
\[
\frac{d\lambda_{100,y}^k}{dt} = -y\lambda_{100,y}^k \left[ k_{p3}^* C_{PDB} + (k_{ic}^* + k_{at}^*) R_{tot} \right] + k_{p3}^* M y\lambda_{100,y}^k - k_{p3} y\lambda_{101,y}^k R_{tot} \\
+ k_{p3}^* \left[ y\lambda_{100,y}^k \sum_{h=0}^{k-1} \mu_{001}^h + y\lambda_{100,y}^k \sum_{h=0}^{k-1} \mu_{010}^h \right] \\
+ k_{p3}^* \left[ \mu_{001} \sum_{h=0}^{k-1} y\lambda_{100,y}^h + \mu_{010} \sum_{h=0}^{k-1} y\lambda_{100,y}^h \right] \\
+ k_{p3}^* \left[ y\lambda_{100,y}^{k-1} \mu_{011}^{k-1} + y\lambda_{100,y}^{k-1} \mu_{011}^{k-1} \right] \\
+ k_{p3}^* \sum_{z=1}^{y-1} \left[ z\lambda_{100,z}^k \sum_{h=0}^{k-1} \lambda_{101,z-y}^{h} + z\lambda_{100,z}^k \sum_{h=0}^{k-1} \lambda_{101,z-y}^{h} \right] \\
+ k_{p3}^* \sum_{z=1}^{y-1} \left[ \lambda_{100,z}^{k-1} \lambda_{101,z-y}^{k-1} + \lambda_{100,z}^{k-1} \lambda_{101,z-y}^{k-1} \right] \\
+ k_{p3}^* \sum_{z=1}^{y-1} \left[ z\lambda_{100,z}^{k-1} \lambda_{101,z-y}^{k-1} + z\lambda_{100,z}^{k-1} \lambda_{101,z-y}^{k-1} \right] \\
+ k_{ic}^* R_{tot} \left( y + 1 \right) \lambda_{100,y+1}^k \delta \left( y < N_{rad} \right) \\
+ k_{ic}^* \left\{ \sum_{z=1}^{y-z+2} \lambda_{100,y-z+2}^k \sum_{h=0}^{k-1} \lambda_{000,z}^{h} + \sum_{z=1}^{y-z+2} \lambda_{100,y-z+2}^k \sum_{h=0}^{k-1} \lambda_{000,z}^{h} \right\} \\
+ \frac{1}{2} k_{ic}^* \left\{ \sum_{z=1}^{y-z+2} \lambda_{100,y-z+2}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,z}^{h} + \sum_{z=1}^{y-z+2} \lambda_{100,y-z+2}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,z}^{h} \right\}
\]

(B15)
\[
\frac{d\lambda_{200,y}^k}{dt} = -y\lambda_{200,y}^k\left[k_{p3}C_{PDB} + (k_{tc} + k_{td})R_{tot}\right] + k_{p3}^*M_y\left[2\lambda_{100,y}^k + \lambda_{201,y}^k - k_{p3}^*\lambda_{201,y}^kY_{000}\right]
+ k_{p3}^*y\left[\mu_{201}^{k-1}\lambda_{201,y}^{k-1}\sum_{h=0}^{k-1}\lambda_{201}^h\lambda_{201,y}^h + 2\mu_{101}^{k-1}\lambda_{100,y}^h + \mu_{101}^{k-1}\sum_{h=0}^{k-1}\lambda_{101,y}^h\lambda_{101,y}^h\right]
+ k_{p3}^*y\left[\mu_{201}^{k-1}\lambda_{201,y}^{k-1}\sum_{h=0}^{k-1}\lambda_{201}^h\lambda_{201,y}^h + 2\mu_{101}^{k-1}\lambda_{100,y}^h + \mu_{101}^{k-1}\sum_{h=0}^{k-1}\lambda_{101,y}^h\lambda_{101,y}^h\right]
+ k_{p3}^*y\left[\mu_{201}^{k-1}\lambda_{201,y}^{k-1}\sum_{h=0}^{k-1}\lambda_{201}^h\lambda_{201,y}^h + 2\mu_{101}^{k-1}\lambda_{100,y}^h + \mu_{101}^{k-1}\sum_{h=0}^{k-1}\lambda_{101,y}^h\lambda_{101,y}^h\right]
+ k_{p3}^*y\left[\mu_{201}^{k-1}\lambda_{201,y}^{k-1}\sum_{h=0}^{k-1}\lambda_{201}^h\lambda_{201,y}^h + 2\mu_{101}^{k-1}\lambda_{100,y}^h + \mu_{101}^{k-1}\sum_{h=0}^{k-1}\lambda_{101,y}^h\lambda_{101,y}^h\right]
+ k_{id}R_{tot}(y + 1)\lambda_{200,y+1}^k\delta(y < N_{rad})
+ k_{tc}^*\sum_{z=1}^{y+1}((y - z + 2)\lambda_{200,y-z}^k\lambda_{200,0}^z + 2\lambda_{100,y-z}^k\lambda_{101,0}^z + \lambda_{200,y-z}^k\lambda_{201,0}^z + \lambda_{101,y-z}^k\lambda_{100,0}^z)\right]}
+ \frac{1}{2}k_{tc}^*\sum_{z=1}^{y+1}((y - z + 2)\lambda_{200,y-z}^{k-1}\lambda_{200,0}^{k-1} + 2\lambda_{100,y-z}^{k-1}\lambda_{101,0}^{k-1} + \lambda_{200,y-z}^{k-1}\lambda_{201,0}^{k-1} + \lambda_{101,y-z}^{k-1}\lambda_{100,0}^{k-1})\right]} \tag{B16}
\]

Linear Dead chains

\[
\frac{d\mu_{000}^0}{dt} = -k_{p3}^*R_{tot}\mu_{001}^0 + \frac{1}{2}k_{tc}^*\left[\lambda_{000,1}^0\right]^2 + k_{id}^*R_{tot}\lambda_{000,1}^0 \tag{B17}
\]

\[
\frac{d\mu_{100}^0}{dt} = -k_{p3}^*R_{tot}\mu_{101}^0 + k_{tc}^*\lambda_{100,1}^0\lambda_{000,1}^0 + k_{id}^*R_{tot}\lambda_{100,1}^0 \tag{B18}
\]

\[
\frac{d\mu_{200}^0}{dt} = -k_{p3}^*R_{tot}\mu_{201}^0 + \frac{1}{2}k_{tc}^*\left[\lambda_{200,1}^0\lambda_{001,1}^0 + 2\lambda_{101,1}^0\lambda_{100,1}^0 + \lambda_{201,1}^0\lambda_{100,1}^0\right] + k_{id}^*R_{tot}\lambda_{200,1}^0 \tag{B19}
\]

Dead branched chains (generation 1)

\[
\frac{d\mu_{000}^1}{dt} = -k_{p3}^*R_{tot}\mu_{001}^1 + k_{tc}^*\lambda_{000,1}^1\lambda_{000,1}^0 + k_{id}^*R_{tot}\lambda_{000,1}^1 \tag{B20}
\]
\[
\frac{d \mu_{100}^i}{dt} = -k_{p3}^* R_{tot} \mu_{101}^i + k_{n}^* \left[ \lambda_{000,1}^{1} \lambda_{100,1}^{0} + \lambda_{100,1}^{1} \lambda_{000,1}^{0} \right] + k_{id}^* R_{tot} \lambda_{100,1}^1
\] (B21)

\[
\frac{d \mu_{200}^i}{dt} = -k_{p3}^* R_{tot} \mu_{201}^i + k_{n}^* \left[ \lambda_{000,1}^{1} \lambda_{200,1}^{0} + 2 \lambda_{100,1}^{1} \lambda_{100,1}^{0} + \lambda_{200,1}^{1} \lambda_{000,1}^{0} \right] + k_{id}^* R_{tot} \lambda_{200,1}^1
\] (B22)

Dead branched chains (generation k)

\[
\frac{d \mu_{000}^k}{dt} = \frac{1}{2} k_{n}^* \lambda_{000,1}^{k-1} \lambda_{000,1}^{k-1} + k_{n}^* \lambda_{000,1}^{k} \sum_{h=0}^{k-1} \lambda_{000,1}^{h} + k_{id}^* R_{tot} \lambda_{000,1}^{k} - k_{p3}^* R_{tot} \mu_{001}^k
\] (B23)

\[
\frac{d \mu_{100}^k}{dt} = k_{n}^* \lambda_{000,1}^{k-1} \lambda_{100,1}^{k-1} + k_{n}^* \lambda_{100,1}^{k} \sum_{h=0}^{k-1} \lambda_{000,1}^{h} + k_{id}^* R_{tot} \lambda_{100,1}^{k} - k_{p3}^* R_{tot} \mu_{101}^k
\] (B24)

\[
\frac{d \mu_{200}^k}{dt} = \frac{1}{2} k_{n}^* \left[ \lambda_{000,1}^{k-1} \lambda_{200,1}^{k-1} + 2 \lambda_{100,1}^{k-1} \lambda_{100,1}^{k-1} + \lambda_{200,1}^{k-1} \lambda_{000,1}^{k-1} \right]
\]
\[
+ k_{n}^* \left[ \lambda_{000,1}^{k} \sum_{h=0}^{k-1} \lambda_{200,1}^{h} + 2 \lambda_{100,1}^{k} \sum_{h=0}^{k-1} \lambda_{100,1}^{h} + \lambda_{200,1}^{k} \sum_{h=0}^{k-1} \lambda_{000,1}^{h} \right]
\] (B25)
\[
+ k_{id}^* R_{tot} \lambda_{200,1}^{k} - k_{p3}^* R_{tot} \mu_{201}^k
\]

**Moments with respect to bridges**

**Active Chains**

\[
\frac{d \lambda_{010,y}^0}{dt} \equiv 0
\] (B26)
\[
\frac{d \lambda_{010,y}^1}{dt} = -k_{p3}^* y \lambda_{010,y}^1 C_{PDB} - \left( k_{c}^* + k_{d}^* \right) y \lambda_{010,y}^1 R_{tot} - k_{p3}^* \lambda_{011,y}^1 R_{tot} \\
+ k_{p3}^* y \lambda_{010,y}^1 \left( \lambda_{000,y}^0 \mu_{011}^0 + \lambda_{010,y}^0 \mu_{011}^0 + \lambda_{000,y}^0 \mu_{011}^0 \right) \\
+ \sum_{z=1}^{y-1} k_{p3}^* \left( \lambda_{000,z}^0 \lambda_{011,y-z}^0 + \lambda_{010,z}^0 \lambda_{011,y-z}^0 + \lambda_{000,z}^0 \lambda_{011,y-z}^0 \right) \\
+ k_{d}^* R_{tot} \left( y + 1 \right) \lambda_{010,y}^1 \delta \left( y < N_{rad} \right) \\
+ k_{c}^* \sum_{z=1}^{y+1} \left\{ (y-z+2) \lambda_{010,y-z+2}^0 \lambda_{010,y}^1 + (y-z+2) \lambda_{010,y-z+2}^0 \lambda_{010,y}^1 \right\}
\]

(B27)

\[
\frac{d \lambda_{010,y}^k}{dt} = -k_{p3}^* y \lambda_{010,y}^k C_{PDB} - \left( k_{c}^* + k_{d}^* \right) y \lambda_{010,y}^k R_{tot} - k_{p3}^* \lambda_{011,y}^k R_{tot} \\
+ k_{p3}^* \lambda_{010,y}^k \left( \sum_{h=0}^{k-1} y \lambda_{000,y}^h \mu_{011}^h + \sum_{h=0}^{k-1} y \lambda_{010,y}^h \mu_{011}^h \right) \\
+ \sum_{z=1}^{y-1} k_{p3}^* \lambda_{010,y-z}^k \lambda_{001,y-z}^k + \lambda_{010,y-z}^k \lambda_{001,y-z}^k + \lambda_{000,y-z}^k \lambda_{001,y-z}^k \\
+ k_{d}^* R_{tot} \left( y + 1 \right) \lambda_{010,y}^k \delta \left( y < N_{rad} \right) \\
+ k_{c}^* \sum_{z=1}^{y+1} \left\{ (y-z+2) \lambda_{010,y-z+2}^0 \lambda_{010,y}^k + (y-z+2) \lambda_{010,y-z+2}^0 \lambda_{010,y}^k \right\}
\]

(B28)

Dead Chains
\[
\frac{d \mu_{010}}{dt} = 0
\]  
\hspace{1cm} (B29)

\[
\frac{d \mu_{010}^1}{dt} = -k_p \mu_{011}^1 R_{\text{tot}} + k_c^* \left( \lambda_{000,1}^0 \lambda_{010,1}^0 + \lambda_{010,1}^0 \lambda_{000,1}^0 \right) + k_{\text{id}}^* \lambda_{010,1}^1 R_{\text{tot}}
\]  
\hspace{1cm} (B30)

\[
\frac{d \mu_{010}^2}{dt} = \frac{1}{2} k_c^* \left( \lambda_{010,1}^{k-1} + \lambda_{000,1}^{k-1} \right) + k_c^* \left( \lambda_{010,1}^{k} \sum_{h=0}^{k-1} \lambda_{000,1}^{h} + \lambda_{000,1}^{k} \sum_{h=0}^{k-1} \lambda_{010,1}^{h} \right) + k_{\text{id}}^* \lambda_{010,1}^k R_{\text{tot}} - k_p \mu_{011}^2 R_{\text{tot}}
\]  
\hspace{1cm} (B31)

**Moments with respect to pendant double bonds**

\[
\frac{d \lambda_{001,y}^0}{dt} = -y \lambda_{001,y}^0 \left[ k_p C_{\text{PDB}} + (k_c^* + k_{\text{id}}^*) R_{\text{tot}} \right] + k_p M_2 \lambda_{000,0,0}^0 y \lambda_{000,0,0}^1 y - k_p R_{\text{tot}} \lambda_{002,y}^0
\]  
\hspace{1cm} (B32)

\[
\frac{d \lambda_{001,y}^1}{dt} = -y \lambda_{001,y}^1 \left[ k_p^* C_{\text{PDB}} + (k_c^* + k_{\text{id}}^*) R_{\text{tot}} \right] + k_p^* M_2 \lambda_{000,0,0}^1 - k_p R_{\text{tot}} \lambda_{002,y}^1
\]  
\hspace{1cm} (B33)

\[
R_{\text{tot}}(y + 1) \lambda_{001,y+1}^1 \delta(y < N_{\text{rad}})
\]  
\hspace{1cm} (B33)
\[
\frac{d\lambda_{001,y}^k}{dt} = -y\lambda_{001,y}^k \left[ k_{p3}^r C_{PDB} + (k_{c}^r + k_{ad}^r) R_{tot} \right] + k_{p3}^r M_y \lambda_{001,y}^k - k_{p3}^r R_{tot} \lambda_{002,y}^k \\
+ \frac{1}{2} k_{c}^r \left\{ \sum_{y=1}^{y+1} \left( y - z \right) \lambda_{001,y-z+2}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,0}^h + \sum_{z=1}^{z+1} \left( y - z \right) \lambda_{000,0}^{k+1} \right\} \\
+ k_{c}^r \left\{ \sum_{z=1}^{z+1} \lambda_{001,y-z}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,0}^h + \sum_{y=1}^{y+1} \lambda_{000,0}^{k+1} \right\} \\
+ k_{c}^r \sum_{y=1}^{y+1} \left\{ (y - z + 2) \lambda_{001,y-z+2}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,0}^h + \sum_{z=1}^{z+1} (y - z + 2) \lambda_{000,0}^{k+1} \right\} \\
+ \frac{1}{2} k_{c}^r \left\{ \sum_{y=1}^{y+1} (y - z + 2) \lambda_{001,y-z+2}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,0}^h + \sum_{z=1}^{z+1} (y - z + 2) \lambda_{000,0}^{k+1} \right\}
\]

\( (B34) \)

\[
\frac{d\mu_{001}^0}{dt} = -k_{p3}^r R_{tot} \mu_{002}^0 + k_{c}^r \lambda_{001,1}^{0} \lambda_{001,1}^{0} + k_{ad}^r R_{tot} \lambda_{001,1}^{0} 
\]

\( (B35) \)

\[
\frac{d\mu_{001}^1}{dt} = -k_{p3}^r R_{tot} \mu_{001}^1 + k_{c}^r \left[ \lambda_{001,1}^{1} \lambda_{001,1}^{0} + \lambda_{001,0}^{1} \lambda_{001,0}^{0} \right] + k_{ad}^r R_{tot} \lambda_{001,1}^{1} 
\]

\( (B36) \)

\[
\frac{d\mu_{001}^k}{dt} = k_{c}^r \lambda_{001,1}^{k-1} \lambda_{001,1}^{k-1} + k_{c}^r \lambda_{001,1}^{k-1} \sum_{h=0}^{k-1} \lambda_{000,0}^h + k_{c}^r \lambda_{001,1}^{k-1} \sum_{h=0}^{k-1} \lambda_{001,1}^h + k_{ad}^r R_{tot} \lambda_{001,1}^{k-1} - k_{p3}^r R_{tot} \mu_{002}^k
\]

\( (B37) \)

Mixed-order moments

\[
\mu_{101} = \frac{\mu_{001}}{\mu_{001}} \mu_{200}
\]

\( (B38) \)
\[ \mu_{201} = \frac{\mu_{001}}{\mu_{400}} \mu_{300} \]  
(B39)

\[ \mu_{011} = \frac{\mu_{010}}{\mu_{400}} \mu_{300} \]  
(B40)

\[ \mu_{002} = \left(\frac{\mu_{001}}{\mu_{400}}\right)^2 \mu_{200} \]  
(B41)

**Overall quantities**

\[ I^* = \frac{2k_d f I_2}{k_{p1} M_1 + k_{p2} M_2} \]  
(B42)

\[ I_2 = I_2(t = 0) \exp(-k_d t) \]  
(B43)

\[ \frac{dR_{\text{tot}}}{dt} = +2k_d f I_2 - \left(k_{ic}^* + k_{id}^*\right) \left(R_{\text{tot}}^*\right)^2 \]  
(B44)

\[ \frac{dR_1}{dt} = k_{p1}^* M_1 I^* + k_{p2} R_4 M_1 + k_{p3} R_4 M_1 - k_{p12} R_4 M_2 - k_{p13} R_4 C_{PDB} - \left(k_{ic}^* + k_{id}^*\right) R_1 R_{\text{tot}} \]  
(B45)

\[ \frac{dR_2}{dt} = k_{p2}^* M_2 I^* + k_{p12} R_1 M_2 + k_{p3} R_4 M_2 - k_{p21} R_4 M_1 - k_{p23} R_4 C_{PDB} - \left(k_{ic}^* + k_{id}^*\right) R_2 R_{\text{tot}} \]  
(B46)

\[ \frac{dR_3}{dt} = k_{p3} R_4 C_{PDB} + k_{p3} R_4 C_{PDB} - k_{p3} R_4 M_1 - k_{p32} R_4 M_2 - \left(k_{ic}^* + k_{id}^*\right) R_3 R_{\text{tot}} \]  
(B47)

\[ \frac{dM_1}{dt} = -k_{p1}^* M_1 R_{\text{tot}} - k_{p1}^* M_1 I^* \]  
(B48)

\[ \frac{dM_2}{dt} = -k_{p2}^* M_2 R_{\text{tot}} - k_{p2}^* M_2 I^* \]  
(B49)

\[ \frac{dW_{100}}{dt} = k_p^* M R_{\text{tot}} + 2k_d f I_2 \]  
(B50)
\[
\frac{dC_{PDB}}{dt} = k^*_p M^2_2 R^*_{tot} - k^*_p R^*_{tot} C_{PDB} + k^*_p M^2 I^*
\]  \hspace{1cm} \text{(B51)}

\[
\frac{dC_{\text{bridges}}}{dt} = k^*_p R^*_{tot} C_{PDB}
\]  \hspace{1cm} \text{(B52)}

**Formulas for interesting properties:**

**Gel and sol fraction**

\[
x_{gel} = \frac{W_{100} - \left( \sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{100,y}^k \right)}{W_{100}}
\]  \hspace{1cm} \text{(B53)}

\[
x_{sol} = 1 - x_{gel}
\]  \hspace{1cm} \text{(B54)}

**Number and weight average degree of polymerization**

\[
DP_n = \frac{\sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{100,y}^k}{\sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{100,y}^k}
\]  \hspace{1cm} \text{(B55)}

\[
DP_w = \frac{\sum_{k=0}^{N_{\text{gen}}} \mu_{200}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{200,y}^k}{\sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{100,y}^k}
\]  \hspace{1cm} \text{(B56)}

**Crosslinking densities**

\[
\rho_{\text{sol}} = \frac{\sum_{k=0}^{N_{\text{gen}}} \mu_{010}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{010,y}^k}{\sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{\text{rad}}} \lambda_{100,y}^k}
\]  \hspace{1cm} \text{(B57)}

\[
\rho_{\text{cross}} = \frac{W_{010}}{W_{100}}
\]  \hspace{1cm} \text{(B58)}
\[ \rho'_{\text{cross}} = \frac{W_{010} - \left( \sum_{k=0}^{N_{\text{gen}}} \mu_{010}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{y0}} \lambda_{010,y}^k \right)}{W_{010} - \left( \sum_{k=0}^{N_{\text{gen}}} \mu_{100}^k + \sum_{k=0}^{N_{\text{rad}}} \sum_{y=1}^{N_{y0}} \lambda_{100,y}^k \right)} \] (B59)

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\text{PDB}} )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Overall Pendant double bonds</td>
</tr>
<tr>
<td>( C_{\text{PDBC}}^* )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Pendant double bonds on active chains</td>
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<tr>
<td>( D P_{e} , D P_w )</td>
<td>–</td>
<td>Number and weight degrees of polymerization</td>
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<tr>
<td>( D P_{w}^{\text{MAX}} )</td>
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<td>Weight degree of polymerization at the gel point</td>
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<tr>
<td>( f^* )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Initiator decomposition efficiency</td>
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<tr>
<td>( I_2 )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Initiator Concentration</td>
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<td>( I^* )</td>
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<td>( 1/s )</td>
<td>Initiator decomposition constant</td>
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<td>( k_{p_j} )</td>
<td>( \text{cm}^3/\text{(mol s)} )</td>
<td>Propagation constant of radical ( i ) with monomer of type ( j )</td>
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<tr>
<td>( k_{p1}^<em>, k_{p2}^</em>, k_{p3}^* )</td>
<td>( \text{cm}^3/\text{(mol s)} )</td>
<td>Pseudo-propagation constants, defined as (B1)-(B3)</td>
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<tr>
<td>( k_{d0}^<em>, k_{d0}^</em> )</td>
<td>( \text{cm}^3/\text{(mol s)} )</td>
<td>Combination and Disproportionation termination constants at zero conversion</td>
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<tr>
<td>( k_{c}, k_{id}^* )</td>
<td>( \text{cm}^3/\text{(mol s)} )</td>
<td>Pseudo- Combination and disproportionation constants</td>
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<td>Mono-vinyl monomer</td>
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<tr>
<td>( M_2 )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Di-vinyl monomer</td>
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<td>Number of equations to be solved</td>
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<td>Number of non-linear sol generations</td>
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<td>Maximum number of active sites per chain</td>
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<td>( P_{\text{MR}} )</td>
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<td>Probability of multiradical formation</td>
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<td>( P_{d,b,i} )</td>
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<td>Dead chains of length ( r ), having ( b ) bridges and ( i ) PDB</td>
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<td>( p_{r,b,i}^k )</td>
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<td>( P_{r,b,i} ) belonging to the ( k \text{th} ) generation</td>
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<td>( R_1, R_2, R_3 )</td>
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<td>Radicals of type 1, 2 and 3</td>
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<td>( R_{\text{tot}} )</td>
<td>( \text{mol/cm}^3 )</td>
<td>Overall radical concentration</td>
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<tr>
<td>( x_{\text{sol}}, x_{\text{gel}} )</td>
<td>–</td>
<td>Sol and gel fractions</td>
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Greek Letters

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<th>Units</th>
<th>Meaning</th>
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<td>( \delta )</td>
<td>–</td>
<td>Kronecker Delta</td>
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</table>
\( \lambda_{ij,y} \) \( \text{mol} / \text{cm}^3 \) moment over active chains \((h^{th} \text{ order on chain length}, i^{th} \text{ order on bridges}, j^{th} \text{ order on PDB}), \text{belonging to the } k^{th} \text{ generation, having } y \text{ active sites}\)

\( \mu_{ij} \) \( \text{mol} / \text{cm}^3 \) moment over dead chains \((h^{th} \text{ order on chain length}, i^{th} \text{ order on bridges}, j^{th} \text{ order on PDB}), \text{belonging to the } k^{th} \text{ generation}\)

\( \rho_{\text{sol}}, \rho_{\text{gel}}, \rho_{\text{tot}} \) – Sol, gel and total crosslinking densities

\( \phi_1, \phi_2, \phi_3 \) – Radical fraction of monomer types 1, 2 and 3

\( \chi \) – Monomer conversion
Appendix C

Appendix

General definitions

Pseudo-kinetic constants

\[ kp_1^* = kp_{11}\phi_1 + kp_{21}\phi_2 + kp_{31}\phi_3 \]  
\[ kp_2^* = kp_{12}\phi_1 + kp_{22}\phi_2 + kp_{32}\phi_3 \]  
\[ kp_3^* = kp_{13}\phi_1 + kp_{23}\phi_2 + kp_{33}\phi_3 \]  

Sol and gel fractions

\[ X_{gel} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (nR_{gel}^{i} + nP_{gel}^{i})}{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (nR_{gel}^{i} + nP_{gel}^{i})} \]  
\[ X_{sol} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (nR_{sol}^{i} + nP_{sol}^{i})}{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (nR_{sol}^{i} + nP_{sol}^{i})} \]  

Average degrees of polymerization

\[ DP_{sol}^n = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (nR_{sol}^{i} + nP_{sol}^{i})}{\sum_{n=1}^{\infty} \sum_{i=0}^{\infty} (R_{sol}^{i} + P_{sol}^{i})} \]
\[ DP_w^{\text{sol}} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (n^2 R_{n,i}^{\text{sol}} + n^2 P_{n,i}^{\text{sol}})}{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (nR_{n,i}^{\text{sol}} + nP_{n,i}^{\text{sol}})} \]  

(C7)

Crosslinking densities

\[ \rho_{\text{cross}}^{\text{gel}} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (iR_{n,i}^{\text{gel}} + iP_{n,i}^{\text{gel}})}{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (nR_{n,i}^{\text{gel}} + nP_{n,i}^{\text{gel}})} \]  

(C8)

\[ \rho_{\text{cross}}^{\text{sol}} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (iR_{n,i}^{\text{sol}} + iP_{n,i}^{\text{sol}})}{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (nR_{n,i}^{\text{sol}} + nP_{n,i}^{\text{sol}})} \]  

(C9)

\[ \rho_{\text{cross}}^{\text{tot}} = \frac{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (iR_{n,i}^{\text{tot}} + iP_{n,i}^{\text{tot}})}{\sum_{n=1}^{\infty} \sum_{i=0}^{n} (nR_{n,i}^{\text{tot}} + nP_{n,i}^{\text{tot}})} \]  

(C10)

The GF model

\[ \frac{dG_1}{dt} = k_{p_{11}} c_{M_1} s_{X_1} c_{R_0} - 2k_{c_c} G_1 + \left[ k_{p_{11}} c_{M_1} \left( s_{X_1} - 1 \right) - k_{p_{12}} c_{M_1} - k_{p_{13}} c_B \right] G_1 \]  

(C11)

\[ + \left( k_{p_{21}} G_2 + k_{p_{22}} G_3 \right) c_{M_1} s_{X_1} \]

\[ \frac{dG_2}{dt} = k_{p_{22}} c_{M_2} s_{B} s_{X_2} c_{R_0} - 2k_{c_c} G_2 + \left( k_{p_{12}} G_1 + k_{p_{22}} G_3 \right) c_{M_2} s_{B} s_{X_2} \]  

(C12)

\[ + \left[ k_{p_{22}} c_{M_2} \left( s_{B} s_{X_2} - 1 \right) - k_{p_{23}} c_{M_2} - k_{p_{23}} c_B \right] G_2 \]
\[
\frac{dG}{dt} = k_{p_{02}} c_{R_0} G_B - 2k_c c_R G_3 +\left(k_{p_{13}} G_1 + k_{p_{23}} G_2\right) G_B + \left[k_{p_{23}} (G_B - c_B) - k_{p_{31}} c_{M_1} - k_{p_{32}} c_{M_2}\right] G_B
\]

\[
\frac{dG_B}{dt} = \left(k_{p_{02}} c_{M_2} s_B s_B s_{X_2} - k_{p_{04}} G_B\right)c_{R_0} + \left(k_{p_{12}} G_1 + k_{p_{22}} G_2 + k_{p_{32}} G_3\right) c_{M_2} s_B s_{X_2} - \left(k_{p_{31}} c_R + k_{p_{23}} c_{R_2} + k_{p_{33}} c_{R_3}\right) G_B
\]

\[
\frac{dG_{X_1}}{dt} = \left(k_{p_{00}} c_{R_0} + k_{p_{11}} G_1 + k_{p_{21}} G_2 + k_{p_{31}} G_3\right)c_{M_1} s_{X_1}
\]

\[
\frac{dG_{X_2}}{dt} = \left(k_{p_{02}} c_{R_0} + k_{p_{11}} G_1 + k_{p_{21}} G_2 + k_{p_{31}} G_3\right)c_{M_2} s_B s_{X_2}
\]

\[
\frac{dG}{dt} = \left(k_{p_{00}} c_{M_1} s_{X_1} + k_{p_{00}} c_{M_2} s_B s_{X_2}\right)c_{R_0} - k_t \left(G_1 + G_2 + G_3\right)^2 - \left(k_{p_{31}} G_1 + k_{p_{23}} G_2 + k_{p_{33}} G_3\right)s_{X_2} G_B
\]

\[
\frac{ds_1}{dt} = 2k_i \left(c_R s_1 - G_1 - G_2 - G_3\right) + k_{p_{11}} c_{M_1} \left(1 - s_{X_1}\right) s_1 + k_{p_{22}} c_{M_2} \left(s_1 - s_B s_{X_2}\right) + k_{p_{33}} \left(c_B s_1 - s_B G_B\right)
\]

\[
\frac{ds_2}{dt} = 2k_i \left(c_R s_2 - G_1 - G_2 - G_3\right) + k_{p_{11}} c_{M_1} \left(s_2 - s_{X_1} s_1\right) + k_{p_{22}} c_{M_2} \left(1 - s_B s_{X_2}\right)s_2 + k_{p_{23}} \left(c_B s_2 - s_B G_B\right)
\]

\[
\frac{ds_3}{dt} = 2k_i \left(c_R s_3 - G_1 - G_2 - G_3\right) + k_{p_{11}} c_{M_1} \left(s_3 - s_B s_{X_2}\right)s_1 + k_{p_{22}} c_{M_2} \left(s_3 - s_B s_{X_2}\right)s_1 + k_{p_{33}} \left(c_B - G_B\right)s_3
\]

\[
\frac{ds_B}{dt} = k_{p_{00}} c_{R_0} \left(s_B - s_3\right) + k_{p_{11}} \left(c_R s_B - s_3 G_1\right) + k_{p_{22}} \left(c_R s_1 - s_3 G_3\right) + k_{p_{33}} \left(c_R s_B - s_3 G_3\right)
\]

\[
\frac{ds_{X_1}}{dt} = \frac{ds_{X_2}}{dt} = \frac{ds_C}{dt} = 0
\]
\[ G_{j' \rightarrow 0} = G_{j' \rightarrow 0} = 0 \quad j = 1, 2, 3, b, x_1, x_2, c \]  
(C24)

\[ s_{j' \rightarrow t_j} = s_{f_j} \quad j = 1, 2, 3, b, x_1, x_2, c \]  
(C25)

\[
\frac{dG_{11}}{dt} = 2k_f \left[ (G_{11} + G_{12} + G_{13})^2 - 2c_R G_{11} \right] - 2k_{p_{12}} c_{M_2} G_{11} + 2k_{p_{22}} c_{M_1} G_{12} 
+ 2k_{p_{13}} c_{M_3} G_{13} + 2k_{p_{23}} (s_3 G_{11} G_{1B} - c_B G_{11}) + 2k_{p_{33}} s_3 G_{12} G_{1B} + 2k_{p_{43}} s_3 G_{13} G_{1B} 
\]  
(C26)

\[
\frac{dG_{12}}{dt} = 2k_f \left[ (G_{11} + G_{12} + G_{13}) (G_{11} + G_{22} + G_{23}) - 2c_R G_{12} \right] + k_{p_{11}} c_{M_1} (G_{22} - G_{12}) + k_{p_{22}} c_{M_2} (s_B - 1) G_{12} + k_{p_{32}} c_{M_3} G_{23} + k_{p_{42}} s_B G_{13} 
+ k_{p_{13}} s_3 (G_{11} G_{2B} + G_{12} G_{1B}) - c_B G_{12} \right] + k_{p_{23}} \left[ s_3 (G_{12} G_{2B} + G_{22} G_{1B}) - c_B G_{12} \right] 
+ k_{p_{33}} \left[ s_3 (G_{13} G_{2B} + G_{23} G_{1B}) \right] 
\]  
(C27)

\[
\frac{dG_{13}}{dt} = 2k_f \left[ (G_{11} + G_{12} + G_{13}) (G_{13} + G_{23} + G_{33}) - 2c_R G_{13} \right] - k_{p_{12}} c_{M_2} G_{13} 
+ k_{p_{13}} c_{M_1} (G_{33} - G_{13}) - k_{p_{22}} c_{M_2} G_{13} + k_{p_{33}} \left[ s_3 (G_{11} G_{3B} + G_{13} G_{1B}) + G_{13} G_B + G_{1B} G_1 - c_B G_{13} \right] 
+ k_{p_{23}} \left[ s_3 (G_{12} G_{3B} + G_{23} G_{1B}) + G_{12} G_B + G_{1B} G_1 \right] 
+ k_{p_{33}} \left[ s_3 (G_{13} G_{3B} + G_{33} G_{1B}) + G_{13} G_B + G_{1B} G_1 - c_B G_{13} \right] 
\]  
(C28)

\[
\frac{dG_{1B}}{dt} = 2k_f \left[ (G_{11} + G_{12} + G_{13}) (G_{1B} + G_{2B} + G_{3B}) - 2c_R G_{1B} \right] - k_{p_{00}} c_{R_0} G_{1B} + k_{p_{22}} c_{M_2} \left( s_2 G_{11} - G_{1B} \right) 
+ k_{p_{22}} c_{M_2} G_{1B} + k_{p_{23}} c_{M_3} G_{12} + k_{p_{23}} c_{M_3} G_{23} + k_{p_{33}} s_3 G_{13} + k_{p_{43}} \left[ s_3 (G_{11} G_{BB} + G_{1B} G_B) - (c_R + c_B) G_{1B} \right] 
+ k_{p_{33}} \left[ s_3 (G_{12} G_{BB} + G_{1B} G_{2B}) - c_R G_{1B} \right] + k_{p_{43}} \left[ s_3 (G_{13} G_{BB} + G_{1B} G_{3B}) - c_R G_{1B} \right] 
\]  
(C29)
\[
\frac{dG_{1X_1}}{dt} = 2k_1 \left[ (G_{11} + G_{12} + G_{13}) \left( G_{1X_1} + G_{2X_1} + G_{3X_1} \right) - 2c_R G_{1X_1} \right] + k_{p_{11}} c_M c_M + k_{p_{11}} c_M \left( G_1 + s_1 G_{11} \right) \\
-k_{p_{22}} c_{M_2} G_{1X_1} + k_{p_{22}} c_{M_2} \left( G_2 + s_1 G_{12} + G_{2X_1} \right) + k_{p_{31}} c_{M_1} \left( G_3 + s_1 G_{13} + G_{3X_1} \right) \\
+k_{p_{33}} s_3 \left( G_{11} G_{BX_2} + G_{1B} G_{1X_1} \right) - c_B G_{1X_1} \right] + k_{p_{23}} s_3 \left( G_{12} G_{BX_2} + G_{22} G_{1B} \right) \\
+k_{p_{33}} s_3 \left( G_{2X_1} G_{BX_2} + G_{3X_1} G_{1B} \right) \\ 
(C30)
\]

\[
\frac{dG_{1X_2}}{dt} = 2k_1 \left[ (G_{11} + G_{12} + G_{13}) \left( G_{1X_2} + G_{2X_2} + G_{3X_2} \right) - 2c_R G_{1X_2} \right] + k_{p_{12}} c_{M_2} \left( s_2 s_B G_{11} - G_{1X_2} \right) \\
+k_{p_{11}} c_{M_1} G_{2X_2} + k_{p_{22}} c_{M_2} s_2 s_B G_{12} + k_{p_{31}} c_{M_1} G_{3X_2} + k_{p_{32}} s_3 s_B G_{13} \\
+k_{p_{33}} s_3 \left( G_{11} G_{BX_2} + G_{1B} G_{1X_2} \right) - c_B G_{1X_2} \right] + k_{p_{23}} s_3 \left( G_{12} G_{BX_2} + G_{1B} G_{22} G_{X_2} \right) \\
+k_{p_{33}} s_3 \left( G_{13} G_{BX_2} + G_{1B} G_{3X_2} \right) \\ 
(C31)
\]

\[
\frac{dG_{22}}{dt} = 2k_1 \left[ (G_{12} + G_{22} + G_{23})^2 - 2c_R G_{22} \right] + 2k_{p_{12}} c_{M_2} s_B G_{12} - 2k_{p_{11}} c_{M_1} G_{22} + 2k_{p_{12}} c_{M_2} \left( s_B - 1 \right) G_{22} \\
+2k_{p_{32}} c_{M_2} s_B G_{23} + 2k_{p_{33}} s_3 G_{12} G_{2B} + 2k_{p_{23}} s_3 G_{22} \left( G_{2B} - c_B G_{22} \right) + 2k_{p_{33}} s_3 G_{23} G_{2B} \\ 
(C32)
\]

\[
\frac{dG_{33}}{dt} = 2k_1 \left[ (G_{12} + G_{22} + G_{23}) \left( G_{13} + G_{23} + G_{33} \right) - 2c_R G_{23} \right] + k_{p_{13}} c_{M_3} S_B G_{13} + k_{p_{13}} c_{M_3} \left( s_B - 1 \right) G_{23} \\
+k_{p_{13}} c_{M_3} G_{23} + k_{p_{23}} c_{M_2} \left( s_B G_{33} - G_{23} \right) + k_{p_{33}} s_3 \left( G_{13} G_{3B} + G_{13} G_{2B} \right) + G_{12} G_{1B} + G_{2B} G_{1} \\
+k_{p_{23}} s_3 \left( G_{23} G_{3B} + G_{23} G_{2B} \right) + G_{22} G_{2B} + G_{2B} G_{2} - c_B G_{23} \\
+k_{p_{33}} s_3 \left( G_{23} G_{3B} + G_{33} G_{2B} \right) + G_{33} \ G_{2B} + G_{2B} G_{3} - c_B G_{23} \\ 
(C33)
\]
\[
\frac{dG_{2B}}{dt} = 2k_1 \left[ (G_{11} + G_{22} + G_{23}) \left( G_{11} \right) + G_{21} + G_{22} + G_{23} \right] - 2c_R G_{2B} + c_R \left[ k_{p_1} c_{M_2} - k_{p_0} G_{2B} \right] \]
\[-k_{p_1} c_{M_1} G_{2B} + k_{p_2} c_{M_2} \left[ G_2 + s_1 G_{22} + (s_B - 1) G_{2B} \right] + k_{p_1} c_{M_2} \left[ G_3 + s_2 G_{23} + s_B G_{3B} \right] \]
\[+ k_{p_1} \left[ s_3 \left( G_{11} G_{2B} + G_{1B} G_{2B} \right) - c_{R_1} G_{2B} \right] + k_{p_2} \left[ s_3 \left( G_{22} G_{2B} + G_{2B}^2 \right) - (c_{R_2} + c_B) G_{2B} \right] \]
\[+ k_{p_0} \left[ s_3 \left( G_{22} G_{B} + G_{23} G_{3B} \right) - c_{R_3} G_{2B} \right] \]
\]

(C34)

\[
\frac{dG_{2X_1}}{dt} = 2k_1 \left[ (G_{11} + G_{12} + G_{13}) \left( G_{1X_1} + G_{2X_1} + G_{3X_1} \right) - 2c_R G_{2X_1} \right] + k_{p_1} c_{M_1} s_1 G_{1X_1} + k_{p_2} c_{M_2} s_B G_{1X_1} \]
\[+ k_{p_2} c_{M_1} \left( s_1 G_{22} - G_{2X_1} \right) + k_{p_2} c_{M_2} \left( s_B - 1 \right) G_{2X_1} + k_{p_1} c_{M_1} s_1 G_{23} + k_{p_2} c_{M_2} s_B G_{3X_1} \]
\[+ k_{p_1} s_3 \left( G_{12} G_{2X_1} + G_{1X_1} G_{2B} \right) + k_{p_2} s_3 \left[ s_3 \left( G_{22} G_{2X_1} + G_{2X_1} G_{2B} \right) - c_B G_{2X_1} \right] \]
\[+ k_{p_3} \left( G_{22} G_{2X_1} + G_{3X_1} G_{2B} \right) \]
\]

(C35)

\[
\frac{dG_{2X_2}}{dt} = 2k_1 \left[ (G_{12} + G_{22} + G_{23}) \left( G_{1X_2} + G_{2X_2} + G_{3X_2} \right) - 2c_R G_{2X_2} \right] + k_{p_2} c_{M_2} s_B \]
\[+ k_{p_1} c_{M_2} s_B \left( G_{R_0} + s_2 G_{12} + G_{1X_2} \right) - k_{p_1} c_{M_1} G_{2X_2} \]
\[+ k_{p_2} c_{M_2} \left[ s_B \left( G_{R_0} + s_2 G_{22} \right) + (s_B - 1) G_{2X_2} \right] \]
\[+ k_{p_3} c_{M_2} s_B \left( G_{R_0} + s_2 G_{23} + G_{3X_2} \right) + k_{p_3} s_3 \left( G_{22} G_{2X_2} + G_{1X_2} G_{2B} \right) \]
\[+ k_{p_3} \left[ s_3 \left( G_{22} G_{2X_2} + G_{2B} G_{2X_2} \right) - c_B G_{2X_2} \right] + k_{p_3} \left( G_{23} G_{2X_2} + G_{2B} G_{3X_2} \right) \]
\]

(C36)

\[
\frac{dG_{33}}{dt} = 2k_1 \left[ (G_{13} + G_{23} + G_{33})^2 - 2c_R G_{33} \right] + 2k_{p_0} c_{M_2} G_{3B} + k_{p_0} c_{M_2} G_{33} - k_{p_2} c_{M_2} G_{33} \]
\[+ 2k_{p_1} \left( s_3 G_{13} G_{3B} + G_{13} G_{B} + G_{3B} G_{1} \right) + 2k_{p_3} \left( s_3 G_{23} G_{3B} + G_{23} G_{B} + G_{3B} G_{2} \right) \]
\[+ 2k_{p_3} \left( s_3 G_{33} G_{3B} + G_{33} G_{B} + G_{3B} G_{3} - c_B G_{33} \right) \]
\]

(C37)
\[
\frac{dG_{3B}}{dt} = 2k_i \left[ (G_{13} + G_{23} + G_{33})(G_{1B} + G_{2B} + G_{3B}) - 2c_R G_{3B} \right] + k_{p1i} c_{R_i} (G_{BB} - G_{3B}) + k_{p2i} c_{M_i} s_i G_{13} \\
+ k_{p2i} c_{M_1} s_2 G_{23} - k_{p1i} c_{M_1} G_{1B} + k_{p2i} c_{M_2} (s_2 G_{33} - G_{3B}) \\
+ k_{p1i} \left[ s_3 (G_{13} G_{BB} + G_{1B} G_{3B}) + G_{1B} G_B + G_{BB} G_i - c_R G_{3B} \right] \\
+ k_{p2i} \left[ s_3 (G_{23} G_{BB} + G_{2B} G_{3B}) + G_{2B} G_B + G_{BB} G_2 - c_R G_{3B} \right] \\
+ k_{p3i} \left[ s_3 (G_{33} G_{BB} + G_{3B} G_B) + G_{3B} G_B + G_{BB} G_3 - (c_R + c_B) G_{3B} \right]
\]

(C38)

\[
\frac{dG_{3X_1}}{dt} = 2k_i \left[ (G_{13} + G_{23} + G_{33})(G_{1X_1} + G_{2X_1} + G_{3X_1}) - 2c_R G_{3X_1} \right] + k_{p0i} c_{R_0} G_{BX_1} + k_{p1i} c_{M_1} s_i G_{13} \\
+ k_{p2i} c_{M_1} s_i G_{23} + k_{p1i} c_{M_1} s_i G_{33} - k_{p2i} c_{M_2} G_{3X_1} \\
+ k_{p1i} \left[ s_3 (G_{1X_1} G_{3B} + G_{13} G_{BX_1}) + G_{1X_1} G_B + G_{BX_1} G_i \right] \\
+ k_{p2i} \left[ s_3 (G_{2X_1} G_{3B} + G_{23} G_{BX_1}) + G_{2X_1} G_B + G_{BX_1} G_2 \right] \\
+ k_{p3i} \left[ s_3 (G_{3X_1} G_{3B} + G_{33} G_{BX_1}) + G_{3X_1} G_B + G_{BX_1} G_3 - c_B G_{3X_1} \right]
\]

(C39)

\[
\frac{dG_{3X_2}}{dt} = 2k_i \left[ (G_{13} + G_{23} + G_{33})(G_{1X_2} + G_{2X_2} + G_{3X_2}) - 2c_R G_{3X_2} \right] + k_{p0i} c_{R_0} G_{BX_2} + k_{p1i} c_{M_1} s_2 G_{13} \\
+ k_{p2i} c_{M_1} s_2 G_{23} + k_{p1i} c_{M_1} s_2 G_{33} + k_{p2i} c_{M_2} (s_2 G_{33} - G_{3X_2}) \\
+ k_{p1i} \left[ s_3 (G_{1X_2} G_{3B} + G_{13} G_{BX_2}) + G_{1X_2} G_B + G_{BX_2} G_i \right] + k_{p2i} \left[ s_3 (G_{2X_2} G_{3B} + G_{23} G_{BX_2}) + G_{2X_2} G_B + G_{BX_2} G_2 \right] \\
+ k_{p3i} \left[ s_3 (G_{3X_2} G_{3B} + G_{33} G_{BX_2}) + G_{3X_2} G_B + G_{BX_2} G_3 - c_B G_{3X_2} \right]
\]

(C40)

\[
\frac{dG_{BB}}{dt} = 2k_i \left[ (G_{1B} + G_{2B} + G_{3B})^2 - 2c_R G_{BB} \right] + 2k_{p0i} c_{R_0} G_{BB} + 2k_{p1i} c_{M_1} s_2 G_{1B} + 2k_{p2i} c_{M_2} s_2 G_{2B} \\
+ 2k_{p2i} c_{M_2} s_2 G_{3B} + 2k_{p1i} (s_3 G_{1B} G_{BB} - c_R G_{BB}) \\
+ 2k_{p2i} (s_3 G_{2B} G_{BB} - c_R G_{BB}) + 2k_{p3i} (s_3 G_{3B} G_{BB} - c_R G_{BB})
\]

(C41)
\[
\frac{dG_{Bx_i}}{dt} = 2k_t \left[ (G_{1B} + G_{2B} + G_{3B})(G_{1X_i} + G_{2X_i} + G_{3X_i}) - 2c_R G_{Bx_i} \right] - k_{p_0} c_{R_0} G_{Bx_i} + k_{p_{i3}} c_{M_i} s_i G_{1B} \\
+ k_{p_{i2}} c_{M_i} s_i G_{1X_i} + k_{p_{i1}} c_{M_i} s_i G_{2B} + k_{p_{i2}} c_{M_i} s_i G_{2X_i} + k_{p_{i3}} c_{M_i} s_i G_{3B} + k_{p_{i2}} c_{M_i} s_i G_{3X_i} \\
+ k_{p_{i3}} \left[ s_i (G_{1X_i} G_{BB} + G_{1B} G_{Bx_i}) - c_{R_i} G_{Bx_i} \right] + k_{p_{i3}} \left[ s_i (G_{2X_i} G_{BB} + G_{2B} G_{Bx_i}) - c_{R_i} G_{Bx_i} \right] \\
+ k_{p_{i3}} \left[ s_i (G_{3X_i} G_{BB} + G_{3B} G_{Bx_i}) - c_{R_i} G_{Bx_i} \right]
\]

(C42)

\[
\frac{dG_{Bx_i}}{dt} = 2k_t \left[ (G_{1B} + G_{2B} + G_{3B})(G_{1X_i} + G_{2X_i} + G_{3X_i}) - 2c_R G_{Bx_i} \right] + k_{p_{i2}} c_{R_i} c_{M_i} s_i - k_{p_0} c_{R_0} G_{Bx_i} \\
+ k_{p_{i2}} c_{M_i} s_i \left( G_1 + s_b G_{1B} + G_{1X_i} \right) + k_{p_{i2}} c_{M_i} s_i \left( G_2 + s_b G_{2B} + G_{2X_i} \right) \\
+ k_{p_{i2}} c_{M_i} s_i \left( G_3 + s_b G_{3B} + G_{3X_i} \right) + k_{p_{i3}} \left[ s_i \left( G_{1X_i} G_{BB} + G_{1B} G_{Bx_i} \right) - c_{R_i} G_{Bx_i} \right] \\
+ k_{p_{i3}} \left[ s_i \left( G_{2X_i} G_{BB} + G_{2B} G_{Bx_i} \right) - c_{R_i} G_{Bx_i} \right] \\
+ k_{p_{i3}} \left[ s_i \left( G_{3X_i} G_{BB} + G_{3B} G_{Bx_i} \right) - c_{R_i} G_{Bx_i} \right]
\]

(C43)

\[
\frac{dG_{X_i X_i}}{dt} = 2k_t \left[ (G_{1X_i} + G_{2X_i} + G_{3X_i})^2 - 2c_R G_{X_i X_i} \right] + 2c_{M_i} s_i \left( k_{p_{i1}} G_{1X_i} + k_{p_{i2}} G_{2X_i} + k_{p_{i3}} G_{3X_i} \right) \\
+ 2s_i G_{Bx_i} \left( k_{p_{i3}} G_{1X_i} + k_{p_{i3}} G_{2X_i} + k_{p_{i3}} G_{3X_i} \right)
\]

(C44)

\[
\frac{dG_{X_i X_i}}{dt} = 2k_t \left[ (G_{1X_i} + G_{2X_i} + G_{3X_i})(G_{1X_i} + G_{2X_i} + G_{3X_i}) - 2c_R G_{X_i X_i} \right] \\
+ c_{M_i} s_i \left( k_{p_{i1}} G_{1X_i} + k_{p_{i2}} G_{2X_i} + k_{p_{i3}} G_{3X_i} \right) + c_{M_i} s_i s_i \left( k_{p_{i2}} G_{1X_i} + k_{p_{i2}} G_{2X_i} + k_{p_{i2}} G_{3X_i} \right) \\
+ k_{p_{i3}} s_i \left( G_{1X_i} G_{Bx_i} + G_{1X_i} G_{Bx_i} \right) + k_{p_{i3}} s_i \left( G_{2X_i} G_{Bx_i} + G_{2X_i} G_{Bx_i} \right) \\
+ k_{p_{i3}} s_i \left( G_{3X_i} G_{Bx_i} + G_{3X_i} G_{Bx_i} \right)
\]

(C45)

\[
\frac{dG_{X_i X_i}}{dt} = 2k_t \left[ (G_{1X_i} + G_{2X_i} + G_{3X_i})^2 - 2c_R G_{X_i X_i} \right] + 2c_{M_i} s_i s_i \left( k_{p_{i2}} G_{1X_i} + k_{p_{i2}} G_{2X_i} + k_{p_{i2}} G_{3X_i} \right) \\
+ 2s_i G_{Bx_i} \left( k_{p_{i1}} G_{1X_i} + k_{p_{i2}} G_{2X_i} + k_{p_{i3}} G_{3X_i} \right)
\]

(C46)
\begin{equation}
G_{ij,a} = 0 \quad i, j = 1, 2, 3, B, X_1, X_2
\end{equation}

In the previous equations, the quantities \(c_I, c_{M_i}, c_{M_2}, c_{B_i}, c_{R_1}, c_{R_0}, c_C, c_{R_i}\) are evaluated from the conventional material balances; these same equations are actually present in all the kinetic models explored in this work.
Appendix D

CFD simulations

For the present CFD analysis laminar flow conditions were applied and the system, composed of cup and stator, was divided in $3 \times 10^6$ mesh elements. The liquid volume considered was 1.5 ml to reproduce the experimental conditions employed, while a constant density of 1000 kg/m$^3$ and a constant viscosity of 0.15 Pa·s were chosen as representative measures of the Inverse Latex (IL) under investigation.

The results of the CFD analysis can be seen in Figure D1, where the shear rate profile on the stator surface can be seen. From Figure D1, as expected, the lowest shear rates are found in the centre of the stator, while the highest are seen at its edges.

To properly quantify the values of the shear rate that the fluid undergoes in the different sections of the cup, we identify three zones (indent of Figure D2). The corresponding shear rate distributions can be observed in histogram form in Figure D2. Notably, the distribution of shear rates is weighted on the volume fractions, where each distribution has been normalized on the volume of its own zone.

As expected, the highest shear rate is found in the bottom part of the rheometer (zone 3), while in zones 2 and 1 the shear rates become progressively lower, as the distance towards the wall increases. Interestingly, the overall average shear rate is only 581 s$^{-1}$, which is substantially smaller than the shear rate (2000 s$^{-1}$) of the standard geometries we used at which no gelation occurred (see discussed in Section 5.2.2). This means that the gelation typically observed in the IL is due to the maximum shear rate, which lies around 5600 s$^{-1}$.
The aforementioned CFD simulations have been performed to identify the real shear rate profiles in other two cases applied (IL 235 was sheared also at two other shear rates). These turned out to be 5100 s\(^{-1}\) and 6200 s\(^{-1}\).

Figure D1
Contours of Shear Rate by CFD

Figure D2
Shear rate distribution of the three different volume portions
Ostwald Ripening of surfactant E₁ in oil

Figure D3
Emulsifier E₁ contains water impurities: upon solution of E₁ in oil, 30 nm water-swollen micelles are observed. These particles undergo Ostwald ripening in time, showing a size increase

Scaling of gelation time with shear rate

As mentioned in Subsection 5.3.2.2, IL 235 has been sheared at three different shear rates, and it is found that the gelation time decreases as the shear rate increases. In addition, the gelation time scales exponentially with the shear rate, as can be seen in Figure D3, where the gelation time, \( t_{gel} \) of IL 235, is plotted as a function of shear rate. The continuous line represents an exponential fit, with an \( R^2 = 0.99 \).
The $t_{gel}$ values of IL 235 (squares) as a function of shear rate, gamma ($\dot{\gamma}$). The line represents an exponential fit in the form of $t_{gel} = Ae^{-\dot{\gamma}}$. 
Appendix E

The discretized differential operator $\mathcal{I}_A$ has the form:

$$\mathcal{I}_A \mathbf{a}(t) = \mathbf{A}^{-1} \mathbf{D} \mathbf{a}(t)$$

(E1)

where:

$$(\mathbf{D})_{i,j} = -\left( \frac{\partial v(x,y)}{\partial y} \phi_j(x,y) + \frac{\partial \phi_j(x,y)}{\partial y} v(x,y) [y_i \neq y_{\min}] \right)_{x=x_i, y=y_j}$$

$$= \tau^{-1}(1)x_i^{-1/3}(1-2\sigma_j(x_i-x_j)(y_{\max} - y_i)[y_i \neq y_{\min}]) \phi_j(x_i,y_i)$$

(E2)

$$(\mathbf{A})_{i,j} = \phi_j(x_i,y_i)$$

where the Iverson bracket $[y_i \neq y_{\min}]$ equals one if the conjunction is true and zero otherwise.

The bracket implements the boundary condition (7.10).

The approximation of the consumption term $\mathcal{I}_B$ is implemented as:

$$(\mathcal{I}_B \mathbf{a}(t))_i = \sum_{k=1}^{n} a_{i,k} \mathbf{a}(t) \mathbf{C}_k^- \mathbf{a}(t),$$

(E3)

where:

$$(\mathbf{C}_k^-)_{i,j} = -\phi_i(x_k,y_k) \int_{y_{\min}}^{y_{\max}} \beta(x_k,x,y) \phi_j(x,y) \, dx \, dy,$$

(E4)

and $a_{i,j}$ are the coefficients of the inverse interpolation matrix (E2):

$$a_{i,j} = (\mathbf{A}^{-1})_{i,j}.$$

(E5)
The nonlinear transformation $\mathcal{C}$ is used to approximate the convolution integral $\mathcal{I}_c$:

$$\mathcal{I}_c \, a(t) = \sum_{k=1}^{n} a_{t,k} \, C_k^+ \, a(t). \quad (E6)$$

where $C_k^+$ is a collection of $n \times n$ matrices whose generic element is:

$$(C_k^+)^{i,j} = \frac{1}{2} \int_0^t \int_{t_0}^t \beta(x, x_k - x, y_1(x, x_k - x, h, y_k), y_2(x, x_k - x, h, y_k))$$

$$\times \phi_j\left(x, y_1(x, x_k - x, h, y_k)\right) \phi_j\left(x_k - x, y_2(x, x_k - x, h, y_k)\right) \times J(x, x_k - x, h, y_k) dhdx. \quad (E7)$$

The discretization for the term $\mathcal{I}_D$ has the form:

$$\mathcal{I}_D \, a(t) = 2 \, s(t)^2 \, a_{2,m} + \frac{1}{2} \, s(t) \, A^{-1} \, C^l \, a(t), \quad (E8)$$

$$(C^l)^{i,j} = \beta(1, x - 1, y_2(1, x - 1, y_j))$$

$$\times \phi_j\left(x_i - 1, y_2(1, x - 1, y_j)\right) - \beta(1, x_i, y_j) \phi_j\left(x_i, y_j\right). \quad (E9)$$

Here $a_{2,m}$ resembles the expansion of the type (7.25) for distribution of doublets $(2,m)$:

$$a_{2,m} = A^{-1}(s_1, s_2, \ldots, s_n)^T;$$

$$s_i = \begin{cases} 1, & x_i = 2, y_i = m; \\ 0, & \text{otherwise}. \end{cases} \quad (E10)$$

The discretization for the term $\mathcal{I}_E$ reads as:

$$\mathcal{I}_E \, a(t) = \sum_j a_j(t) \int_{0}^{y_{\text{min}}} \int_{y_{\text{min}}}^{y_{\text{max}}} \beta(x, 1, y, y_{\text{max}}) \phi_j(x, y) dx dy. \quad (E11)$$
Bibliography


Curriculum Vitae

Personal Data
- Date and place of Birth: June 24th, 1985, Milan, Italy

Work Experience
- 2010-present **Swiss Federal Institute of Technology (ETH Zurich)**
  - Research Assistant in the group of Prof. Morbidelli at the Institute of Chemical and Bioengineering
  - Projects: Polymerization Modeling (EU), Colloidal Stability (BASF)
- 2009-2010 **Mario Negri Institute for Pharmacological Research, Milan**
  - Bioengineering Researcher in the group of Dr. Salmona in the Department of Biochemistry and Molecular Pharmacology
  - Project: Nanoparticle Pharmacokinetic Modeling

Education
- 2008-2009 **Politecnico di Milano**
  - Master of Science degree cum laude in Chemical Engineering
- 2004-2008 **Politecnico di Milano**
  - Bachelor’s degree in chemical engineering, grade: 105/110
- 2004 **German School of Milan**
  - High School diploma

Awards & Fellowships
- **Chemistry Travel Award 2014** (sponsor: Swiss Chemical Society)
- “**Macro Award” 2013** for best contribution at the 2nd Working Party for Polymer Reaction Engineering, 24/05-26/05/2013, Hamburg, Germany (sponsor: Wiley)
- **Marie Curie Fellowship** in the frame of the European (FP7) project “NANOPOLY” (PITN-GA-2009-238700, 2010-2013)

Teaching activities
- Teaching assistant in the course “Polymer Reaction and Colloid Engineering” at ETH Zurich, Fall Semester (2011-2014)
- Thesis Supervisor of 4 master students and 1 bachelor student at ETH Zurich (2011-2014)

Languages
- Italian: Mother tongue
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Publications

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