Heterogeneity of polymer network micro-regions as formed by end-linking processes.

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Abstract

Polymerization and formation of crosslinked polymer networks are important processes in manufacturing, materials fabrication, and in the case of hydrated polymer networks, biomedical materials, drug delivery, and tissue engineering applications. While considerable research has been devoted to the modeling of polymer networks to determine “average” mean-field properties, studies that specifically examine the variance and distribution of large collections of polymer network strands (micro-gels) within the larger polymer network are limited. In the present study, we mathematically model
polymer networks composed of bifunctional $A_2$ network strands that undergo an end-linking gelation process. We introduce a Master Equation that allows for the inclusion of stochastic effects. The distribution of the network strands contained within individual micro-gel configurations is examined as a function of time and the extent of reaction. We specifically focus on the dynamics of polymeric end-linking gel formation, and the structural heterogeneity of micro/nano-regions within the gel. We also consider binding biases as end-groups may differentially link to the network, and possible annealing effects. Our results allow for a more detailed and thorough understanding of the dynamics of polymer network formation.

1 Introduction

The study and development of crosslinked polymer networks has been important in a wide range of applications from heavy industry to biomedical research. Crosslinked polymer networks can be formed by various techniques, leading to different structures and properties. Of these network types, considerable attention has been paid to those formed by a process termed “end-linking”. During end-linking gelation, polymer strands with two or more reactive ends bind at branch points/cross-links to form an infinite polymer network. For example, poly(ethylene glycol) (PEG) based hydrogels are typically formed through the reaction of its end-groups. The end-groups of the bifunctional $A_2$ PEG polymer precursor can either react through: a binary condensation reaction with a multifunctional ($> 2$) junction/crosslink/branchpoint; or if the end-groups are polymerizable, to multiple other end-groups – e.g., free-radical polymerization of vinyl end-groups. As this end-linking process proceeds, the respective reactive polymeric strands may exist in one of many states. In the case of bifunctional $A_2$ polymeric strands, each polymeric strand may exist in one of three states (see Figure 1): (i) the strand may be “free” where neither of the reactive ends have bound; (ii) the strand may “dangle” where only a single end has bound and the strand dangles from the rest of the network; or (iii) the strand may be “intact” where both ends are
Figure 1: Schematic of polymer network micro-gel configuration evolution. During the formation of an end-linking polymer network composed of A₂ polymeric strands, the network strands may exist in one of three states: “free” – neither end-group is bound (s₀-strand); “dangling” – a single end-group is bound (s₁-strand); or “intact” – both end-groups are bound (s₂-strand). (a) During network formation, all network strands are initially in the s₀-state. (b-d) As end-linking proceeds, the configuration of network strands can follow many paths. For example, when the extent of reaction $p = 0.5$, the is a finite probability that many different network micro-gel configurations will exist. At the extremes, the different micro-gel configurations could be composed of network strands that (b) all exist as s₁-strands, (c) exist as a combination of s₀-, s₁-, and s₂-strands, or (d) exist only s₀- and s₂-strands. (e) When the extent of reaction of complete ($p = 1$), only one micro-gel configuration is possible where all network strands exist in the s₂-state.

bound to the larger polymer network and bridge two different crosslink centers. Strands with both ends bound, may form a loop, where both ends are bound to the same crosslink center. In water-swollen polymeric networks, the proportion of these network strand states has important implications with regards to the material modulus, mesh size, and swelling.


1.1 Examining the configuration of network micro-regions

While the average number of network strand states in the mean-field can be calculated as a function of the extent of reaction $p$,\textsuperscript{12,11,13,14} there is no one-to-one correspondence between the number of end-groups that have bound and the exact tallies of respective network strand states. This holds true for both the bulk network and the individual micro-regions within the gel. A single extent of reaction, will instead, only give the probability that a specific network strand state exists. Thus far, mostly “average” network properties, such as the global fraction of different network strand states, have been calculated. Little work has been done to evaluate the individual probabilities of the different possible configurations of a set of network strands. Better quantification of the stochastic properties of the network that can occur through thermal fluctuation of strands (termed “frozen concentration fluctuation”) or heterogeneous distribution of crosslinking may yield a more detailed understanding of the system.\textsuperscript{15–17} A few Monte Carlo simulations have been performed to examine certain heterogeneities of the networks,\textsuperscript{18–24} however, there currently is no work to quantify the probability distributions of different configurations of large collections of polymer network strands (micro-gels). In this work, we attempt to fill this gap by introducing a Master Equation to study the dynamics and probability distributions of network micro-gel configurations due to random end-linking.

As proposed by Stepto and coworkers\textsuperscript{25–27} the population of molecular species in the network-forming polymerizing mixture may be realized as a population of states, or “sub-graphs,” of the monomeric network strands, where only a subset of the states is needed to describe the polymerization process. The existence probabilities of these states can be formulated. This subset of states approach has been expanded to examine topological defects of the polymer networks.\textsuperscript{28} However, to the best of our knowledge, there is a lack of investigations examining analytical solutions to higher order combinations of network strands, e.g., where the number of network strands in each individual micro-gel region is $\gtrsim 10$. The structural heterogeneity of micro-gels with high-network strand numbers is particularly important when the extent of reaction $p$ is incomplete ($p < 1$), where $p$ is defined as the fraction
of end-groups that have bound to the network. At incomplete extents of reaction, variability of micro-gel populations will be highest. In this work, we consider and model the formation and configuration of very large collections of polymer network strands (micro-gels).

We examine the reaction of bifunctional $A_2$ polymer precursors, and also look more generally at higher order functional polymer precursors $A_N$ where $N$ is the number of reactive end-groups on each polymer precursor. For simplicity, we allow the reaction of multifunctional $A_N$ polymer precursors to bind without restriction to the number of end-groups that can combine at the crosslink/branchpoint (Figure 1). Accordingly, the total number of branch-points in a single micro-gel has no effect on this model and can be subsequently incorporated to determine network physical properties. We simply examine the distribution of network strand states only. Based on models examining stochastic self assembly and nucleation,$^{29,30}$ we produce a Master Equation that is more complete than current mathematical methods to not only find average quantities of the network strand states, but also the entire probability distribution of the different possible micro-gel configurations. This Master Equation allows us to further calculate quantities such as variance and first passage times. We also use the Master Equation to account for different reactivities of different network strand states during gelation, and we devise a model where the network strand end-groups can dynamically rearrange within the network.

Table 1: Summary of variables used.

| Symbol | Representation                                      |
|--------|----------------------------------------------------|
| $N$    | Number of reactive end-groups per polymer precursor|
| $\ell$ | Number end-groups that have bound per polymer precursor|
| $s_\ell$ | Designation of strand type with $\ell$ bound end-groups |
| $N_s$ | Number polymer strands per micro-gel               |
| $n_0$ | Number of $s_0$-polymer strands per micro-gel      |
| $n_1$ | Number of $s_1$-polymer strands per micro-gel      |
| $n_2$ | Number of $s_2$-polymer strands per micro-gel      |
| $m$   | Total number of end-groups that have bound per micro-gel |
| $p$   | Extent of reaction, $m/(N_sN)$                      |
| $P(n_1,n_2)$ | Probability of micro-gel with configuration $\{n_0,n_1,n_2\}$ |
2 Current combinatoric models

2.1 Bounded strand probability

Thus far the most common analyses of networks formed by end-linking of multi-functional strands have used combinatoric approaches which we here review.\[13,31–34\] For convenience, we refer to the different strand types in the network as $s_\ell$-strands where $\ell$ is the number of strand end-groups that have bound to a branchpoint/crosslink center and, thus, to the greater network. We also assume that a maximal number of $N$ end-groups per strand can bind the network so that $0 \leq \ell \leq N$. Hence, an unbound “free” strand where no reactive ends have bound is an $s_0$-strand; a singly-bound “dangling” strand where only one end-group has bound is a $s_1$-strand; a $k$-bound “partial” strand with $k < N$ end-groups bound is a $s_k$-strand. Finally, if all $N$ end-groups have reacted and bound we have a fully integrated $s_N$-strand. It is typical to define the extent of reaction $p$ as the percentage of all possible end-groups bound to the network at equilibrium. The value of $p$ can also be interpreted as the probability that any end-group has bound to the overall network. We can evaluate the probability $P_\ell(p)$ of finding $s_\ell$-strands with $0 \leq \ell \leq N$ bound end-groups as

$$P_\ell(p) = \binom{N}{\ell} p^\ell (1-p)^{N-\ell}, \quad (1)$$

which assumes that of $N$ end-groups, $\ell$ are bound and $N - \ell$ are not. The binomial formula ensures that the above probabilities are normalized to one

$$\sum_{\ell=0}^{N} P_\ell(p) = \sum_{\ell=0}^{N} \binom{N}{\ell} p^\ell (1-p)^{N-\ell} = (p + 1 - p)^N = 1. \quad (2)$$

This combinatoric approach yields the probability of observing a given total number of different network strand states at equilibrium assuming that the fraction of bound end-groups is fixed. In Figure 2 we show schematics of $A_2$ and $A_3$ networks and corresponding probability plots of of finding $s_\ell$-strands $P_\ell(p)$ as a function of the extent of reaction $p$. 6
Equation 1 is the basis for many other end-linking gelation models which assume that all end-groups carry the same reactivity, regardless of the state of the strand they are attached to. This may not always be the case in realistic scenarios. For example, the end-groups of an unbound \( s_0 \)-strand might bind more readily than that of dangling \( s_1 \)-strands since diffusion may allow the \( s_0 \)-strand to more freely navigate the environment and find an appropriate reaction site. Additionally, end-group binding to form a \( s_2 \)-strand from a \( s_1 \)-strand may be hindered by negative allosteric effects (uncooperative) which has been shown for rigid network strands.\(^{23}\) Conversely, in other realizations, the unbound end-group of a dangling \( s_1 \)-strand might more readily bind forming an \( s_2 \)-strand due to its proximity to the overall polymerizing network, especially when the polymer concentration is dilute. Cooperative binding is at play here.

Furthermore, network formation may occur in a different settings: it may be a “quenched” forward processes that follows a specific path that is highly dependent on the initial conditions; but it may also be a dynamic phenomenon where rearrangements of end-group binding may be possible. Finally, one may be interested in the probability distribution of the specific micro-gel configurations, where the number of nul, single, \( k \), or \( N \) bound end-groups is specified, or in the time-evolution of the system. The goal of this paper is to present a mathematical framework to support a more detailed analysis of the system allowing us to go beyond Equation 1. We will do this via a Master Equation where we include different reactivities of unbound or partially bound end-groups, where dynamic or quenched binding events can be distinguished, and where explicit time-dependence is included.

### 2.2 Equilibrated distribution

Before introducing our Master Equation, we determine the equilibrium probability distribution for a given set of network strands based on combinatoric arguments with complete dynamic end-group binding. We consider a pool (or solution) of \( N_s \) polymeric network strands, where at most \( N \) end-groups per strand can bind, resulting in a total of \( N_sN \) available end-
groups. For simplicity we set $N = 2$, the most representative experimental scenario. Our goal is to determine the number of ways one can distribute $n_0$ unbound $s_0$-strands, $n_1$ singly bound $s_1$-strands, and $n_2$ doubly bound $s_2$-strands among the total number of strands $N_s$, given that a specific number of end-groups $m$ have bound. The above quantities are related by $n_0 + n_1 + n_2 = N_s$ since all strands must be accounted for, and by $n_1 + 2n_2 = m$ to include the contribution of each strand type to the total end-group count. Hence a given micro-gel with configuration $\{n_0, n_1, n_2\}$ can be equivalently described by $\{N_s, m, n_2\}$. The extent of reaction $p$ can also be determined from $\{N_s, m, n_2\}$ via $p = m/2N_s$; by definition $0 \leq p \leq 1$ since the number of bound end groups $m$ cannot exceed the total number of available ones $2N_s$. If we now assume that the reactive end-groups bind and unbind dynamically while maintaining constant $m$, we can write the number of ways $\mathcal{N}(n_0, n_1, n_2)$ to realize a given micro-gel configuration $\{n_0, n_1, n_2\}$ at equilibrium through a simple combinatoric
\[ N(0,1,2) = 2^n_1 \binom{N_s}{n_0,n_1,n_2} \] (3)

Here, the \( 2^n_1 \) factor arises from the fact that bound end-groups on \( s_1 \)-strands can be arranged in two configurations per strand. The above can be rewritten using \( n_0 = N_s - m + n_2 \) and \( n_1 = m - 2n_2 \) as follows

\[ N(N_s,m,n_2) = \frac{2^{m-2n_2}N_s!}{(N_s-m+n_2)!(m-2n_2)!n_2!} \] (4)

Upon summing over \( n_2 \) we derive \( Z_{N,s,m} \) the partition function for all possible configurations, once \( N_s,m \) are fixed

\[ Z_{N,s,m} = \sum_{n_2=0}^{[m/2]} N(N_s,m,n_2), \] (5)

where \([·]\) indicates the integer part of its argument. The equilibrium probability distribution can now be calculated as \( P_{N,s,m}(n_2) = \frac{N(N_s,m,n_2)}{Z_{N,s,m}} \), from which we can derive the following average strand populations

\[ \langle n_2 \rangle = \sum_{n_2=0}^{[m/2]} n_2 P_{N,s,m}(n_2), \] (6a)

\[ \langle n_1 \rangle = m - 2\langle n_2 \rangle, \] (6b)

\[ \langle n_0 \rangle = N_s - m + \langle n_2 \rangle. \] (6c)

The expression for \( P_{N,s,m}(n_2) \) can be useful to also determine other quantities of interest, such as the variance and higher moments. So far, we have assumed that the binding and unbinding of any strand end-group is independent of the number of bound end-groups already present on a strand. As mentioned above, at times bound end-groups may promote or hinder the binding of other end-groups, leading to so called cooperative or uncooperative binding. We
thus write

\[ \mathcal{N}(N_s, m, n_2, \alpha) = \frac{(2/\alpha)^{m-2n_2}N_s!}{(N_s - m + n_2)!(m - 2n_2)!n_2!}, \]  

(7)

where \( \alpha \) represents the reactivity parameter. Here, \( \alpha > 1 \) represents cooperative binding, which penalizes configurations with \( n_1 = m - 2n_2 \) partially bound strands, thus favoring \( s_1 \rightarrow s_2 \) events. The case \( \alpha < 1 \) represents the opposite case of uncooperative binding where \( s_0 \rightarrow s_1 \) events are favored. Finally, the probability distribution at equilibrium \( P_{N_s, m, \alpha}(n_2) \) can be written as

\[ P_{N_s, m, \alpha}(n_2) = \mathcal{N}(N_s, m, n_2, \alpha) \sum_{n_2=0}^{[m/2]} \mathcal{N}(N_s, m, n_2, \alpha). \]  

(8)

3 Master Equation

In this section we introduce the Master Equation to describe the time evolution for the probability \( P(n_0, n_1, n_2, t) \) of finding a micro-gel with the \( \{n_0, n_1, n_2\} \) configuration at time \( t \). The transition rates between configurations are dictated by a reaction matrix as we will outline below. Since the total number of strands is constant, the overall constraint \( n_0 + n_1 + n_2 = N_s \) will be obeyed. We will consider various realizations, including quenched/dynamic binding, and the possibility of end-group binding cooperativity. We will compare equilibrium or steady state solutions to Equation1 and Equation8; where possible we will also determine the full time-dependent solution.

3.1 Quenched end-group binding to the network

The first case we consider is that of irreversible attachment, whereby once an end-group has bound to the network, it will not detach. We also assume the binding rate \( \lambda \) is constant; cooperative binding effects may be included. Under these conditions, the Master Equation for the probability \( P(n_1, n_2, t) \) of a micro-gel configuration with \( n_1 \) network strands bound
at one end and $n_2$ network strands bound at both ends at time $t$, evolves according to

$$\frac{dP(n_1,n_2, t)}{dt} = 2\lambda(N_s - n_1 - n_2 + 1)P(n_1 - 1, n_2, t) + \lambda\alpha(n_1 + 1)P(n_1 + 1, n_2 - 1, t) - \lambda[2(N_s - n_1 - n_2) + \alpha n_1]P(n_1, n_2, t),$$

where we have explicitly used the $n_0 = N_s - n_1 - n_2$ constraint. The parameter $\alpha$ represents possible cooperative effects: $\alpha > 1$ implies that the $s_1 \to s_2$ binding event is more likely than the $s_0 \to s_1$ event; the reverse is true for $\alpha < 1$. The first term on the right hand side of Equation 9 represents the process of an unbound strand attaching to the network structure to form a singly bound dangling strand ($s_0 \to s_1$, Figure 3a), which gives the micro-gel configuration transition $\{n_0 + 1, n_1 - 1, n_2\} \to \{n_0, n_1, n_2\}$ (Figure 3b). The multiplicative factor $N_s - n_1 - n_2 + 1$ represents the number $s_0$-strands in the previous micro-gel configuration that have the ability to bind to the network; the 2 prefactor is also included since a $s_0$-strand can bind to the network at either of its two unbound end-groups. Similarly, the second term represents an unbound end-group from a singly bound strand binding to the network and forming a doubly bound strand ($s_1 \to s_2$, Figure 3a). The related transition is $\{n_0, n_1 + 1, n_2 - 1\} \to \{n_0, n_1, n_2\}$ (Figure 3b). The multiplicative factor $n_1 + 1$ represents the number of $s_1$-strands that can bind to the network to form an $s_2$-strand. Finally the last term describes the processes that drives the system out of the $\{n_0, n_1, n_2\}$ configuration, where either an $s_0 \to s_1$ transition, with $\{n_0, n_1, n_2\} \to \{n_0 - 1, n_1 + 1, n_2\}$, or a $s_1 \to s_2$ transition, with $\{n_0, n_1, n_2\} \to \{n_0, n_1 - 1, n_2 + 1\}$, occur (Figure 3b). Due to the forward nature of the end-group binding, at $t \to \infty$ the system will consist of only $s_2$-network strands $P(n_1, n_2, t \to \infty) = 0$ for all $\{n_1, n_2\} \neq \{0, N_s\}$ and $P(0, N_s, t \to \infty) = 1$.
Figure 3: Schematic of the process of end-group binding.  (a) End-groups bind to the overall network causing a transition in network strand states. An unbound \( s_0 \)-strand initially binds to the overall network at one of its two end-groups to form a \( s_1 \)-strand. This \( s_1 \)-strand can undergo further binding via the unbound end-group to form a \( s_2 \)-strand that is fully bound to the network. (b) A schematic of potential micro-gel configuration transitions where \( N_s = 6 \) network strands is shown. In this schematic we examine, as an example, the “ground state” where \( \{n_0, n_1, n_2\} = \{2,2,2\} \), and the paths in which the configuration of the specific micro-gel can transition. Configuration transitions from left-to-right represent the process of more end-groups binding to the network. The \( \{n_0, n_1, n_2\} \) configuration can be formed, or modified. In the case of dynamic end-group rearrangement, the number of bound groups is constant, but the micro-gel can be reconfigured (vertical direction).

(Figure 1f). We rescale time in Equation 9 via \( \lambda \alpha t \rightarrow t' \) to give

\[
\frac{dP(n_1, n_2, t)}{dt} = z(N_s - n_1 - n_2 + 1)P(n_1 - 1, n_2, t) +
(n_1 + 1)P(n_1 + 1, n_2 - 1, t) -
[z(N_s - n_1 - n_2) + n_1]P(n_1, n_2, t),
\]

where \( z = 2/\alpha \) and where we have dropped the prime notation \( (t' \rightarrow t) \) for simplicity. We can now define the average number of strand types \( \langle n_\ell(t) \rangle \) via

\[
\langle n_\ell(t) \rangle = \sum_{n_1, n_2} n_\ell P(n_1, n_2, t),
\]

(10)
for $\ell = 1, 2$, under the constraint that $0 \leq n_1 + n_2 \leq N_s$. The corresponding mass action equations can be derived by multiplying Equation 10 by $n_\ell$ and by summing over $n_1, n_2$ under the same constraint so that

$$
\frac{d\langle n_0(t) \rangle}{dt} = -z\langle n_0 \rangle, \quad (12a)
$$
$$
\frac{d\langle n_1(t) \rangle}{dt} = z\langle n_0 \rangle - \langle n_1 \rangle, \quad (12b)
$$
$$
\frac{d\langle n_2(t) \rangle}{dt} = \langle n_1 \rangle. \quad (12c)
$$

Equation 12 can be solved under the initial condition $n_0(0) = N_s$, modeling an initially totally unbound network. We find

$$
\langle n_0(t) \rangle = N_s e^{-zt}, \quad (13a)
$$
$$
\langle n_1(t) \rangle = N_s \frac{z}{z-1} (e^{-t} - e^{-zt}), \quad (13b)
$$
$$
\langle n_2(t) \rangle = N_s \left(1 + \frac{e^{-zt} - ze^{-t}}{z-1}\right), \quad (13c)
$$

from which it can be seen that $\langle n_\ell(t \to \infty) \rangle \to 0$ for $\ell = 0, 1$ and $\langle n_2(t \to \infty) \rangle \to N_s$. To connect Equations 13 to Equation 1 we evaluate $\langle m \rangle = \langle n_1 \rangle + 2\langle n_2 \rangle$ to find

$$
\langle m(t) \rangle = \frac{N_s}{z-1} [(2-z)e^{-zt} - ze^{-t} + 2(z-1)]. \quad (14)
$$

Inverting the above transcendental equation is not possible, however upon setting $z = 2$, that is, under neutral cooperative conditions $\alpha = 1$, we find

$$
\langle m(t) \rangle = 2N_s [1 - e^{-t}], \quad (15)
$$
which can be inverted to yield

\[ e^{-t} = 1 - \frac{\langle m(t) \rangle}{2N_s} = 1 - \langle p \rangle, \quad (16) \]

where we have identified the average extent of the reaction \( \langle p \rangle \) with \( \langle p \rangle = \langle m(t) \rangle / 2N_s \), and where \( t \) and \( \langle p \rangle \) are monotonic functions of each other. Equations 13 can be now recast as

\[
\begin{align*}
\langle n_0(p) \rangle &= N_s(1 - \langle p \rangle), \\
\langle n_1(p) \rangle &= 2N_s \langle p \rangle (1 - \langle p \rangle), \\
\langle n_2(p) \rangle &= N_s \langle p \rangle^2.
\end{align*}
\quad (17a,b,c)
\]

As can be seen upon comparison with Equation 1, Equations 17 obey the following identity \( \langle n_\ell(p) \rangle = N_s P_\ell(p) \), implying that the standard combinatoric approach is recovered when we consider a time-dependent forward binding process described by Equation 10 without cooperative effects, \( \alpha = 1 \). The Master Equation 10 however is much more powerful as it allows us to follow the time dynamics of the system and offers much more information than Equation 1. For example, Equation 10 can be solved directly to find the probability distribution of the micro-gel configurations at all times, \( P(n_1, n_2, t) \). To do this we introduce the generating function \( G(x, y, t) \) defined as

\[
G(x, y, t) = \sum_{n_1, n_2} P(n_1, n_2, t)x^{n_1}y^{n_2},
\quad (18)
\]

under the constraint \( 0 \leq n_1 + n_2 \leq N_s \). Upon multiplying Equation 10 by \( x^{n_1}y^{n_2} \) and summing over \( n_1, n_2 \), under the same constraint, we find the following differential equation for \( G(x, y, t) \)

\[
\frac{\partial G}{\partial t} = -z(x - y) \frac{\partial G}{\partial x} - (y - 1) \frac{\partial G}{\partial y}.
\quad (19)
\]
Equation 19 is coupled to the corresponding initial condition \( G(x, y, t = 0) = x^{N_s} \). Using the method of characteristics we find

\[
G(x, y, t) = \left[ xe^{-zt} + \frac{zy}{z-1}(e^{-t} - e^{-zt}) + \left(1 - \frac{1}{z-1}(ze^{-t} - e^{-zt})\right)\right]^{N_s}.
\] (20)

After performing a Taylor series expansion in \( x, y \) and upon comparison with Equation 18 we find

\[
P(n_1, n_2, t) = \left(\frac{N_s}{n_1, n_2}\right) e^{-z(N_s-n_1-n_2)t} \left(\frac{ze^{-t} - ze^{-zt}}{z-1}\right)^{n_1} \left(1 - \frac{ze^{-t} - e^{-zt}}{z-1}\right)^{n_2}.
\] (21)

Note that \( P(n_1, n_2, t \to \infty) = 0 \) for \( \{n_1, n_2\} \neq \{0, N_s\} \) and that \( P(0, N_s, t \to \infty) = 1 \) as expected from a forward process. Also note that the time-dependent solution for \( P(n_1, n_2, t) \) in Equation 21 depends on the initial conditions.

### 3.2 Dynamic end-group rearrangement/redistribution

We now include an equilibration process that allows the bound end-groups to dynamically rearrange their binding sites on the network if the extent of reaction is not complete and \( m < N_sN \) (Figure 3b). In this scenario, the network strand end-groups attach and detach from the greater network. Given that the total number of bound end-groups within a given micro-gel is constant, the configuration of network strands within the micro-gel is allowed to equilibrate. For example, a \( s_2 \)-network strand may detach at one of its ends to form a \( s_1 \)-strand, Simultaneously, in order to maintain constant \( m \), a \( s_0 \)-strand binds to the network to form another \( s_1 \)-strand. The reverse process where two \( s_1 \)-strands become a \( s_2 \)-and \( s_0 \)-strand is also possible. Note that since we assume that the total number of bound end-groups per micro-gel \( m = n_1 + 2n_2 \) is fixed, the system readjusts the manner in which these bound end-groups divide to form \( s_1 \)- or \( s_2 \)-network strands. Since the equilibration process yields a distribution that is independent of the initial configuration, we can select...
any starting point that yields \( m \) bound-ends. We write the equilibration Master Equation for \( P(n_1, n_2, t) \) as follows:

\[
\frac{dP(n_1, n_2, t)}{dt} = -2\kappa \alpha^2 \left( \begin{array}{c} n_1 + 2 \\ 2 \end{array} \right) P(n_1 + 2, n_2 - 1, t) + 4\kappa (N_s - n_1 - n_2 + 1)(n_2 + 1)P(n_1 - 2, n_2 + 1, t) - 2\kappa \alpha^2 \left( \begin{array}{c} n_1 \\ 2 \end{array} \right) P(n_1, n_2, t) - 4\kappa n_2 (N_s - n_1 - n_2)P(n_1, n_2, t),
\]

(22)

where \( \kappa \) is the rate at which network strand end-groups rearrange within the network, which we assume for simplicity to be constant. The first term on the right hand side of Equation 22 accounts for the process of forming a \( s_2 \)-strand and a \( s_0 \)-strand from two \( s_1 \)-strands \( (2s_1 \rightarrow s_0 + s_2; \text{Figure 3b}) \). In this process the bound end-group of one of the two \( s_1 \)-strands “hops” to the unbound end-group of the other \( s_1 \)-strands to give the micro-gel configuration transition \( \{n_0 - 1, n_1 + 2, n_2 - 1\} \rightarrow \{n_0, n_1, n_2\} \). The combinatorial factor accounts for how many pairs of \( s_1 \)-strands are available for this process, while the 2 prefactor is due a bound end-group being able to “hop” from either of the two \( s_1 \)-strands to the other. The binding factor \( \alpha \) is squared, since the formation of an \( s_2 \)-strand arises from the binding of two \( s_1 \)-strands. The second term on the right hand side represents the reverse process, a bound end-group “hops” from a \( s_2 \)-strand and relocates to an unbound end-group on a \( s_0 \)-strand, \( \{n_0 + 1, n_1 - 2, n_2 + 1\} \rightarrow \{n_0, n_1, n_2\} \) (Figure 3b), giving rise to two \( s_1 \)-strands. The factors \((N_s - n_1 - n_2 + 1)(n_2 + 1)\) represent the number of \( s_0 \)- and \( s_2 \)-network strands available, respectively. The 4 prefactor accounts for the number of possible bond movements: either of the two bound end-groups on the \( s_2 \)-strand can relocate to either of the two unbound end-groups of the \( s_0 \)-strand, yielding a total of four combinations. The last two terms represent the the same two processes described above, but driving the system away from the configuration \( \{n_0, n_1, n_2\} \) as shown in Figure 3b. Note that in Equation 22 there are no terms that represent the process of network bonds leaving a \( s_2 \)-strand to populate a \( s_1 \)-strand; this
transition would not change the overall the micro-gel configuration \( \{n_0, n_1, n_2\} \). Finally, the probability \( P_b(m, t) \) of having \( m \) bound-ends at time \( t \) can be written as

\[
P_b(m, t) = \sum_{n_2=0}^{[m/2]} P(m - 2n_2, n_2, t),
\]

(23)

where the weight of all possible \( n_1, n_2 \) combinations that yield \( m = n_1 + 2n_2 \) bound-ends are added. Equation 22 ensures that \( dP_b(m, t)/dt = 0 \); that is that \( m \) does not change once the rearrangement dynamic is at play as expected.

In addition to the \( n_1 + 2n_2 = m \) constraint, the number of strands is also fixed so that \( n_0 + n_1 + n_2 = N_s \). As a result of these two relationships we can cast Equation 22 in terms of only one of the network strand populations \( \{n_0, n_1, n_2\} \). We choose \( n_2 \) and determine the steady state \( P(n_2, t \to \infty) \equiv P^*(n_2) \) by imposing detailed balance between the first and the last term on the right hand side, or equivalently, the second and the third. One can verify that the conditions are the same. We find

\[
\frac{P^*(n_2 - 1)}{P^*(n_2)} = \frac{4n_2(N_s - m + n_2)}{\alpha^2(m - 2n_2 + 2)(m - 2n_2 + 1)},
\]

(24)

which can be solved to yield

\[
P^*(n_2) = \frac{1}{Z_{m,N_s}} \frac{(2/\alpha)^{m-2n_2} N_s!}{(m - 2n_2)! n_2!(N_s - m + n_2)!},
\]

(25)

where \( Z_{m,N_s} \) is the normalization constant

\[
Z_{m,N_s} = \sum_{n_2=0}^{[m/2]} \frac{(2/\alpha)^{m-2n_2} N_s!}{(m - 2n_2)! n_2!(N_s - m + n_2)!}.
\]

(26)

As can be seen, this result is the same as in Equation 7, confirming that the combinatoric result evaluated through the equilibrated distribution, is equivalent to allowing for relaxation
4 Numerical Results And Discussion

4.1 Equilibrated distributions of micro-gel configurations

In this section we present and discuss results from the numerical evaluation of the equilibrated distribution in Equations 4 and 7 and related quantities. The equilibrium distribution $P_{N_s,m}(n_2)$ is plotted as a function of the extent of reaction $p = m/2N_s$, for different numbers of $n_2$ $s_2$-strands (Figures 4a–c) for three different values of the cooperative factor $\alpha$. We choose this representation since the number of “intact” or “elastically effective” $s_2$-network strands determines both the mechanical modulus and swelling behavior of the polymer network. Note that as $\alpha$ increases, the probability of finding micro-gel configurations with more $s_2$-strands, at lower values of $m$, increases as might be expected. Accordingly, in Figure 4d we plot the average strand fractions $\langle n_\ell \rangle/N_s$ as evaluated via Equations 6 for $N_s = 40$ and as a function of the extent of reaction $p$. Under neutral conditions, for $\alpha = 1$, the resulting average strand probabilities closely follow that of Figure 2c as calculated by the combinatorial approach in Section 2.1. Similarly to Equations 6 one can also calculate the second moments of the strand populations $\langle n_\ell^2 \rangle = \sum_{n_\ell=0}^{N_s} n_\ell^2 P(n_\ell)$ and the resulting variance $\text{Var}(n_\ell) = \langle n_\ell^2 \rangle - \langle n_\ell \rangle^2$. Figure 4e shows $\text{Var}(n_2)$ as a function of $p$ for different values of $\alpha$. In each panel, the maximum variance occurs when half of all possible end-groups have bound. As $\alpha$ deviates from 1, the bias towards certain bond types causes the variance to decrease. Interestingly, when $\alpha$ is equal to a number and that number’s reciprocal, the maximum variance is equal. The shape of the two curves, however, differ as shown by the solid and dotted lines of the same color. We also examine how the size of the micro-gel affects the variance of micro-gel configuration. The variance of the fraction of $s_2$-strands $\text{Var}(n_2/N_s)$ is shown in Figure 4f at different values of $N_s$. Clearly, as the number of strands in the micro-gel increases, the variance in the fraction of strands in the $s_2$-state decreases.
Figure 4: Micro-gels as produced by the equilibrated distribution. (a-c) The distribution of micro-gel configuration probabilities $P_{N_s,m}(n_2)$ in a system with 10 network strands is plotted as a function of the number of bound end-groups $m$ or the extent of reaction $p$. Each data point represents a different micro-gel configuration $\{n_0, n_1, n_2\}$. The individual configuration probabilities are calculated given (a) $\alpha = 0.5$, (b) $\alpha = 1$, and (c) $\alpha = 2$. Configurations with the same number of $s_2$-strands are connected with lines. (d) Average micro-gel strand populations $\langle n_\ell \rangle/N_s$ when $N_s = 40$ given (dotted line) $\alpha = 0.5$, (solid line) $\alpha = 1$, and (dashed line) $\alpha = 2$ are plotted. (e) The variance of $n_2$ as a function of $p$ with variable $\alpha$ and $N_s = 40$ is plotted. Dotted lines indicate the inverse value of the solid lines of the same color. (f) To compare the strand variance across different micro-gel configurations of increasing $N_s$, the variance of the fraction of strands in the $s_2$-state ($n_2/N_s$) is plotted when $\alpha = 1$. The fractional strand variance across the possible micro-gel configurations maintains a maximum at $p = 0.5$ and decreases as the micro-gel grows in size.

4.2 Solution to the Master Equation

4.2.1 Quenched end-group binding

While the equilibrated distribution method is an improvement over the combinatoric approach, it still assumes that end-group binding is dynamic, where the end-groups can bind and unbind in order to achieve thermodynamic equilibrium. Thus, the model’s results are independent to the path/history in which the network was formed and not representative of
networks formed by “quenched” (non-dynamic) end-group binding. Additionally, end-group binding is a stochastic process. At a single time point, an individual micro-gel configuration will not have the same number of bound end-groups as every other possible micro-gel configuration. Rather, there will be a probability distribution of $m$ across the different possible micro-gel configurations as a function of time. The equilibrated distribution approach only gives the probability distribution of the micro-gel configuration when $m$ is fixed.

Evaluation of Equation 13 is shown in Figures 5a-c. The average strand number fractions $\langle n_{\ell} \rangle / N_s$ are plotted as a function of time where $N_s = 40$ at different values of $\alpha$. Similar to the equilibrated distribution approach, formation of $s_1$-strands is favored at smaller $\alpha$, and formation of $s_2$-strands is favored at higher $\alpha$. These figures can subsequently plotted against the average extent of reaction $\langle p \rangle$ of the system (Figure 5d-f), where

$$\langle p(t) \rangle = \frac{2\langle n_2(t) \rangle + \langle n_1(t) \rangle}{2N_s}. \quad (27)$$

When plotted in this manner, the strand probabilities take on a distinctly different shape from previous models when $\alpha \neq 1$. Most noticeably, the $\langle n_1 \rangle$ probability loses its symmetric behavior as observed previously in Figure 4d and becomes skewed (Figures 5d,f). As shown in Figure 8d, this skewed behavior of $\langle n_1 \rangle$ as evaluated by Equation 21 exists at all $\alpha \neq 1$. Dotted lines represent $\langle n_1 \rangle$ evaluated by Equations 6 and 7 with variable $\alpha$ and solid lines represent the corresponding evaluations of Equation 21.

Evaluation of the Master Equation 9 and it’s solution Equation 21 allows us to directly calculate the probability distribution of individual configurations of a micro-gel region. Figure 6 shows the probability of individual configurations $P(n_1, n_2)$ of $N_s = 3$ micro-gels plotted against $\langle p \rangle$ at different values of $\alpha$. Due to the stochastic nature of end-group binding, we find that at even very small values of $\langle p \rangle$ there exists a small, but finite, probability that all network strands will be in the $s_2$-state: $P(n_1 = 0, n_2 = 3)$. In order to point out differences between the plots of Figure 6 three different configurations are highlighted by bold lines.
Figure 5: Solutions to Equation 13. Solutions to Equation 13 as a function of (a-c) time and (d-f) the extent of reaction $\langle p \rangle$ (Equation 27), where different reactivity biases $\alpha$ were tested: (a,d) $\alpha = 0.5$, (b,e) $\alpha = 1$, and (c,f) $\alpha = 2$.

\{n_0, n_1, n_2\} = \{3, 0, 0\}; \{1, 1, 1\}; or \{0, 0, 3\}. As an example, we can solve for $P(n_1, n_2)$ when $N_s = 3$, $\alpha = 1$, and $\langle p \rangle = 0.5$ to give:

\begin{align*}
P(0, 0) &= 0.0143, \quad P(1, 1) = 0.1874, \\
P(0, 1) &= 0.0455, \quad P(1, 2) = 0.0994, \\
P(0, 2) &= 0.0482, \quad P(2, 0) = 0.1820, \\
P(0, 3) &= 0.0171, \quad P(2, 1) = 0.1930, \\
P(1, 0) &= 0.0883, \quad P(3, 0) = 0.1249.
\end{align*}

(28)

One of the main benefits of the Master Equation approach, is our ability to explore the behavior of micro-gels with very high strand numbers and investigate the probability
Figure 6: Solutions to Equation 21. Solutions to Equation 21 to find the individual micro-gel configuration probabilities $P(n_1, n_2)$, where (a) $\alpha = 0.5$, (b) $\alpha = 1$, (c) $\alpha = 2$ are plotted. To highlight differences between the above plots, three different configurations are indicated by bold lines: $\{n_0, n_1, n_2\} = \{3, 0, 0\}$ (black), $\{1, 1, 1\}$ (magenta), or $\{0, 0, 3\}$ (blue).

distribution and variability of their configurations. Figure 7 plots the micro-gel configuration probabilities $P(n_1, n_2)$ with increasing $N_s$. When $N_s = 40$, as given by $\binom{N_s+2}{2}$ there exists 861 distinct $\{n_0, n_1, n_2\}$ micro-gel configurations, all with a non-zero probability when $0 < t < \infty$.

Calculation of micro-gel configuration probabilities when $N_s$ is larger than 40 is possible, but graphically difficult to display. Figure 7 shows how heterogeneous the configuration of these micro-gels can be at intermediate values of $\langle p \rangle$.

From these micro-gel configuration probabilities we can, again, look at the configuration variance. Figure 8a plots $\text{Var}(n_2)$ at different values of $\alpha$ when $N_s = 40$ as a function of the average extent of reaction $\langle p \rangle$. In comparison to Figure 4e, we notice two main distinctions. First, the variance of $n_2$ is larger for the micro-gels calculated using the Master Equation when $N_s$ is fixed. This outcome can be expected from the simple physical argument we outline below. At each time point (and thus at each individual value of $\langle p \rangle$), there exists a probability distribution, not only of the different possible combinations of $\{n_0, n_1, n_2\}$ for a single value of $m$, but a distribution of $m$ itself. The total number of possible micro-gel configurations at any given point in time further increases. Figure 8b shows the variance of $m$, again, with variable $\alpha$ when $N_s = 40$. $\text{Var}(m)$ reaches a maximum as $\alpha \to \infty$ and a minimum as $\alpha \to 0$, the latter of which gives a bimodal distribution of $\text{Var}(m)$. When
α ≪ 1 all end-group binding will initially only occur on $s_0$-strands. Therefore, when $p = 0.5$ all network strands will have transitioned to the $s_1$-state and the variance is at a minimum.

Second, we notice that the variance of $n_2$ is no longer symmetric with $\langle p \rangle$ for all $\alpha$. Rather, when $\alpha = 1$ the variance reaches a maximum when $p \approx 0.7$. Similar to Figure 4f, Figure 8c shows that as $N_s$ increases and the micro-gel size increases, $\text{Var}(n_2/N_s)$ decreases. The shape of the $\text{Var}(n_2/N_s)$ does not change as the size of the micro-gel increases, only decreases in magnitude.

### 4.2.2 Dynamic end-group redistribution

From here, we can use the Master Equation to observe a system where the network strand end-groups are able to bind and unbind, eventually reaching thermodynamic equilibrium. For example network strand end-groups can be bound together by reversible hydrazone bonds, imine bonds, or guest-host interactions. Under the condition that the total number of bound end-groups in each micro-gel remains constant, rearrangement of the micro-gel configuration occurs according to Equation 22. Its steady state solution is the equilibrated
Figure 8: Micro-gel configuration variance. The variance of the number of (a) $s_2$-strands and number of (b) bound end-groups $m$ across the various possible micro-gel configurations with variable $\alpha$ and $N_s = 40$ are plotted. For $\alpha > 80$ and $\alpha < 1/80$ the variance curves to not change significantly from those displayed. (c) The variance of the fraction of $s_2$-strands $\text{Var}(n_2/N_s)$ across the various possible micro-gel configurations with variable $N_s$ and $\alpha = 1$ is shown. (d) Plots comparing $\langle n_1 \rangle$ as calculated using (dotted lines) the thermodynamic equilibrium approach and (solid lines) the Master Equation with variable $\alpha$ ($\alpha = 1/8, 1/2, 1, 2, \text{or} 8$) is shown.

distribution Equation 25. We combine the bond formation and bond redistribution differential equations (Equations 9 and 25, respectively) to model both processes simultaneously. A full time-dependent solution to this equation (corresponding to Equation 21 when bond rearrangement is not included) could not be found.

In Figure 9 we compare the results of the Master Equation with and without dynamic end-group rearrangement. The solution and evaluation to the system of coupled linear differential equations $dP(n_1, n_2, t)/dt$ is plotted against $\langle p \rangle$ and shown in Figure 9 with $N_s = 3$, $\alpha = 2$, and $\kappa \gg \lambda$. This solution is directly compared to the case where end-group binding is quenched ($\kappa = 0$, Figure 9a). Figure 9b shows the redistribution of micro-gel configuration probabilities due to the dynamic nature of the bonds. To evaluate this redistribution, we considered the variance of the different strand types $\text{Var}(n_\ell)$. When $\alpha = 1$, bond reversibility produces no change in the variance curves. When $\alpha = 2$, dynamic end-
Micro-gel configuration probabilities $P(n_1, n_2)$ are plotted against $\langle p \rangle$. Micro-gel configuration probabilities $P(n_1, n_2)$ are plotted against $\langle p \rangle$ for (a) quenched end-group binding ($\kappa = 0$), and (b) dynamic end-group binding ($\kappa \gg \lambda$) when $\alpha = 2$ and $N_s = 3$. The variance in the number of strand types $\text{Var}(n_\ell)$ is plotted for (c) quenched end-group binding and (d) dynamic end-group binding. For the variance plots, $\alpha = 2$ and $N_s = 10$.

Group binding produces only slight differences in the variance curves (Figure 9d) as compared to the quenched case (Figure 9c). As $\alpha$ deviates further from 1, the magnitude of $\text{Var}(n_\ell)$ for networks with dynamic bonds decreases slightly, and the shape of the variance curves deviate more. In this sense, the bond reversibility works to “anneal” the micro-gels when $\alpha \neq 1$.

This “annealing” process can be more closely observed if we plot only the micro-gel configurations where $m$ is fixed. Figure 10 shows the micro-gel configuration probabilities $P(5, 0)$, $P(3, 1)$, and $P(1, 2)$ plotted against $\langle p \rangle$ for a $N_s = 5$ system. When dynamic binding is introduced (solid lines), the probability curves shift, and become scalar multiples of one another. That is, the ratio $P(5, 0):P(3, 1):P(1, 2)$ is fixed for all time, and hence all $\langle p \rangle$.

This result is expected given the steady-state micro-gel configuration probabilities when $m$ is fixed. Equation 25 calculates the distribution of configuration probabilities for given $m$ and is independent of the network’s average extent of reaction, or the time of the network formation process. The steady state solution only requires that $t$ be sufficiently large or
Figure 10: Probability of micro-gel configurations with dynamic binding. The probability of individual micro-gel configurations \( P(n_1, n_2) \) when \( \alpha = 2 \), and \( N_s = 5 \). Only the micro-gel configurations with fixed \( m = 5 \) are shown (\( \{n_0, n_1, n_2\} = \{0, 5, 0\}, \{1, 3, 1\}, \text{or} \{2, 1, 2\} \)). Comparison is drawn between micro-gels formed with dynamic end-group binding (solid lines) and quenched end-group binding (dotted lines).

\( \kappa \gg \lambda \) in order for the equilibrated micro-gel configuration probabilities to emerge.

Redistribution of micro-gel configurations can be further observed when the average strand probabilities \( \langle n_\ell \rangle / N_s \) are calculated according to Equation 11 as shown in Figure 11. Similar to Figure 5d-f, the strand probabilities are plotted when \( \alpha = 0.5, 1, \text{or} 2 \). When \( \alpha = 1 \), we find that dynamic end-group binding has no effect on these curves. However, when \( \alpha \neq 1 \), introduction of dynamic binding reverts this solution back to the solution observed using the equilibrated distribution (Figure 4d). The most noticeable feature is the symmetry of \( \langle n_1 \rangle \) as a function of \( \langle p \rangle \) even when \( \alpha \) has deviated far from 1 (Figure 11d). This symmetry highlights an important distinction between models where end-group binding is quenched versus models where the end-groups are allowed to dynamically rearrange their binding. The properties of networks that form via a quenched end-group binding process should not be determined by models that assume the network strands can redistribute themselves as is the case in Equations 1 and 8.
Figure 11: Strand probabilities when with dynamic binding. The average strand fractions $\langle n_\ell \rangle / N_s$ for networks with dynamic end-group binding. Strand probabilities are plotted for (a) $\alpha = 1$, (b) $\alpha = 0.5$, and (c) $\alpha = 2$. (d) When dynamic binding is introduced, the plot of $\langle n_1 \rangle / N_s$ becomes symmetric with $\langle p \rangle$ for all $\alpha$ ($\alpha = 1/8$, 1/2, 1, 2, or 8). For all figures, $N_s = 10$.

5 Applications in polymer science

5.1 Probability distribution of micro-gel configurations as spatial heterogeneity.

In this work we use the Master Equation to produce probability distributions of polymer network micro-gel configurations. Our results can now be applied towards simulating and modeling the spatial heterogeneity of larger polymer networks. We consider a scenario where a macroscopic polymer network is comprised of a collection of smaller three-dimensional micro-regions, all with the same number of network strands. Upon evaluation of the Master Equation for a micro-gel of a specific number of network strands, a probability distribution of the network micro-gel configurations will be calculated. This probability distribution can be utilized to create a “simulated” macroscopic network, where the micro-gel configuration probability is translated into a spatial distribution of micro-gel configurations. That is, the number density of specific micro-gel configurations $\{n_0, n_1, n_2\}$ within the simulated larger
network will follow the probability distribution of micro-gel configurations as calculated by the Master Equation. This process of simulating macroscopic polymer networks is useful to investigate the spatial heterogeneity of networks across multiple length scales. For example, nano/micrometer scale differences in the polymer network properties can affect the fate of cells that are cultured on them as well as the mechanical properties of high-performance materials. Note that our model does not examine heterogeneous mixing, but fixes each micro-gel to have the same number of polymer strands $N_s$. Future iterations of this work should include variations in $N_s$.

5.2 Elasticity

According to the phantom network theory, the shear modulus $G$ of an ideal network is related to the number density of “elastically effective” network strands $\nu$ by $G = (1 - 2/f)\nu k_B T$ where $f$ is the functionality of the network’s crosslink/branchpoint centers, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. In this simple estimation, we assume that all $s_2$-strands are elastically effective, and that there is no formation of loops. Loops do not act as elastically effective strands, however, the formation of loops can be incorporated into the Master Equation in future models. By simulating the spatial distribution of micro-gel configurations with different numbers of $s_2$-strands as outlined above, we can simulate a spatial distribution map of elasticity.

5.3 Models of network degradation

In the past two decades, degradable sites have been increasingly incorporated into end-linking polymeric network strands. These degradable network strands allow for a reverse gelation process that can occur after the initial gelation process. The degradable sites typically cleave by enzymatic, hydrolytic, photolytic, or other chemical mechanisms. Initially, the network strands exist in the “intact” state where both ends are considered “un-reacted.” After a single end has reacted/degraded, the network strand is a “dangle,” and after both ends have

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reacted/degraded, the network strand is “free.” Mathematical models of reverse gelation have been formulated by adapting models of gelation. In particular, our group is interested in photodegradable networks as they are uniquely suited to pattern network stiffness as a function of time and space. End-groups are degraded by exposure to light, a process that follows exponential decay.

Mean-field mathematical models of photodegradable networks have been proposed. However, they offer less insight than the stochastic formulation presented in this work such as the evaluation of network micro-gel distributions, quenched network de-gelation reactions, and incorporation of a reactivity factor where certain network strands react more readily than others. In the case of network degradation, one might assume that the undegraded end-groups of a network strand that is bound at both ends to the network, might degrade more readily due to the stress that is normally induced in swollen polymeric networks. Once one of the end-groups has cleaved, and the network strand dangles, the stress is removed rendering the remaining undegraded end-group less susceptible to degradation. This cooperative process can again be modeled by the reactivity factor $\alpha$. Models that predict de-gelation behavior largely ignore this notion. Furthermore, in such degradable networks, incomplete extents of reaction are especially important and useful where network heterogeneity is highest. As we have shown in this work, simple combinatoric models do not properly model such polymer networks. The current model can be very simply adopted to study degradable networks by labeling “intact” network strands as $s_0$-strands (0 degraded end-groups), “dangling” network strands as $s_1$-strands (1 degraded end-group), and “free” network strands as $s_2$-strands (2 degraded end-groups).

6 Conclusions

In this work we developed and explored the use of a Master Equation to model the formation of micro-regions within a larger polymer network. The networks examined were composed
of bifunctional $A_2$ network strands that undergo an end-linking gelation process. Since most mathematical models of polymer networks only determine “average” mean-field properties, we specifically examined the variance and distribution of finite collections of polymer network strands (micro-gels) within the larger polymer network. Using a Master Equation that allows for stochastic events during network strand end-linking, probability distributions of micro-gel configurations were determined as a function of both time and extent of reaction. The calculated probability distributions were used to examine micro-gel heterogeneity with a large number of network strands per micro-gel. The Master Equation approach has allowed for the inclusion of a binding bias, or reactivity parameter $\alpha$, to model the degree of reactivity of the two end-groups on a single network strand. Dynamic binding/un-binding of the network strand end-groups was also studied, leading to “annealed” configurations. This work may be extended to incorporate network degradation, a larger number of end groups per strand, and other variants. We hope it is a first step in better understanding of the relationship between network extent of reaction and the heterogeneity of specific collections of network strand states on a microscopic level.

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