Kinetics of bond formation in cross-linked gelatin gels

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In chemical cross-linking of gelatin solutions, two different time scales affect the kinetics of the gel formation in the experiments. We complement the experimental study with Monte Carlo numerical simulations of a lattice model. This approach shows that the two characteristic time scales are related to the formation of single bonds cross linker–chain and of bridges between chains. In particular their ratio turns out to control the kinetics of the gel formation. We discuss the effect of the concentration of chains. Finally, our results suggest that, by varying the probability of forming bridges as an independent parameter, one can finely tune the kinetics of the gelation via the ratio of the two characteristic times.

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I. INTRODUCTION

Among biopolymers, gelatin gels have received great attention \(^{[1]}\) because of their numerous applications in pharmaceutical, photographic, and food industries. When a semi-diluted gelatin solution is cooled below room temperature, the coils start to form triple helices and progressively a connected network is built. The triple helices are reminiscent of the structure of native collagen, which gave origin to gelatin by means of a denaturation process. The gel is thermoreversible, i.e., by raising the temperature the sol state is recovered. Biodiversity due to chemical composition of the native collagen, molecular weight distribution, solution properties such as concentration or pH, influences the temperature of helix formation in the physical gel \(^{[2]}\). The shear modulus shows universal scaling behavior with a critical exponent \(f\) close to 2 versus the distance from the critical concentration of helices \(^{[3]}\). On the other hand, gelatin solutions show an even richer phenomenology since chemical gelation or a combination of chemical and physical gelation can be observed. In fact, if the system is kept above the helix formation temperature, amino-acids present along the gelatin chain can react with cross-linking molecules added to the solution. In this case helices cannot form and a permanent network appears due to cross-links between reactant and chains, leading to the onset of an elastic response. Recently, extended studies have been performed on systems of gelatin in solution with bisvinyl-sulphonemethyl (BVSM) reactant \(^{[4]}\), able to establish double covalent bonds with the lysine, the hydroxysine and possibly with other amine groups of gelatin chains. The chemical reaction is schematically shown in Fig.\(^{[1]}\) The influence of various parameters, as gelatin or reagent concentration and solution pH, on bond formation was investigated. For instance, increasing the pH activates more amine groups able to react with BSVM along the gelatin chains. Microcalorimetry measurements were able to monitor the development of the chemical reaction in time by detecting the exothermic enthalpy change during the formation of \(C - N\) bonds. Then the kinetics of cross-link formation was found to follow a double exponential decay with two characteristic times, whereas a simple exponential decay was detected at low pH.

However, when counting the number of cross-links binding BVSM and gelatin, the method could not discriminate between bonds established by free reactants with a chain and bonds leading to a bridge between two gelatin chains, nor else bonds leading to a loop within a chain. This lack of information on the kinetics leading to the gel formation crucially affects the characterization of the gel structure and therefore its mechanical properties. Finally, it may reflect onto the location of the gelation threshold and the determination of the critical exponent of the elastic modulus (the critical behavior of the shear modulus was measured at low frequency, giving a critical exponent \(f = 3.4 \pm 0.3\)\(^{[4]}\), close to the expected value for the vulcanization of long chains). As a consequence, a deeper comprehension of the bond formation kinetics is essential, requiring alternative investigations. In particular the primary question is to understand how the two time scales controlling the kinetics depend on the formation of single-bonds and bridges between the cross-linkers and the chains, or else to loops within the chains. Moreover it would be crucial to understand how these time scales are related to the properties of the gelatin solution.

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(concentration, pH...) and of the cross-linking molecules (concentration, reactivity...).

In this paper we analyze the role of concentration and reactivity of cross-linking molecules in the kinetics of bond formation, by complementing the experimental observations with a numerical study. In gelling systems numerical approaches to the study of rheological and dynamical properties have revealed to be extremely useful for a better understanding of experimental data. Both Monte Carlo and molecular dynamics simulations have been applied in the last years to the study of different chemical gelation processes. Here we have used Monte Carlo simulations on the cubic lattice of a simple model to analyze the kinetics of bond formation in chemical cross-linking of a gelatin solution. We have considered a solution of polymer chains at different concentrations. Reactant monomers can diffuse in the solution forming bonds with the active sites along the chains, producing the cross-linking. Within this approach we have followed the kinetics of the gel formation varying the gelatin concentration, the cross-linker concentration and its bonding probability (i.e. reactivity). Our data reproduce extremely well the experimental findings. They show that the two time scales detected in the experiments correspond respectively to the average time of forming single bonds reactant-chains and bridges chains-chains via cross-linkers. The ratio of these two characteristic times controls the kinetics of the bond formation: Varying the concentration and the cross-linker reactivity strongly affect this ratio and therefore the kinetics of the gelation process.

The paper is organized as follows: In section II the results of microcalorimetry measurements are presented, whereas in section III the numerical study is described and the results on bond formation are discussed. Finally in section IV the kinetics of bond formation is analyzed and the concluding remarks are given in section V.

II. MICROCALORIMETRY MEASUREMENTS

In experiments, the kinetics of the reaction between amine groups of gelatin chains and BVSM has been monitored by microcalorimetry measurements. The gelatin sample is a photographic grade of gelatin extracted from lime processed ossein with an average molecular weight \( M_w \sim 165300g/mole \), an index of polydispersity \( I_p \) = 2.06 and an isoelectric point \( pI \) = 4.9. The granules contain approximately 10% humidity and the concentrations are corrected accordingly. The BVSM can create covalent \( C-N \) bonds with amine groups of gelatin chains, so that a permanent network is formed at \( T \geq 40°C \), where the triple helices structure of gelatin gels does not form. D. Hellio-Serughetti and M. Djabourov analyzed the relation between elastic properties and system parameters was analyzed. The exothermal reaction between amine groups and BVSM has been monitored by measuring the enthalpy change. We have performed several experiments at temperature \( T = 40°C \), using solutions with different concentrations of gelatin and reactant, for different values of pH. In Fig. 2 we plot the released heat \( Q(t) \) as a function of time for a solution with gelatin concentration \( C_{gel} \) = 12% g/cm\(^3\), BVSM concentration \( C_{BVSM} \) = 0.15% g/cm\(^3\) and \( pH \) = 6.7. Normalizing the released heat by the enthalpy change \( \Delta H = -40\text{kJ/mol} \) due to the formation of one \( C-N \) bond, the curve represents at any time the total number of bonds formed between gelatin chains and BVSM. By writing \( Q(t) = A(1 - f(t)) \), where \( A \) is a dimensional coefficient proportional to \( \Delta H \), we introduce the function \( f(t) \) which represents the fraction of bonds that remain to form at time \( t \). In Fig. 3 \( f(t) \) is plotted as a function of time. Data have been fitted with the sum of two exponentials:

\[
f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

with \( \tau_1 = 520s \), \( \tau_2 = 9000s \) so that \( \tau_2/\tau_1 = 17.31 \) (the apex "m" is an abbreviation for "microcalorimetry"). It is worth to notice that microcalorimetry experiments do not allow to discriminate between single-bonds and bridges or loops within a chain, where only bridges between different chains contribute to the increase of connectivity in the system. For this reason computer simulations are a fundamental step for a deeper understanding of the kinetics of bonds formation.

III. MODEL AND NUMERICAL STUDY

We have performed Monte Carlo simulations on a cubic lattice of a system made of bi-functional monomers, i.e. the reactant and linear chains, which are represented...
by a sequence of $n = 10$ linked monomers. One monomer of the chain models a Kuhn segment \[^{10}\] , and therefore represents more units. The length of a Kuhn segment in a gelatin chain has been measured \[^{11}\] to be of the order of 40 Å, corresponding to about 10 amino-acids. As compared to the experiments, our chains correspond to shorter gelatin chains, containing only about 100 amino-acids. Each monomer occupies simultaneously the eight sites of the lattice elementary cell and, to take into account the excluded volume interaction, two occupied cells cannot have any site in common. Some monomers along the chain are active sites which may bind to the reactant in order to compose complex clusters of chains leading to the formation of a gel. The active sites are tetra-functional. Two bonds are formed with the neighbors along the chain and two are not saturated at the beginning of the simulation. The number of active sites per chain, $n_{as}$, corresponds to a fixed pH of the solution. In fact, in experiments the increasing of the pH activates more amine groups able to react with the BVSM along the chain, therefore in simulations $n_{as}$ could be varied to study the effect of the pH. Although the number of amine groups in a gelatin chain actually linked to reactant cannot be measured experimentally, it is estimated that at most a fraction of 20% can react. Therefore we have performed most of the simulations for $n_{as} = 5$, which corresponds to a fraction of 10% of active amino-acids in our chain.

Chains are randomly distributed on the lattice and diffuse via random local movements. The excluded volume interaction and the self avoiding walk condition for polymer clusters restrict the possibility of monomer movements: to satisfy these two requirements the bond lengths vary into a set of permitted values according to bond-fluctuation dynamics \[^{12}\]. On a cubic lattice the allowed bond lengths are $l = 2, \sqrt{3}, \sqrt{6}, 3, \sqrt{10}$. At each Monte Carlo step the time is increased by $\delta t = 1$ and one random move is selected on average for each monomer: if the move satisfies the bond-fluctuation dynamics and excluded volume conditions, it is executed, otherwise it is rejected. These simple laws for local movements give rise to a dynamics which takes into account the main features of the real dynamics of polymer molecules \[^{12}\].

After chains have diffused and reached equilibrium, we add the reactant to the system and let the solution diffuse towards the stationary state. Due to the diffusion of cross-linkers and chains, when a reactant finds a nearest neighbor unsaturated active site, a bond may form. The process goes on until all the possible bonds are formed.

The bond formation may request to overcome a free energy barrier \[^{13}\] , depending on the nature of the solution, the active sites and the reactant. In particular, it may depend on some specific local orientation of the molecules, some restriction on the value of the angle between two bonds, due to the rigidity of the $C-N$ link, or else may be affected by variations of the effective reactivity of the cross-linker. In our model we have taken into account these effects in the following way: The first bond of a reactant monomer is formed along lattice directions as soon as there is a neighboring active site. The second bond is formed with probability $p_b \leq 1$, since a reactant monomer is expected to have less chance to react when is already bonded to a chain, compared to when it is free. In the same spirit of reaction limited aggregation models \[^{14}\] , $p_b$ is an independent parameter which influences the time of formation of bridges between gelatin active sites. The value of $p_b$ should be determined by the features of cross-linking reagent. Moreover, although varying the bridge probability $p_b$ does not affect the gelation transition, it has a crucial effect on the velocity of the reaction, which can be easily enlightened in the numerical simulation as discussed later.

We have performed numerical simulations of the model for different lattice sizes ($L = 50, 100, 200$), where the unit length is the lattice spacing $a = 1$, with periodic boundary conditions. The chain concentration $C$ and the cross-linker concentration $C_r$ are defined as the ratio between the number of monomers/reactant and the maximum number of monomers $N_{max} = L^3/8$ in the system. Using the percolation approach we identify the gel phase as the state in which there is a percolating cluster, which spans the whole system \[^{15}\]. For a fixed set of parameters we generate a number of configurations of the system and monitor the reaction. In order to locate the gelation transition we analyze the percolation probability $\Pi$, defined as the fraction of configurations leading to a percolating cluster, and we identify the transition with the line $\Pi = 0.5$ \[^{16}\]. We have determined a qualitative phase diagram (Fig.4) by varying the chain and cross-linker concentrations, $C$ and $C_r$ respectively, for a fixed $n_{as} = 5$. In experiments the total amount of reactant has been consumed at the end of the reaction.

![FIG. 3: The fraction of bonds of the BVSM that remain to form as a function of time, for a solution with $C_{gel} = 12\%$, $C_{BVSM} = 0.15$, $pH = 6.7$ and $T = 40^\circ C$. The continuous line is the fit with Eq.(1).](image-url)
process, i.e. the amount of reactant is much lower than the amount of active sites. The reaction stops when all the reactant are linked to amine groups and the system is in the gel phase. Moreover the experimental system is investigated at gelatin concentrations $C_{gel}$ above the overlap concentration $C_{gel} = 0.005 \, g/cm^3$. In order to reproduce the experimental conditions the crosslinker concentration has been fixed at $C = 0.025$, which corresponds to $C_r \ll C$ at the sol-gel transition. Under this condition, in simulations the gel phase is located at concentrations $C$ above the overlap concentration which in our system is $C^* \approx 0.017$. This choice of parameters guarantees that at the end of the reaction the system is in the gel phase.

With finite size scaling analysis we have obtained the percolation threshold, that for the case $C_r = 0.025$ is $C_c = 0.10 \pm 0.05$, the critical exponents $\nu = 0.9 \pm 0.1$ for the percolation connectivity length $\xi \sim |C - C_c|^{-\nu}$ and $\gamma = 1.78 \pm 0.10$ for the mean cluster size $\chi \sim |C - C_c|^{-\gamma}$. These results are in good agreement with the random percolation critical exponents. The random percolating cluster is characterized by a fractal structure: its mass $M$, i.e. the number of monomers, scales with its linear dimension $\xi$ with a power law behavior $\xi^D$, where $D \simeq 2.5$. The structure of the formed network may depend on model parameters and influences the rheological response of the system.

IV. KINETICS OF BOND FORMATION

In simulations we have investigated the behavior of the number of bonds formed during the reaction process and we have distinguished between:

1. Bonds between a free reactant and an active site (we will refer to the latter type of bond as single-bonds);
2. Bonds between a linked reactant and an active site of another chain;
3. Bonds between a reactant and two active sites of the same chain (which in the following we will call loops).

We have analyzed the kinetics of bond formation for a system of size $L = 100$, with $C_r = 0.025$ and $n_{as} = 5$ varying the chain concentration $C$ and the probability $p_b$ of bridge formation. The time is measured in Monte Carlo unit time $\delta t$.

Since $C_r \ll C$, the total number of bonds at the end of reaction is equal to twice the number of cross-linkers: $N_b = 2C_rL^3/8$. In Fig.6 the total number of bonds $n_b(t)$ is plotted as a function of the time together with the number of single-bonds $n_s(t)$ (bonds of type 1) and bridges $n_{br}(t)$ (i.e. bonds of type 2 or 3) in the case $p_b = 0.01$. The number of bonds has been normalized by $N_b$. As the reaction begins, single-bonds form rapidly, then bridges start to form and the degree of connectivity between chains increases. The behavior of the total number of bonds versus time closely resembles the released heat experimentally measured during the reaction reported in Fig.2. The velocity of the reaction is related to the probability $p_b$ of bridge formation. It governs the mean time of link formation between different chains and strongly influences the duration of the reaction process.

In the inset of Fig.5 $n_s(t)$, $n_s(t)$ and $n_{br}(t)$ are plotted as a function of the time for $p_b = 1$, showing that both single-bonds and bridges form more rapidly as compared to the $p_b = 0.01$ case. The total number of bonds $n_b(t) = n_s(t) + 2n_{br}(t)$, and its time dependence can be written as $n_b(t) = N_b(1 - f(t))$. In Fig.6 the function $f(t) = 1 - n_b(t)/N_b$, representing the fraction of bonds that remain to form, is plotted in a semi logarithmic plot for the case $p_b = 0.01$. The data reproduce extremely well the behavior observed experimentally (Fig.5) and are well fitted by a sum of two exponentials

$$f(t) = a_1e^{-(t/\tau_1)} + a_2e^{-(t/\tau_2)}$$

in agreement with the microcalorimetry measurements (Eq.1). From the fit we obtain $\tau_1 = 20 \pm 2$ and $\tau_2 = 166 \pm 5$, for $p_b = 0.01$ and $C = 0.3$, providing $\tau_2/\tau_1 = 8.3 \pm 0.9$. If the bridge probability $p_b$ varies, the mean time of bridge formation $\tau_2$ changes, and so does the ratio $\tau_2/\tau_1$. In the inset of Fig.5 $f(t)$ is plotted for $p_b = 1$. From the fit we obtain $\tau_1 = 34.4 \pm 1.5$, $\tau_2 = 57.8 \pm 1.5$, and hence $\tau_2/\tau_1 = 1.68 \pm 0.08$.

In order to give a microscopic interpretation for these two characteristic times, we have directly computed the average time of formation of single bonds and bridges respectively, which cannot be done by microcalorimetry measurements. These two times are in agreement with the fitting parameters $\tau_1$ and $\tau_2$ within error bars. Next, we have analyzed the mean square displacement of the reactant monomers when they are free (1) and when they have formed one single bond (2). Interestingly we have observed that the ratio between the corresponding diffu-
We have systematically analyzed the behavior of bridges formation, it influences the average time $\tau_p$ that this effect can be crucial. Indeed, as the kinetics of the bond formation. Remarkably, we find the obtained data: When the bridge probability $p_b$ increases, the average time of bridge formation decreases, and so does the ratio $\tau_2/\tau_1$. For $p_b \geq 0.3$ we find that the ratio decreases more slowly apparently tending to a plateau. In this regime, the bridge probability $p_b$ does not influence the kinetics of bond formation, which is completely governed by the diffusion of the monomers and by their concentration. The value of the ratio between the two characteristic times obtained in the experiments at $pH = 6.7$ (see Fig. 6) corresponds to a reactant with $0.005 \lesssim p_b \lesssim 0.01$ in our simulations. The experimental findings show that the solution pH also affects the kinetics of bond formation, i.e. the ratio $\tau_2^{\text{m}}/\tau_1^{\text{m}}$ decreases as the pH decreases. This is in agreement with the chemistry of reaction, where the non protoned form of the amine is reactive. In fact, one could expect different regimes depending on the chains concentration. Indeed, if decreasing of the number of active sites will in general correspond to an increase of $p_b$, the effect of this variation on $\tau_2$ is likely to strongly depend on chain concentration. At high concentration of chains, if the number of active sites per chain decreases below a certain level, we expect that these will be surrounded by many other sites of the same chain which are not active. As a consequence, due to excluded volume effects, they will hardly be reached by partially linked cross-linkers, i.e. $\tau_2$ will increase as the number of active sites decreases and so will the ratio $\tau_2/\tau_1$. On the other hand, $\tau_2$ strongly depends on the chain mobility and on the formation of loops. Therefore decreasing the pH at low concentrations, leads to an increase of $\tau_1$ that may be balanced by a not so dramatic smaller.
FIG. 7: The ratio $\tau_2/\tau_1$ between the average time of formation of bridges and the average time of formation of single-bonds as a function of bridge probability $p_b$ for different concentrations $C$ of chains, for $C_r = 0.025$ and $n_{as} = 5$.

increase of $\tau_2$, due to the eventual formation of loops. As a consequence one can observe a net decrease of the ratio $\tau_2/\tau_1$. We would like to stress that, although the investigation of the role of pH could be in principle done with this model by varying $n_{as}$, one should use long enough chains to be able to detect the different concentration regimes.

Conversely, when the number active sites increases up to $n_{as} = 10$, in the analyzed concentration range the average time $\tau_1$ does not change appreciably, while $\tau_2$ decreases due to the formation of loops. For bridge probability $p_b$ sufficiently high ($p_b \gtrsim 0.8$), the mean time of bridge formation becomes less than or equal to the mean time of formation of single-bonds: in these cases, the number of bonds $n_b(t)$ may be fitted by a single exponential with the characteristic time $\tau_1$.

To complete our study of the kinetics of bond formation, we have measured the time $t_h$ of formation of half of the total bonds, and the duration of the reaction $t_f$, i.e. the average time needed to form all possible bonds. The data are presented in Fig.8 and show that the ratio $t_f/t_h$ decreases as the concentration increases, tending to a plateau value for $C \gtrsim 0.3$. This behavior is in agreement with the experimental findings: For $C_{BV SM} = 0.3\%$ g/cm$^3$ and $C_{gel}$ ranging from 3% to 6%, the ratio $t_f/t_h$ decreases from $t_f/t_h \sim 27$ to $t_f/t_h \sim 15$. For $C_{gel} \gtrsim 6\%$ the ratio remains constant with the concentration. Comparing the experimental results with simulations, we conclude that the regime of concentration $C \sim 0.3$ for the lattice model corresponds to $C_{gel} \sim 6\%$ of the experiments [1]. This correspondence is coherent with the behavior shown in Fig.s 5,6,7 and support the suggested interpretation. It is worth to notice that $t_f/t_h \gg 1$ for the explored range of parameters: this is a consequence of the fact that in the first half of the reaction most of formed bonds are single-bonds. In the second half, bridges between active sites are established, requiring a longer time. Finally we have analyzed the number of loops which are formed during the cross-linking reaction and may play a crucial role in the mechanical response of the gel. Loops are not detectable in experimental measurements, but can be easily monitored in simulations. Previous numerical simulations of polymerization process in hexamethylene diisocynate-based polyurethane [17] indicate that the number of loops has different roles in the various concentration regimes. Indeed the loss of elasticity due to loops may be outweighed by the increase of topological entanglements, depending on the concentration.

At the end of the reaction we have counted the number of loops, normalized by the maximum number of bridges $N_b/2$, and investigated its behavior as a function of $C$. Data plotted in Fig.9 refer to chain with $n_{as} = 5$ and $n_{as} = 10$. Our results indicate that the number of loops decreases as the chain density $C$ increases. In the range of concentration explored the number of loops decreases following a power law behavior $\sim C^{-l}$ characterized by an exponent $l = 0.75 \pm 0.05$. The behavior appears in-

FIG. 8: The time of reaction end $t_f$ (dots), time of half reaction $t_h$ (squares) and their ratio (triangles) as a function of chain concentration $C$ for $C_r = 0.0025$, $n_{as} = 5$ and $p_b = 0.01$. 
dependent of the bridge probability $p_b$. This result confirms that the bridge probability only influences the kinetics of bond formation but does not strongly affect the morphology of the system. By opportunely tuning $p_b$, i.e. changing the reactant, the velocity of the reaction may be adjusted and the formation of single-bonds and bridges may be tuned in time, but the final geometrical properties of the structure should not be modified. On the other hand, the connectedness of the system may be influenced by the number of active sites per chain $n_{as}$. In particular, when $n_{as}$ increases, the number of loops formed in the system increases and hence the degree of connectedness of the system decreases (Fig.9). Moreover, in the limit of very diluted solutions of chains where all sites are active ($n_{as} = 10$), loops represent about 80% of the total number of bonds and, as a consequence, the viscoelastic properties can be sensibly modified [17].

V. CONCLUSION

In conclusion, our experimental results show that two different timescales affect the kinetics of bond formation in our cross-linked gelatin solution. The numerical data reproduce well the experimental ones and clarify the mechanisms involved in bond formation. Our study shows that the two time scales detected in experiments correspond to the average time of forming single-bonds reactant-chains and bridges chains-chains via cross-linkers. These two times are related to the characteristic times of diffusion of free reactants and reactants which have already formed one bond. Their ratio controls the kinetics of the bond formation: Varying the concentration, the cross-linker reactivity and the pH strongly affect this ratio and therefore the kinetics of the gelation process. Our findings also show that the probability $p_b$ to form a bridge between two active sites allows to finely tune the kinetics of the reaction via the ratio of the two characteristic times. A variation of $p_b$ in our interpretation corresponds to a variation of the free energy barrier to be overcome in order to form the bond, or to different orientations of bonds vectors; hence to vary $p_b$ corresponds to change the reactant agent in the gelatin solution. Moreover, our data indicate that the number of loops formed between two active sites of the same chain, which has an important effect of the viscoelastic properties of the system, increases when the pH of the solution increases. This model represents a useful tool to investigate rheological behavior of gelatin solutions and the relation between the kinetics and gel structures.

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