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Heterogeneity in polymer networks formed by a single copolymerization reaction: I. Gelation and pre-gel structure

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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.

1. 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

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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].

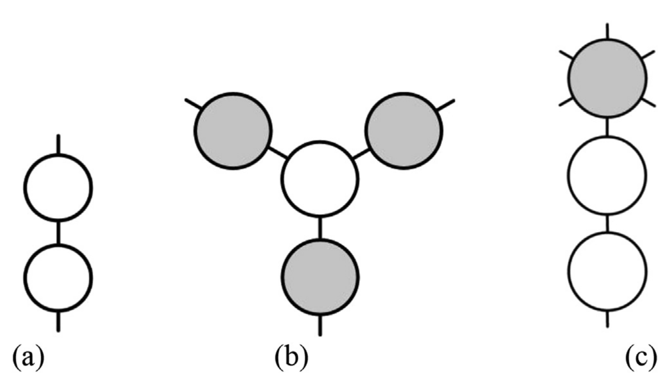

Fig. 1. Illustration of the precursors used in creating networks: (a) dimer, chain extender, (b) 3-functional crosslinker, (c) 6-functional precursor.

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:

$$\begin{aligned} U(r) &= U_{LJ}(r) - U_{LJ}(r_c) \quad && \mathit{for}\ r \le r_c \\ &= 0 && \mathit{for}\ r > r_c \end{aligned}, \tag{1}$$

where

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

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:

$$\begin{aligned} U_{FENE}(r) &= -0.5R_0^2 k \log_e\left[1 - \left(\frac{r}{R_0}\right)^2\right] \quad && r < R_0 \\ &= \infty && r \ge R_0 \end{aligned} \tag{3}$$

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 ε/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 τ $(= \sigma(m/\varepsilon)^{1/2})$ 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 30,000τ to achieve the same. For convenience, the units of temperature will be omitted in the following.