Heterogeneity in Polymer Networks Formed by a Single Copolymerization Reaction: I. Gelation and Pre-Gel Structure

D. M. Kroll¹, S. G. Croll²

1. Department of Physics, North Dakota State University, Fargo, North Dakota 58108-6050

2. Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58108-6050

Abstract

Coarse-grained molecular dynamics simulations of the formation of 3- and 6-functional polymer networks explicitly shows gelation via large dendritic clusters. The heterogeneous network structures are studied in detail; clusters have pendant structures and occupy significant volume fraction. Cluster fractal dimension and the Fisher exponent for cluster size are consistent with percolation theory and kinetic gelation models. Several criteria for determining gelation yield consistent results somewhat higher than the estimate for ideal networks on regular lattices. Almost all crosslink loop formation occurs after gelation just as traditional statistical theories assume. The presence and size of these clusters provide a natural explanation for density variations seen in microscopy studies of crosslinked polymers. The second paper in this series describes how the network structure develops after gelation. Large pendant structures, and more localized defects, persist and comprise a substantial fraction of material that is not contributing to network strength.

Keywords: Networks, gelation, clusters, dendrites, percolation, defects

Introduction

Crosslinked polymer networks are used to produce high performance materials with a variety of applications that support modern infrastructure. They are used as structural materials, insulators, adhesives, sealants, caulks and coatings. All these uses require that they have the necessary strength and durability, and many applications make use of their ability to protect other structural materials from an aggressive environment. In studying the connection between structure and properties a common, simplifying assumption is that the networks are ideal and can be described by the statistical theories originated by Flory and others [1-5]. It was always clear that forming a completely ideal network is impossible in systems that consist of molar quantities of chemical reactive species. In reality, crosslinked networks include molecular chain loops as well as chains or pendants that are incompletely connected to the network [6] so that the performance of the network is less than the ideal. To allow for these imperfections, Flory [7] used cycle rank to characterize network properties in terms of the number of complete loops in the network rather than the simpler approach in terms of the number of chains. Cycle rank is an effective parameter that is used to describe the overall mechanical properties or solvent swelling behavior of the

material, but it conveys only the overall connectivity of a network. The usefulness of a crosslinked polymer may well be defined by its ultimate strength and/or its ability to prevent aggressive fluids from passing. These properties are determined by the size and frequency of flaws, i.e. structural non-idealities that limit the performance.

Statistical models for networks can be used to describe the stress-strain behavior, deduce the molecular weight between crosslinks and determine the degree of swelling when a solvent is introduced. These are macroscopic, bulk properties. Statistical models use probabilistic calculations to estimate the conversion at which gelation occurs by looking for the probability that a chain extends to infinity, i.e. looking for the first opportunity for this to happen. Such approaches have proved to be extraordinarily useful, but focus on single values to characterize the whole system, and there is little appreciation of the variability that might occur within the crosslinking mass as it assembles. In fact, in much of the discussion of the properties of crosslinked polymers or their improvement, it is very unusual to acknowledge departures from ideal network structure.

Given the molar numbers of molecules used to make these networks, the Central Limit theorem indicates that the chemical reactions between polymer precursors, which comprise many random repeated events of the same or very similar probability, will produce results that fall on a distribution. Crosslinking should therefore not be expected to produce an ideal, homogeneous material but to create heterogeneous structures with a characteristic size and dispersion that should to be studied. Previously, Monte Carlo methods on regular lattices have focused on gelation and degree of conversion in targeted crosslinking chemistry [6-8]. In this paper we present the results, including visualizations, of a detailed coarse-grained molecular dynamics study of the pre-gel growth and structures formed during polymerization of two generic, often-used, models with 3- and 6-functional crosslinkers. The structure of the post-gel networks is discussed in the second paper in this sequence. The overall objective is to characterize the heterogeneities created during network formation that may ultimately limit the utility or durability of the crosslinked polymer and to complement others' studies that link composition with performance.

2. Model and Simulation Method.

It is most common for crosslinked polymers to be constructed with organic chemicals in which tetravalent carbon atom forms the basis of a crosslinked junction where 3 chains are joined at a carbon. In principle, the carbon's tetravalency might provide a 4-functional network, but this is uncommon; usually the 4th possible bond is taken by a hydrogen atom or some other small side group. 3-functional networks are included in this study because they are common structures and because it is the minimum functionality needed to form a network. However, it is also a common strategy to attempt to change and improve a network by increasing the reactive functionality of a chemical precursor, so we use a 6-functional system to explore the results that might ensue with that approach.

The simulation details are only briefly reiterated here, since they have been described in detail elsewhere [9, 10]. In our simulations, simple coarse-grained networks are formed from precursors consisting of 'chain extenders' and 'crosslinkers'. 'Chain extenders' are dimers in

which each bead has only one reactive functionality. They are combined in a stoichiometric mixture with either a 3-functional or a 6-functional crosslinker. The 3-functional crosslinker has a central (3-fold coordinated) bead connected to 3 other beads, each with one reactive functionality. The 6-functional crosslinker has a 6-functional bead that has one dimer already attached. These, and similar models have been used by Stevens et al. [11 - 13] to study mechanical properties, including fracture, of polymer networks. It has been shown that the pre-bonding of one dimer chain to the 6-functional bead has no noticeable effect on the resulting network connectivity [10].

Figure 1. Illustration of the precursors used in creating networks: (a) dimer, chain extender, (b) 3-functional crosslinker, (c) 6-functional precursor.

Referring to Fig.1, we assume that the functionality on shaded beads can only react with that on un-shaded beads. In practice, depending on the nature of the chemical precursors, it is possible for a fraction of the dimers or crosslinkers to undergo other reactions, e.g. homopolymerization or secondary reactions, which complicate and expand the number of possible configurations.

The simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [14]. All non-bonded beads interact with a Lennard-Jones (LJ) potential, $U(r)$, cut off at radius, $r_c = 2.5\sigma$, and shifted upward so that the potential is zero at r_c :

$$U(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases}, \quad (1)$$

where

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

σ is the length scale in the LJ potential, r is the distance between bead centers and ϵ is the energy parameter. This potential models van der Waals attractive forces and has a strong repulsive core that defines the extent of the bead. Covalent bonds between beads that were pre-existing or formed during reactions are modeled using a potential that prohibits chain crossing; the potential is the sum of the purely repulsive LJ interaction with a cutoff at $2^{1/6}\sigma$ (the minimum of the LJ

potential) which is shifted upward so that the potential is zero at the cutoff, and a finite-extensible nonlinear elastic (FENE) attractive potential:

$$U_{FENE}(r) = -0.5R_0^2 k \log_e \left[1 - \left(\frac{r}{R_0} \right)^2 \right] \quad r < R_0$$

$$= \infty \quad r \geq R_0 \quad (3)$$

where $k = 30\varepsilon/\sigma^2$ and $R_0 = 1.5\sigma$ as used previously [9, 10, 15].

Networks were formed using stoichiometric mixtures of crosslinkers and dimers with overall system sizes of 11,424 and 114,240 beads, as described elsewhere [9]. Unless otherwise stated, simulations of ten replicas of the 11,424 bead and five replicas of the 114,240 bead systems were performed to allow for adequate averaging and check for finite size effects. Some of the results for the larger networks will be shown here, but in all cases the larger simulations showed the same features and yielded numerical results that were essentially the same as the smaller simulations.

Before crosslinking, the mixture was equilibrated at a high temperature, $T = 1.0 \varepsilon/k_B$ (where k_B is Boltzmann's constant) and zero pressure using a Nosé-Hoover thermostat and barostat with time steps of $\tau/200$, where $\tau (= \sigma(m/\varepsilon)^{1/2})$ is the Lennard-Jones unit of time, in order to generate a well-mixed, liquid precursor solution. Crosslinking was performed at constant temperature and zero load. After every 100 time steps ($\tau/2$) potential bonding partners with unreacted functionalities separated by a distance less than 1.3σ , were identified and are joined with a probability of 10%. This low probability allows the neighborhood around a new bond to equilibrate and permits the next bond to be formed from an unstrained configuration. The 3-functional system reached a high level of conversion that was changing slower than logarithmically with time after 12 million time-steps (60,000 τ), whereas the 6-function system needed only 30,000 τ to achieve the same. For convenience, the units of temperature will be omitted in the following.

A combination of depth-first search and “burning” algorithms [16] were used to identify clusters and determine their structure.

Results and Discussion

In previous work [9] the emphasis was on how the overall network properties were degraded by the number of short loops in the network, or cavitation caused by shrinkage in constrained networks [10]. The focus here is to characterize in more detail the structures that form during the polymerization process, how they grow and how they combine through the gelation transition.

In order to avoid confusion, it is useful to explicitly define some terms we will use to describe these features. We used the term “bead” earlier when describing the structure of the precursors that were used to form the network in the molecular dynamics simulations. In the following

discussion of the resultant topology however, instead of “bead”, we have chosen to use “node” which is a term frequently used when discussing networks to describe a point where more than one bond are joined. Junction” denotes a node where 3 or more bonds are joined. A loop is a network chain or path in which its first and last nodes are identical. An elementary loop is one in which no nodes except the first and last appear twice. In addition, we use the term “primary” loop to denote the minimal, elementary loop formed by a single chain extender molecule that has both ends attached to the same junction. This is a small, local defect. There may be, of course, many larger elementary loops. A “dangling bond” on a crosslinker is an unreacted functionality, whereas a dangling chain, or end, is a pendant that is connected to the backbone of the network by one bond and has more than one node in the chain. A dangling chain can be quite long and may have several unreacted functionalities along its length. There are also more complicated pendants, but they will be described in more detail in the separate discussion of the post-gel structure of a network.

Table 1. The number of precursors in the stoichiometric mixtures used in the simulations. These numbers are for the smaller 11,424 node systems; the larger systems contain exactly ten times the number of each.

System	Crosslinkers	Chain-extender	Total Nodes
3-functional	1632	2448	11,424
6-functional	1632	3264	11,424

Network Growth

Simulations of both models show that molecular growth occurs in clusters which are randomly dispersed throughout the simulation volume. Because of the huge number of chemical precursors used when creating a crosslinking polymer, it is extraordinarily unlikely that each precursor finds a co-reactant at the same time and that all molecules build their molecular weight at the same rate. It is inevitable that the development of polymer molecules proceeds heterogeneously, in many locations, throughout the reacting mass. Although the statistical models of network formation have no means of incorporating this, it has been long appreciated that crosslinked polymers must grow in a heterogeneous fashion [1, 17]; similarly, nodular structures of some tens of nanometers in size, which must be the result of heterogeneous formation, have long been observed in crosslinked networks of a variety of chemistries [18, 19].

Cluster Formation and Internal Structure

Clusters formed during crosslinking in the sol phase have a highly ramified, dendritic structure. Initially, clusters grow by the incorporation of individual precursor molecules and small combined molecules, but as conversion progresses, the accretion of clusters becomes more and more frequent until, close to the gel point, growth is dominated by the aggregation of clusters. Before characterizing the structure of these pre-gel clusters, it is instructive to visualize characteristic clusters during various stages of growth.

Fig. 2 shows snapshots of the largest cluster for both models after crosslinking for 55τ (11,000 time steps) in a system containing 114,240 nodes. For the 3-functional system, the conversion at this point is 0.648 and the cluster contains 366 nodes with arms (pendants) containing 39, 137 and 189 nodes extending from the central node (the larger black sphere). There are 37 dangling bonds (blue), 18 dangling ends (red) and one primary loop (green) in this configuration. There are no other loops.

For the 6-functional system the conversion after 55τ has reached 0.36. The cluster contains 181 nodes and 35 junctions (black bullets). Of the junctions, 5 have a single bond to the cluster, 6 have two bonds, 10 have three, 5 have four, 7 have five and 2 have six. Arms (pendants) extending from the central node (the larger black sphere) contain 2 nodes (a dangling end), 5 nodes, 64 nodes and two with 109 nodes. The last of these forms a 2-pendant a pendant with two connections to the junction, so that there is a closed loop connecting the pendant to the junction. There are 32 dangling ends (red), five primary loops (green) and 96 unsaturated bond sites on junctions, as well as two larger loops in this configuration.

At this early stage of the crosslinking process, growth occurs primarily through the incorporation of individual precursors. The clusters are ramified, essentially tree-like structures reminiscent of percolation clusters.

Figure 2: Snapshot of the largest cluster after 55τ in systems containing 114,420 nodes, (a) 3-functional system (366 nodes). Dangling bonds are blue; dangling ends are red and the one primary loop is green, (b) 6-functional system (230 nodes and 42 junctions as black bullets).

For the 6-functional model, the primary difference is that the greater functionality introduces the possibility that junctions can have a higher coordination number than in the 3-functional model. In spite of this, the clusters look remarkably similar. The 6-functional cluster has fewer nodes but each node has more complex local topology because of the larger number of reactive sites on each crosslinker. Again, there are comparatively few elementary loops because during formation of the cluster there are generally a sufficient number of competing reactive sites on neighboring junctions.

A superimposed sequence of configurations showing the further growth of the clusters illustrated in Fig. 2 is presented in Fig. 3(a) and (b). Snapshots of the clusters after 55τ (as in Fig. 2), 72.5τ ,

77.5τ and 80τ are shown. Spatial coordinates of all nodes are those after 80τ (16,000 crosslinking time steps).

The rapid growth of the 3-functional cluster in the last crosslinking time interval is primarily due to the coalescence of two large clusters. The cluster shown here was the largest cluster after 55τ ; it was the 2nd largest after 72.5τ and 77.5τ . After 80τ it is again the largest, and its size is comparable to that of the simulation cell. Note that two large portions of the cluster are connected by only a single bond. Further information about the structure of the cluster as it grows is given in Tables 2 and 3.

Figure 3: Time sequence showing the further growth of the clusters illustrated in Fig. 2. (a) 3-functional system, (b) 6-functional system. Snapshots of clusters after 55τ , 72.5τ , 77.5τ and 80τ are shown. Positions of all nodes are those after 80τ . Bonds in the initial cluster (after 55τ) are colored blue. The additional bonds created in the cluster over the next 17.5τ are colored green. Bonds created in the interval between 72.5τ and 77.5τ are colored red. Bonds created in the last time interval are colored black. Note that a cluster added to the 3-functional network just prior to gelation is connected by only a single bond.

The 6-functional cluster shown here was the largest cluster after 55τ , it was the 3rd largest after 72.5τ . After 77.5τ and 80τ it is again the largest, and its size is comparable to that of the simulation cell. Note that again in this case, a significant portion of the cluster is attached to the rest of the cluster by only a single bond (towards the top right). Further information about the structure of these clusters is given in Tables 4 and 5. However, in both systems the progress toward gelation accelerates quickly as larger clusters coalesce.

Table 2: The number of nodes, junctions, dangling bonds and ends, primary loops and conversion of the clusters shown in Figs. 2(a) and 3(a) for the 3-functional model.

Time, τ	Nodes	Junctions	Dangling	Dangling	Primary	Conversion
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			Bonds	Ends	Loops	
55	366	55	37	18	1	0.648
72.5	1478	215	116	89	3	0.733
77.5	3732	543	282	213	15	0.752
80	12124	1770	923	657	51	0.762

Table 3: The number of saturated junctions and junctions with elementary loops larger than primary loops in the clusters shown in Figs. 2(a) and 3(a) for the 3-functional model. A saturated junction is one in which all bonds emanating from the junction have paths to all other nodes in the network. They would be the elastically active junctions in a network. Note that there are no saturated junctions in these configurations.

Time, τ	Nodes	Saturated Junctions	Junctions with elementary loops larger than primary loops
55	366	0	0
72.5	1478	0	10
77.5	3732	0	54
80	12124	0	220

As conversion progresses, long loops can be incorporated into the post-gel network when the unreacted sites along their length have an opportunity to react, so a loop can disappear or become shorter. On the other hand, minimal, primary loops will remain as a defect since they contain no unreacted functionality.

Table 4: The number of nodes, junctions, the bond deficit, dangling ends, primary loops and conversion of the clusters shown in Figs. 2(b) and 3(b) for the 6-functional model. The bond deficit is the number of functionalities in the cluster which have not formed bonds.

Time, τ	Nodes	Junctions	Bond Deficit	Dangling Ends	Primary Loops	Conversion
55	230	42	111	47	6	0.361
72.5	1174	216	533	195	50	0.465
77.5	4604	796	1773	805	225	0.491
80	7444	1282	2852	1322	350	0.504

Table 5: The number of saturated junctions and junctions with elementary loops larger than primary loops in the clusters shown in Figs. 2(b) and 3(b). S-3, S-4, S-5 and S-6 are the number of junctions with 3, 4, 5 and 6 saturated functionalities. A saturated functionality is one in for which there is a path to all other nodes in the network. These junctions would be elastically active junctions in a network.

Time, τ	Nodes	S-3	S-4	S-5	S-6	Junctions with elementary loops larger than primary loops
55	230	0	0	0	0	0
72.5	1174	0	0	0	0	60
77.5	4604	3	1	1	0	236
80	7444	8	2	1	0	359

It is important to note that even when these clusters are comparable in size to the simulation cell, just before the gel point, there are no saturated junctions in the configurations for the 3-functional model, although there are a significant number of primary and larger elementary loops. In contrast, clusters for the 6-functional model, because of its greater functionality, do have a small number of saturated junctions near the gel point. At this stage, the clusters are essentially dendritic supermolecules that are part of the “sol”. In practice, it would be very difficult to dissolve or extract these clusters in a solvent due to size, loops and steric hindrance, so that they might be measured as a “gel” particle. Simulations permit a more precise and detailed characterization of the material near the gel point than is possible in an experiment.

Cluster Size and Scaling

Discussions of the scaling behavior of clusters near the gel point have a long history. Stauffer [20] and de Gennes [21] suggested that percolation on a three-dimensional lattice is a good model for the growth and scaling behavior because the theories of Flory [22] and Stockmayer [4] are the same as percolation on a Cayley tree. However, it was subsequently argued that this analogy ignores the fact that standard percolation does not consider the kinetic processes that control cluster growth near the gel point so that kinetic gelation might not be in the same universality class as standard percolation [23]. Kinetic gelation models (reviewed in Ref. [24]) are generally lattice models for irreversible free-radical copolymerization in which the sol consists of small monomers and gelation is initiated by the radicals. It goes beyond the scope of the current paper to present a detailed comparison of the results of these earlier lattice models, but it should be noted that the polymerization process modeled here is different and that the precursors are free to diffuse in continuous space, which is an advantage of molecular dynamics simulations over lattice models.

In the following, the fractal dimension of individual clusters as well as the scaling behavior of the cluster size distribution, n_s , is used to characterize the growth process. Before gelation, the clusters are fractals, with a fractal dimension d_f . The fractal dimension describes how the number of nodes in a large cluster, s , depends on the cluster radius (defined here as the radius of gyration, R_g). For large clusters, it is expected to scale as

$$s \propto R_g^{d_f} \quad (4)$$

The radius of gyration is defined by

$$R_g^2 = \frac{1}{2s^2} \sum_{i,j} (r_i - r_j)^2 = \frac{1}{s} \sum_{i=1}^s (r_i - r_{mean})^2 \quad (5)$$

where r_i is the position vector of the i^{th} node in the cluster and r_{mean} is the mean position of the monomers in the cluster.

For large s , the cluster size distribution decays as a the power law

$$n_s \propto s^{-F} \quad (6)$$

The Fisher exponent, F , characterizes asymptotic scaling behavior of the cluster size distribution, n_s .

Results from the simulations can be seen in Fig. 4, where the radius of gyration, R_g , of the largest clusters at various times before gelation are plotted as a function of their number of nodes. The unit of length here is the LJ characteristic length, σ , and the number of beads in the largest cluster is used as the measure of its size, s .

Figure 4: The radius of gyration, R_g as a function of the cluster size, s , (a) 3-functional system, (b) 6-functional system. R_g was determined for the largest cluster for a range of crosslinking times until the cluster size reached the cell size. Results in red are data from ten independent realizations for the small system size (11424 nodes); results for the larger system size (114240 nodes) obtained from five independent realizations are shown in blue. The black lines show the results of fits of $\ln(s)$ as a function of $\ln(R_g)$ to determine the fractal dimension.

The largest cluster in a 114,240 node simulation shown in Fig. 3 contains 12,124 nodes (approximately 10% of the total system size) at a conversion of 0.76. This configuration was formed after 80τ . Clusters of this approximate size were the largest that could be used for determining the scaling behavior of the radius of gyration, since further crosslinking results in clusters that extend into the image cells and quickly percolate to form a network (gelation). Typically, maximum cluster sizes for the smaller simulations (11424 nodes) were ten times

smaller. Data for very small clusters were also omitted when making the fit for the scaling behavior. The remaining data were fit to the form

$$\ln(s) = d_f \ln(R_g) + a \quad (4)$$

which yielded $d_f = 2.46 \pm 0.06$ for the 3-functional system and 2.48 ± 0.03 for the 6-functional system.

The largest clusters are slightly larger in the 6-functional system than in the 3-functional system and contain more nodes, as one might expect from the greater number of reactive functionalities available. However, the fractal dimension of the clusters is identical to that for the 3-functional system, so the 6-functional pre-gel clusters are no more ramified than in the 3-functional system. Cluster-cluster aggregation provides a good description of the growth process for both the 3-functional and the higher functional network.

Our values for the fractal dimension of the clusters are consistent with those found elsewhere (~ 2.5) for similarly percolating clusters [25 - 27].

Figure 5: Cluster size distribution, n_s , as a function of the cluster size, s , (a) 3-functional, (b) 6-functional. In the smaller system size (11,424 nodes), n_s was evaluated using configurations from ten independent realizations shortly before the linear dimension of the largest cluster reached the size of the simulation cell. For the larger system (114,240 nodes), configurations from five independent realizations were used to determine n_s . In each case, data for the smaller system size are in red, and for the larger system size in blue. The data used in the logarithmic fit for n_s (black line) lie between the arrows in the figure.

Fig. 5 shows the cluster size distributions and the fit to the logarithm of

$$n_s = cs^{-F} \quad (5)$$

When making the fits, data for clusters containing fewer than 32 nodes as well as clusters in the tail of the distribution, where the statistics is poor, were omitted. The result for the Fisher exponent is 2.14 ± 0.05 for the 3-functional model and 2.05 ± 0.10 for the 6-functional model. These values are close to those found in thermoplastic polymer gels, 2.2 [28], and for percolation

on regular lattices, 2.19 [29, 30]. The values for the Fisher exponent and the fractal dimension are also consistent with the hyperscaling relation [30]:

$$F = \frac{d}{d_f} + 1$$

where d is the spatial dimension, 3.

Gelation Point

The gel point is typically defined as the point at which the growing molecular network percolates across the whole system [30]. This definition is used in the statistical models of Flory and others where, after some fraction of the possible crosslinking reactions, it is probable that a chain extends to infinity. This definition suffices for most macroscopic applications. However, simulations are necessarily performed using comparatively small system sizes, typically with periodic boundary conditions. The finite system size complicates the determination of the gelation point; while a detailed finite-scaling analysis can be used to accurately determine the gel point in the limit of infinite system size, it is convenient to have a simpler and faster way to estimate its location. Table 5 gives values of conversion at gelation based on several possible criteria. The first criterion is that the single largest cluster must span the simulation volume in all three Cartesian directions. The second is the point at which the second largest cluster attains its largest size; the justification for this criterion is that this should happen close to the point at which the clusters coalesce to form the gel [31, 32]. The third criterion is that the largest cluster percolates in one Cartesian direction, while the fourth is that a percolating network is found in all three spatial dimensions.

Table 5: Four criteria for conversion at the gel point. The first row contains values for the conversion obtained by averaging over results from ten replicas of simulations containing 11,424 nodes. The values in the second row are obtained by averaging data from five replicas of systems containing 114,240 nodes. Criterion 1: the largest cluster spans the simulation cell in all three dimensions; criterion 2: peak in the size of the second largest cluster; criterion 3: the network percolates in one spatial dimension; criterion 4: the network percolates in all three dimensions

(a) 3-functional system

System size	Criterion 1	Criterion 2	Criterion 3	Criterion 4
11424	0.747 ± 0.012	0.760 ± 0.016	0.778 ± 0.014	0.796 ± 0.012
114240	0.754 ± 0.07	0.762 ± 0.011	0.770 ± 0.007	0.788 ± 0.008

(b) 6-functional system

System size	Criterion 1	Criterion 2	Criterion 3	Criterion 4
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11,424	0.502 ± 0.027	0.507 ± 0.027	0.533 ± 0.021	0.557 ± 0.015
114,240	0.517 ± 0.010	0.517 ± 0.011	0.524 ± 0.007	0.535 ± 0.007

Results show that the averages for the smaller and larger simulations are within one standard deviation of each other. The Tables are arranged so that the values of conversion at which the system meets the various gelation criteria increase from left to right. They all provide roughly similar values; however, the first criterion is at the lowest conversion because it merely requires that linear dimensions of the largest cluster exceed those of the simulation cell, without requiring that the cluster is actually connected through the simulation boundaries. A similar argument is true for the second criterion; when the two largest clusters coalesce, there is no guarantee that the resulting cluster is a percolating network, so the second criterion also provides a lower bound for the gelation point. The third and fourth criteria require that the network percolates, so the search for connections passes the periodic boundaries and finds connections. The third and fourth criteria require percolation to be present, so they must be an upper bound for the point of gelation. It is not surprising that requiring the network to percolate in all three Cartesian directions yields a slightly higher value for the conversion at the gel point than does requiring that it percolates only in one dimension. While the fourth criterion is clearly a rigorous choice for very large systems [33], it appears to overestimate the conversion at the gel point in finite systems. This can be seen from the fact that the estimated conversion decreases with increasing system size; this is also the case for the estimate provided by criterion 3.

Scaling behavior can also be used to determine the gel point. At the percolation threshold, the number of nodes in the incipient infinite cluster, $M(L)$, where L is the linear dimension of the system, should scale as $M(L) \sim L^{d_f}$ for large L . Our previous analysis of the radius as a function of the cluster size yielded d_f in the range 2.46 to 2.48. In a plot of the cluster size data divided by L^{d_f} as a function of conversion, results for the different system sizes should cross at the percolation threshold. Using data from the two simulation sizes we studied, this was found to occur at percolation thresholds of 0.76 and 0.52 for the 3- and 6-functional models, respectively; the conversion at the crossing point exhibited only a weak dependence on the value of d_f . These values are consistent with those deduced using the other criteria. A more detailed analysis using this approach for a range of system sizes would provide insight into the importance of finite size effects and corrections to scaling on the resulting values for the conversion at gelation.

The criteria for the gel point show that it probably occurs at a conversion between 0.762 and 0.770 for the 3-functional system. In the following we will use 0.77 for the conversion at the gel point, which is the average rounded to two significant figures. The pattern of differences between the estimates is the same for the 6-functional system, so in a similar manner, we have chosen 0.52 as a best estimate for the conversion at the gel point for the 6-functional system.

Miller-Macosko [34] used recursion theory to generalize the Flory-Stockmayer estimate of the conversion at gelation, p_c , in an ideal crosslinking system with two reactive precursors of average functionalities, f and g :

$$rp_c^2 = \frac{1}{(f-1)(g-1)} \quad (6)$$

where r = stoichiometric ratio, which is equal to one in our simulations. The dimer has a functionality of two, so the prediction for the gel point conversion is 0.707 for the 3-functional system and 0.447 for the 6-functional system. This approach assumes ideal network formation on a Bethe lattice without allowing for loops or steric barriers. It is not surprising that the MD estimates for the conversion at the gel point are slightly higher, because an amorphous network may produce higher percolation thresholds than a regular lattice [35] and more crosslinks are required to produce a non-ideal network that percolates.

The ratio of the MD to the Miller-Macosko estimate for the gel point in the 6-functional model, 1.16, is higher than the corresponding ratio, 1.07, for the 3-functional network. A comparison of values for the elastically active network chain density, cycle rank etc. for these two models reported elsewhere also indicates that networks for the 6-functional model are further from ideality than those of the 3-functional model [9]. Departure from ideality at the gelation point persists at higher conversions. However, it is interesting to note that the absolute difference in the conversion at the gel point is approximately the same in both cases ($\sim 7\%$).

Network development

As already noted, clusters in the sol phase are tree-like structures with few loops. However, as crosslinking continues, cluster aggregation becomes more common and the frequency of loops and non-ideal features increases. Following the evolution of these features through the sol and into the gel phase provides insight into how the network forms and defects are created and persist.

Fig. 6 shows the conversion (red squares) and the fraction of nodes in the largest cluster (black squares) as a function of time (crosslinking time steps) for both functionalities.

Figure 6: Conversion (red squares) and the fraction of nodes in the largest cluster (black squares) as a function of time, τ (200 time steps), for (a) 3-functional model, and (b) the 6-functional model. Data for the smaller 11424 node system (open symbols) are averages over ten independent replicas; data for the larger 114240 node system (filled symbols) are averages over five independent replicas. Lines show estimates for the conversion at the gel point and the

corresponding time when this conversion is attained. Inserts show how the data evolve during the later stages of conversion.

Fig. 7 shows the fraction of functionalities on junctions in the largest cluster that are saturated. For the 3-functional model, a crosslinker is saturated if all three paths emanating from the junction connect to the entire cluster. In the gel phase, a saturated junction would be an elastically active junction unless it was located in a pendant. It can be seen that, at gelation, there are only a very small number of saturated junctions, which is consistent with results in Table 2 that there are no saturated junctions at 80τ (16,000 time steps), even for a conversion of 0.762 (just below the gel point for the 3-functional model). The number of saturated junctions then increases rapidly as conversion increases beyond the gel point and the elastically active network is generated.

For the 6-functional system, a junction does not have to have all of its functionalities saturated, i.e. with 6 paths to the network, to be part of the elastically active network. Figure 7(b) shows the trends for the 3-, 4-, 5- and 6-fold saturated junctions. In all cases, there are very few multi-connected nodes at the gel point, so the spanning cluster contains little crosslinked material and is therefore not a network; rather, it is a tenuous, ramified, primarily branched structure. Conversion beyond the gel point is required to further connect neighboring nodes and create a highly interconnected network. This is the case found in smaller Monte Carlo simulations of 4-functional networks [36].

Figure 7: (a) 3-functional model showing the number of nodes (as a fraction of the total number of nodes) in the largest cluster (red squares) and the fraction of junctions that are saturated (black squares). For a junction to be saturated, non-primary loops must be present so that there are paths that connect to other junctions in the network. (b) 6-functional model showing the reduced number of nodes in the largest cluster (red squares) and the reduced number of junctions with three (green circles), four (orange triangles), five (pink inverted triangles) and six (grey hexagons) saturated functionalities. Data for the smaller 11424 node system (open symbols) are averages over ten independent replicas; data for the larger 114240 node system (filled symbols) are averages over five independent replicas. The lines again indicate the gel point and show the corresponding estimate for the gel content at the gel point.

Fig. 7 (or Fig. 6) can be used to estimate the amount of the material in the gel at the gelation point. The curves are steep at the transition so it is difficult to be precise, but approximately 36 % of the nodes are in the gel in the 3-functional model when it first forms and approximately 24 % in the case of the 6-functional model. Due to the functionality of the junctions, the fractional conversion at the gel point will be greater than the fraction of nodes in the gel. It is also possible to estimate these quantities in a simple way. Gelation in the 3-functional system is at a conversion of 0.77 and the values in Table 1 show that, on average, every node (bead) has a functionality of 2.14 ($2^{1/7}$); 36% ($= 0.77 \div 2.14$) of the nodes should therefore be in the initial gel cluster, as found in the diagram. The gel point for the 6-functional system is 0.52, and each node (bead) averages 2.57 ($2^{4/7}$) bonds, so the gel cluster should contain 20% of the nodes ($= 0.52 \div 2.57$). The discrepancy in the higher functional model could be because there are some functionalities used in loops formed early that cannot contribute to the percolation.

Molecular dynamics allows us to count the nodes in the gel using the selected criterion of gelation. If we retained percolation descriptions in the thermodynamic limit, the reduced number of nodes in the largest cluster vanish and is non-analytic at the transition but, in practice, if solvent extraction of material was being used to gauge the gel point, the difficulty of dissolving the large pre-gel clusters broadens this transition into something measurable. Percolation theory, molecular dynamics and experiment all provide perspective. However, the very simple approach above demonstrates that one could approximately calculate the fraction of material in the initial gel, in such simulations at least.

Figure 7b shows that the gelled material develops 6-fold saturated junctions only slowly, as was shown in less detail [9] previously. For some time after gelation, inevitably there are more junctions with low connectivity than with high connectivity; but as the conversion proceeds towards completion, 6-fold connected junctions become most common. Smaller simulations of a 4-functional model also demonstrated this expected behavior [36].

Molecular dynamics simulations illustrate in detail how crosslinked networks develop heterogeneously, via the coalescence of highly ramified clusters. It is more obvious in the 6-functional model, but Fig. 7 shows that there is a considerable variation in the extent to which each junction becomes connected as conversion proceeds. This is likely to be true in any similar crosslinking chemistry, as has been proposed in other studies [7, 37]. In both systems examined here, clusters become large and thus immobile, so that there is considerable steric hindrance for the remaining unreacted functionalities to react, in the sol, even before the gel point. As conversion proceeds after the gel point, the dendritic branches on neighboring clusters will find it more difficult to completely intertwine and complete the overall conversion. The network polymer that forms between these clusters will be imperfect and not as densely crosslinked as the material closer to the center of a cluster, where it started. This is consistent with nanoscale density variations or nodules seen in cured polymer networks [18, 19, 38, 39]. This and other consequences of how curing occurs will be discussed in the following paper.

Summary

Statistical models of crosslinked polymer formation provide a description of the properties of a network based on the probability of what happens to individual precursor molecules or functionalities. They provide estimates for the conversion at the gel point as well as the connection between mechanical or swelling properties and the predicted value for the concentration of elastically active chains or cycle rank. However, these models provide only average values and do not describe the intrinsic variability in network structure and the defects created during crosslinking. On the other hand, molecular dynamics simulations track every elementary unit during the crosslinking process and therefore provide detailed information about the growth and aggregation of the ramified pre-gel clusters as well as the subsequent heterogeneous structures which evolve after gelation. Initially, cluster growth occurs primarily through the incorporation of individual precursor molecules, but as reactions continue the aggregation of clusters becomes increasingly important until it dominates at gelation. Further crosslinking after gelation strengthens the network by forming inter-cluster bonds.

We also examined four different methods for ascertaining when a spanning percolating cluster has formed in order to estimate the conversion at the gel point and found that they produced very similar results. The fractional conversion at gelation predicted by the Miller-Macosko theory was found to be a good estimate, but too low because the networks produced in the simulations are not ideal and do not form on a regular lattice. This must also be true for real crosslinking polymers. Reactions take place in an inhomogeneous fashion with increasing steric hindrance as the conversion progresses, even in the sol material. At gelation, simulations show that neither the 3-functional nor the 6-functional system has any significant amount of crosslinked material in the clusters. This bears out one of the underlying assumptions of the statistical models of crosslinked polymer formation. Crosslinking to form an elastically active network comes after the gel point. Just prior to gelation, molecular clusters are dendritic, non-crosslinked macromolecules, without the extensive loop structure characteristic of elastically active networks. However, although not crosslinked, these clusters will be very difficult to dissolve and could cause an experimental measurement of the gel point to find a lower value of conversion than it perhaps should. The fraction of nodes in the largest cluster just prior to, or at, gelation is 24% (6-functional) or 36% (3-functional) of the total nodes in the simulation which can be estimated approximately from the conversion at the gel point and the average functionality on any node. The fractional conversion at the gel point, which is an expression of the number of chemical reactions possible, is greater than the fraction of nodes in the gel at that point because each node has more than two functionalities on average, which must be true in a network-forming system. Immediately after the system has gelled, via a percolating cluster, the sol content is diminished by the amount of material in that cluster.

It might be expected that large system sizes are needed to provide a quantitative description of the cluster structure and behavior near gelation. However, we have found that simulations for systems containing 11,424 and 114,240 particles yielded essentially the same results for the cluster fractal dimension and Fisher exponent, and confirm that percolation on a three-dimensional lattice is a good model for the scaling behavior of the clusters prior to gelation. Nevertheless, it should be emphasized that the fractal dimension of the pre-gel 6-functional clusters is identical to that for the 3-functional system, so in spite of their potentially richer structure, the 6-functional pre-gel is no more ramified than in the 3-functional system. Both the fractal dimension of the large clusters and the Fisher exponent for the scaling of the cluster size,

prior to gelation, are consistent with percolation theory and results found for kinetic gelation models.

Large super-molecular aggregates form via cluster-cluster aggregation near the gel point, so steric hindrance is always present and must become more severe after gelation. Following the conversion process after gelation shows that there is considerable variation in the degree to which the 6-functional junctions are incorporated into the network and shows that there is considerable opportunity for heterogeneity to remain in the final material. Further, extensive regions of low crosslinking density must remain over those parts of a cluster surface that are particularly restricted in mobility. Defects that remain in the crosslinked material after gelation will be examined in more detail in the second paper in this series, together with a discussion of their possible effect on macroscopic properties and durability.

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