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A reactive coarse-grained model for polydisperse polymers

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ABSTRACT

Most existing particle-based polymeric models are non-reactive, and usually constructed to be monodisperse. This deficiency limits the utilization of these models to understand the dependency of polymer properties on polydispersity. Here we report a coarse-grained model with pairwise interactions, yet is reactive and capable of *in silico* synthesis of polydisperse polymers in a step-wise manner. The polymerization of linear, branched, cross-linked and network polymers can be described by this reactive model. The chain length distribution of the resulting linear polymer agrees well with the Flory-Schulz distribution. The importance of polydispersity in polymer behaviors is highlighted in terms of kinetic (self-diffusivities of linear polymer melts) and mechanical properties (stress-strain responses of linear polymer glasses under uniaxial tension).

1. Introduction

Polymers have been widely utilized since the dawn of civilization, being inexpensive, versatile and bio-compatible. Consequently, there are considerable research efforts on polymers with a wide range of applications, such as polymer-based composite filled with carbon nanotube (CNT) for coating [1], nanocomposite polymers for self-healing [2], polymeric nanofibers for drug delivery [3] and new porous polymers for CO_2 capture [4]. Among different polymers, those from step-growth polymerization are particularly relevant to the research presented here, including nylons, polyesters, polyimides, and dendrimers [5–8]. However, due to the intrinsic complexity of polymeric systems, many fundamental questions regarding the structure-property relations remain unanswered, hindering the optimization of existing polymers and the rational design of new polymers. Particularly, how the polydispersity affects polymer properties has not been quantitatively understood [9–11]. This particular issue is challenging to investigate experimentally as it is difficult to synthesize polymers with an arbitrary chain length distribution.

Computer simulations [12–21], on the other hand, have become invaluable tools in polymer researches, with microscopic structural and time-dependent information of polymers. There are two classes of particle-based simulation models for polymers each focusing on different spatial and length scales: lattice model [20,22,23] and off-lattice model [24]. In lattice models, polymer chains are represented by random walk or self-avoiding walk on a crystal lattice such as simple cubic, face-centered cubic and diamond lattices [22,25–27]. Monte Carlo (MC) is usually the method of choice for lattice models [28,29], which has been used to study polymer melt dynamics [23,30], polymer blends [24,31], and glass transition [32].

In off-lattice models, molecular dynamics simulations (MD) have been instrumental in understanding both static and dynamic properties of polymers [15,24,28,33]. Off-lattice models for polymers include all-atom models, united atom models and coarse-grained models. Chemically realistic all-atom models [13,34] describe constituent atoms explicitly using sophisticated force fields such as DREIDING [35] and COMPASS [36]. United atom models [13,14,37] treat each monomer group as individual particles with species-dependent customized interactions [38]. Coarse-grained models [13,17] use a single particle to represent a number of successive monomer groups to further enhance the computational efficiency. The inter-particle interactions in coarse-grained models vary from system to system, including harmonic springs and the FENE potential [21,39,40]. One of the most popular coarse-grained models is the bead-spring model, pioneered by Kremer and Grest [18].

Probably one of the most significant limitations of the above models is the inability to model chemical reactions such as bond formation in polymerization reactions or bond rupture in depolymerization reactions. This deficiency limits the description of important processes such as healing and fracture. Furthermore, without reactive models for polymers, one cannot mimic

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experiments by synthesizing polymers from monomers. Instead, polymer models are usually constructed with a uniform chain length. For this reason, among others, there is a lack of computational efforts aimed at understanding how polydisersity affects polymer properties. The existing simulation studies have mainly dealt with this issue by simply mixing many monodisperse samples to approximate the desired polydispersity [9,15,41–43]. The achieved chain length distribution in many cases only consists of several different chain lengths, which falls short of giving a continuous distribution as it is in many real polymeric systems. Moreover, how polydispersity affects polymer properties have been mostly on equilibrium systems, such as the "living polymer" systems [44–49]. For instance, Milchev et al. [48,49] studied the relaxation, high density and ring formation effect on equilibrium polymers using dynamic MC simulations. However, how polydispersity affects polymer properties out of equilibrium such as the diffusion of quenched polymer melts (out of chemical equilibrium) or the mechanical properties of far-from-equilibrium polymeric glasses have not been well understood.

In this work, we present a reactive, coarse-grained model for polymers. One obvious motivation for using a coarse-grained procedure is to enhance the computational efficiency without compromising the system details needed for the properties of interests. In additional, the common way to dealing with bond create/break in molecular dynamics is to combine MC steps to remove/create bonds. This type of hybrid method is very different from reactive MD simulations. One obvious deficiency is the inability to continuously describe the transition state during reactions [48,49]. A sharp discontinuity is unavoidable at the point of the MC step of forming/breaking bond. Moreover, the specific criteria to remove/create bonds have to be specified a priori (usually set as a constant, yet should vary drastically with local temperature, pressure, and concentration). No such criterion for bond forming/breaking is necessary in reactive MD simulations. This coarse-grained model is a binary system interacting with attractive heterobonds and repulsive homobonds, to control the coordination number of each particle. The interatomic force field used here is a Lennard-Jones (LJ) potential, with the addition of a repulsive bump as the formation barrier of a heterobond. The polymeric reaction of single-particle monomers was found to be a step-wise reaction, with an activation barrier consistent with the repulsive bump set in the force field. It should be noted that this reactive polymeric model presented here is intended to describe dense polymer melts and polymeric glasses. Using MD simulations, mimetic polydisperse polymer models were obtained via *in silico* polymerization of monomers. Linear, branched, cross-linked and network polymers have been successfully synthesized using our coarse-grained model. Taking linear polymer samples as examples, we showed that the polydispersity affects the kinetic properties of polymers, in terms of the self-diffusivities in polymer melts, and affects the mechanical properties of polymeric glasses, in terms of stress-strain responses under uniaxial tension.

2. Simulation methodology

2.1. Coarse-grained polymeric model and interatomic force fields

The coarse-grained model for linear polymer is described below. Models for branched, cross-linked and network polymers can be straightforwardly extended from the linear polymer (details in Section 2.3). In our coarse-grained model for linear polymers, each particle corresponds to one generic monomer. As monomers in linear polymers are bi-functional, the particle in our model must bond to a maximum of two other particles. Fig. 1 shows the illustration of how to control the coordination number (CN) of the particles. To do this, we choose a binary system (A particles and B particles, identical particle attributes except the type) interacting with pair-wise interactions: heterobonds (A-B) are attractive and homobonds (A-A or B-B) are repulsive. Thus, a particle only bonds to the opposite type. Importantly, all particles bonding to the same particle have the same type and repel each other. As shown in Fig. 1, a B particle can have, at most, two A particles as neighbors due to the longer-ranged A-A repulsion. In other words, a third A particle cannot get close to B particle due to the repulsion from the existing two A particles. It is straightforward to see that one can control the coordination number of each particle by adjusting the length and strength of the homobond repulsion. As each particle can bond to two opposite-species particles, one can consider each particle bi-functional. It should be noted that, angular constraints could be used to control the coordination number, which is computationally more costly. As A particles and B particles behave exactly symmetrically, the obtained polymers should be considered homopolymers. The chain length referred in this manuscript counts the number of particles in the linear polymer chain, regardless of the species.

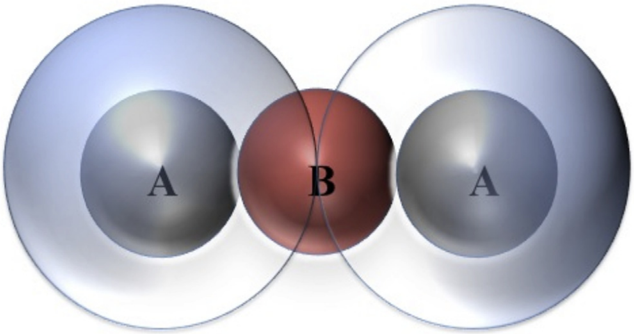

Fig. 1. Illustration of the two types of particles in this polymeric model. Adjacent monomers of different species (A and B) bond together. The effective equilibrium separation of A-A (or B-B, entirely symmetrical) monomers is roughly twice that of the A-B monomers. Consequently, there is no space to fit a third neighbor (or CN cannot exceed 2).

The particle-particle interaction is described by a modified Lennard-Jones (mLJ) potential, which was originally used to model metallic glass systems [50]. The mLJ potential differs from the conventional smoothed LJ form $\varphi_{LJ}^{smooth}(r)$ by the inclusion of a repulsive bump term $b(r)$ outside of the potential well. The pair-wise interaction of $\varphi_{mLJ}(r)$ can be written as,

$$\varphi_{mLJ}(r)=\begin{cases}\varphi_{LJ}^{smooth}(r) & r<r_{\alpha\beta}^{s}\\ \varphi_{LJ}^{smooth}(r)+b(r), & r\geq r_{\alpha\beta}^{s}\\ 0, & r\geq r_{\alpha\beta}^{c}\end{cases} \tag{1}$$

Here $r_{\alpha\beta}^{c}$ is the species dependent cutoff (α, β denotes species of A or B). The bump term $b(r)$ is only applied between the range of $r_{\alpha\beta}^{s}$ and $r_{\alpha\beta}^{c}$. Ensuring the potential energy and its first derivative is continuous at $r_{\alpha\beta}^{c}$, the smoothed LJ function $\varphi_{LJ}^{smooth}(r)$ can be written as,

$$\begin{aligned}&\varphi_{LJ}^{smooth}(r)=\varphi_{LJ}(r)-\varphi_{LJ}\left(r_{\alpha\beta}^{c}\right)-\left(r-r_{\alpha\beta}^{c}\right)\varphi_{LJ}'\left(r_{\alpha\beta}^{c}\right)\\&\varphi_{LJ}(r)=4\varepsilon_{\alpha\beta}\left(\frac{\sigma_{\alpha\beta}^{12}}{r^{12}}-\frac{\sigma_{\alpha\beta}^{6}}{r^{6}}\right)\end{aligned} \tag{2}$$

$\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ provide the energy and length scales for the pair interaction, respectively. The bump term $b(r)$ can be written as,