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Effects of precursor topology on polymer networks simulated with molecular dynamics

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ABSTRACT

Molecular modeling of crosslinked polymers often follows arbitrary pathways for network generation, with different precursor topology from experimental systems. We use coarse-grained molecular simulation to study the effects of precursor choice on the predicted network structure and properties. Three sets of precursors with different molecular architectures are designed such that they would form identical networks at the limit of perfect conversion. Little difference is observed between the resulting networks in typical properties including the radial distribution function, macroscopic statistics of network connectivity, and glass transition behaviors. However, the stress-strain relationship in tensile deformation clearly depends on the formation pathway when compared at the same crosslinking density. The elastic modulus of the network is found to correlate strongly with the number of elastic strands in the network, except at the highly-crosslinked limit where substantial discrepancy is observed between networks from different precursors. Although these final networks contain a similar average density of structural defects, the choice of precursor has significant impact on their spatial distribution, leading to the precursor dependence of their mechanical properties. Uniform defect distribution and fast defect elimination can be achieved by designing precursor units with a proper stoichiometric ratio of different monomers.

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1. Introduction

Network polymers are one of the most important classes of soft materials composed of multiple crosslinked polymer chains which assemble into a percolating three-dimensional structure [1–3]. Interconnection of molecular chains by chemical bonds confers many unique properties to these materials, such as improved elasticity and high resistance to heat and organic solvents [4–6]. Because of their superior performance, network polymers have grabbed much attention in both industrial practice and theoretical research. Typical applications include vulcanized rubber and thermosetting polymers (e.g., epoxy resins and phenolic resins) which have been widely used in the manufacturing of tires, parts, and consumer products; they are also a common ingredient for adhesives and coatings, and remain the focus of both experimental and theoretical research [5,7–10]. Recent attention in hydrogels, crosslinked hydrophilic polymers swollen by water, further extended their application to the biomedical area [11].

Topologically speaking, the same network can be assembled from different sets of precursors, typically either by reaction between multifunctional monomeric precursors or by connecting linear polymer chains with crosslinkers. Both pathways are regularly used in practice. For instance, crosslinked phenolic resins can be synthesized from scratch using phenols and formaldehydes mixed at a proper molar ratio or by curing novolac phenolic resins – uncrosslinked macromolecular precursors – with a crosslinking agent [12]. Effects of precursor topology, if present, on the structure and properties of the prepared polymer networks are not well understood.

Development of computer power and molecular simulation techniques over the past three decades have not only significantly advanced our understanding of polymer materials, but also brought us closer to reliable prediction of their properties [13–16]. Building molecular models representing realistic microscopic structures of polymers is however not a trivial task [17–20] and the difficulty only multiplies for crosslinked polymers. Ideally, it would be best to have a network formation method that resembles the realistic experimental crosslinking process. It is however prohibitively expensive to simulate the motion and diffusion of all molecules

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involved for the entire duration of the formation process using chemically realistic full-atom molecular models. Methods for the “virtual” synthesis of polymer networks found in the literature are thus all artificial in this sense. A typical procedure starts with a liquid structure of corresponding monomers, mixed with crosslinker molecules when applicable; new chemical bonds are added between eligible reacting atom pairs within a specified cutoff distance to form a network [21–23]. In this sing-step approach, optimization techniques are often needed to identify as many potential bonding pairs as possible [24,25]. The resulting structure normally needs to undergo extensive molecular dynamics runs, often with repeated heating and compression cycles, to relax the stress singularities. Alternatively, these steps can be repeated to form a multi-step crosslinking process, in which new bonds are added in batches and between the bond addition steps the structure is relaxed using molecular dynamics (MD) or Monte Carlo (MC) simulations [26,27]. To achieve high crosslinking density, where atom motion becomes topologically constrained, it is often necessary to use unrealistically long cutoff distance to push the conversion close to experimental values [22,27].

Currently there is no standard protocol for the generation of network models. Specific implementation of these methods varies from one research group to another. Meanwhile there is little knowledge of how the choice of formation pathway affects network properties. The only study in this regard is the recent work of Jang et al. [25], which compared a single-step and a multi-step method. Substantial difference was found in the fragment molecular weight between the resulting networks, while all other statistics inspected in the study appear similar.

Model validation is another concern. In most studies, networks in molecular simulation are formed to the same level of crosslinking density as the targeted experimental systems. These models can typically predict volumetric properties such as density and glass transition temperature satisfactorily. However, prediction reliability of many other properties, such as mechanical properties, is not fully examined. As a broader question, if two networks have the same crosslinking density and even the same radial distribution function, does it necessarily ensure their equivalence in all properties? If not, how to detect the discrepancy between a molecular model and its experimental counterpart and which of its predictions are reliable? These questions all remain unexplored.

A realistic reaction-diffusion process for network formation can be simulated at the coarse-grained (CG) level. The earliest CG simulations used a similar approach as the aforementioned full-atom studies, where monomeric precursors are frozen in the space and systematically connected [28,29]. Seminal work of Kremer, Grest, and coworkers [30–32] pioneered the dynamical approach for network synthesis, which is still widely used today [33–35]. Here, diffusion and mobility of polymer chains are fully simulated using MD and crosslinking reaction is assumed to take place when eligible atom pairs fall into a certain cutoff distance. It has been widely used to study the crosslinking kinetics of end-linked polymer networks, i.e., networks formed by connecting the chain ends of linear polymers with multifunctional crosslinkers [30–33,35–37]. Network formation from other precursor architectures has not been reported. CG molecular simulation also provides a powerful tool for understanding the behaviors of network polymers such as their elasticity [38,39], volume phase transitions [40], and interfacial adhesion behaviors [37,41]. The advantage of CG models in simulating crosslinking kinetics makes it naturally suited for studying the effects of network generation conditions. Using a bond-fluctuation model [42], Gilra et al. [43] observed clear dependence of crosslinking conversion on the cutoff distance. Recent development of systematic coarse-graining methods [44–46] makes it possible to map a network model generated at the CG level, using either MD [47] or MC [48], back to a full-atom representation. Following the same idea [49], used dissipative particle dynamics (DPD) [50] to model the reaction-diffusion process of the network formation and mapped the generated network structure to the full-atom level for property characterization.

The goal of our study focuses on the effects of formation pathway on the network structure and properties. Almost all full-atom models in the literature were synthesized from monomeric precursors (with the exception of Abbott et al. [23]), it is of interest to understand if crosslinked materials prepared by curing linear polymer precursors can be represented by such models. We design three sets of model precursors in such a way that at the limit of perfect conversion, they would result in identical networks. Our results indicate that precursor topology has non-trivial impact on the network properties. In particular, a precursor design based on the reaction stoichiometry is most efficient in eliminating network defects. Furthermore, differences between these networks are not captured by typical macroscopic structural characterization. These findings show that effects of formation pathway on the molecular model of a polymer network should not be overlooked and new validation protocols need to be developed to adequately vet models for property prediction.

2. Methodology

2.1. Molecular model and precursor systems

We use the classical bead-spring model of Kremer and Grest [51]: a group of successive repeating units are lumped into one bead (also referred to as one CG “monomer” or atom below), which are connected by finitely-extensible nonlinear elastic (FENE) “bonds” to form a polymer. Interaction between bonded monomers are given by

$$\begin{aligned} U_{\mathrm{FENE}}(r) &= -\frac{1}{2}kR_0^2\ln\left[1-\left(\frac{r}{R_0}\right)^2\right] \\ &+ 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right] \end{aligned} \tag{1}$$

where r is the inter-particle distance. The first term is attractive which models a spring force that diverges at the maximum bond length R_0 ($=1.5\sigma$ in our study); the second term is only included for $r<2^{1/6}$ which captures the repulsion between beads at short distance. The spring constant $k=30\varepsilon/\sigma^2$, which is small enough to allow the use of a relatively large time step while large enough to prevent bonds from cutting through each other [31]. The pairwise interaction between non-bonded beads are calculated with the standard Lennard-Jones (LJ) potential [52]

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

The potential is truncated at $r=2.5\sigma$ and shifted by a constant to ensure continuity at the cutoff. Results in this study will be reported in standard LJ reduced units: i.e., length is scaled by σ, energy by ε, mass by the bead mass m, time by

$$\tau\equiv\sigma\sqrt{m/\varepsilon}, \tag{3}$$

and temperature by ε/k_B, k_B being the Boltzmann constant.

All simulations are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [53]. The equation of motion is integrated by the velocity-Verlet algorithm [52] with a time step of $\Delta t=0.005\tau$. Periodic

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