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).

Key words: molecular dynamics, reactive force field, polydispersity.

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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 CO₂ 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 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 polydispersity 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. Figure 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 Figure 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.

Figure 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 $\phi_{LJ}^{smooth}(r)$ by the inclusion of a repulsive bump term $b(r)$ outside of the potential well. The pair-wise interaction of $f_{mLJ}(r)$ can be written as,

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

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 $\phi_{LJ}^{smooth}(r)$ can be written as,

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

$\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ provide the energy and length scales for the pair interaction, respectively.

The bump term $b(r)$ can be written as,

$$b(r) = e_{ab}^b e_{AB} \cdot \sin^2 \left(\rho \frac{r_{ab}^c - r}{r_{ab}^c - r_{ab}^s} \right) \quad (3)$$

e_{ab}^b is the height of the repulsive bump. Note that the bump term itself and its first derivative are zero at both r_{ab}^s and r_{ab}^c . Therefore, the overall mLJ potential is still

smooth (the potential and the first derivative) after the inclusion of $b(r)$ between $r_{\alpha\beta}^s$ and $r_{\alpha\beta}^c$.

Table 1. Species-dependent parameters for the m LJ force field for various pairs of particles.

	$\varepsilon_{\alpha\beta} / \varepsilon_{AB}$	$\sigma_{\alpha\beta} / \sigma_{AB}$	$\varepsilon_{\alpha\beta}^b / \varepsilon_{AB}$	$r_{\alpha\beta}^s / \sigma_{AB}$	$r_{\alpha\beta}^c / \sigma_{AB}$
A-A	0.1	2.1	0	0	2.9
B-B	0.1	2.1	0	0	2.9
A-B	1.0	1.0	0.45	1.2	1.8

The energy and length units are chosen as ε_{AB} and σ_{AB} for convenience. All particles have the same mass of m_0 . Thus, the temperature unit is ε_{AB}/k_B (k_B is the Boltzmann constant), and the time unit is $t_0 = \sigma_{AB} \sqrt{m_0 / \varepsilon_{AB}}$. Table 1 lists the parameters of the m LJ potential. Only the heterobonds (i.e., A-B interactions) are imposed with the bump term. The homobonds (A-A and B-B interactions) are generally repulsive due to the larger ε_{AA} and σ_{BB} values. Importantly, the homobonds feature relatively low ε_{AA} and ε_{BB} to describe the weak inter-chain van der Waals interactions. Due to the presence of the smoothing function, the actual energy depths ratio of heterobonds ($0.0637 \varepsilon_{AB}$) to homobonds ($0.0127 \varepsilon_{AB}$) is about 50. Figure 2 shows the potential energy curve for both the homobonds and heterobonds. The temperature and pressure (when applicable) are controlled by Nose-Hoover [51,52] thermostat and barostat, respectively. The equations

of motion are numerically integrated using the velocity-Verlet [53] algorithm with a time step of $0.005 t_0$.

Figure 2. The potential energy per particle for the species-dependent pair-wise interactions. Heterobonds (A-B, solid black line) are attractive m LJ potential with an actual bump height of around $0.38 \epsilon_{AB}$. Homobonds (A-A or B-B, dashed red line) are Lennard-Jones smooth potential, which is mostly repulsive, yet with a weak inter-chain VdW attraction.

2.2. Sample preparation procedures for linear polymers

All simulations in this study were carried out using the MD software LAMMPS [54] with our customized force fields mentioned above. The polydisperse linear polymers were generated by simulating the polymerization process of monomers. Periodic boundary conditions (PBC) were applied to all the simulation boxes. The initial system for polymerization reaction consists of isolated monomer liquids (half A and half B particles) in equilibrium at high temperature of $T_{high}=0.5 \epsilon_{AB}/k_B$ with a monomer number density of $0.18 \sigma_{AB}^{-3}$. This temperature was chosen to be high enough that the

polymerization reaction will not commence, yet low enough to avoid unnecessary quenching. In the equilibrium liquid at T_{high} , 55.1% of all particles are monomers, while 29.4% are dimers and 10.3% are trimers.

Figure 3. Extent of reaction (top) from T_{high} to T_{low} during the quenching procedure of preparing $Sample_{FromCooling}^{Glass-2}$. Snapshots of system during quenching were shown (a smaller system with the same quenching procedure was shown for clarity). Black lines are heterobonds formed during the polymerization reaction.

The system was initially quenched isochorically to $T_{intermediate}=0.15 \epsilon_{AB}/k_B$ with a duration of $t_{Polymerization}=150, 750$ and $3750 t_0$, respectively. As shown in Figure 3, the majority of the polymerization occurs during this phase of quenching. The degrees of conversion of the reaction (the number of heterobonds normalized by the maximum number of possible heterobonds) for those three melts are 0.885, 0.900, and 0.911, respectively. Yet, the number average chain lengths are relatively short: 8.7, 10.0 and 11.2, respectively. The resulting polymer melt (termed $Sample_{FromCooling}^{Melt}$) with the

intermediate $t_{\text{Polymerization}}$ at $T_{\text{intermediate}}$ will be used to study how the reaction affects the diffusion properties in Section 3.3. We further quenched the polymer melts from $T_{\text{intermediate}}$ to $T_{\text{low}} = 0.001 \epsilon_{AB}/k_B$ within a duration of $\frac{1}{3}t_{\text{Polymerization}}$ to make polymeric glasses. These polymeric glasses were subjected to an isothermal isobaric relaxation at T_{low} to eliminate the residual stresses (samples now are termed $\text{Sample}_{\text{FromCooling}}^{\text{Glass-1,2,3}}$). $\text{Sample}_{\text{FromCooling}}^{\text{Glass-2}}$ was used for the structural characterization in Section 3.2, and the mechanical tests in Section 3.4. These glasses were then reheated to $T_{\text{intermediate}}$ in $500 \tau_0$ to obtain another set of polymer melts (termed $\text{Sample}_{\text{Reheat}}^{\text{Melt-1,2,3}}$), which contain considerably longer chains (number-averaged chain lengths are, 10.4, 17.4 and 28.8, respectively) than $\text{Sample}_{\text{FromCooling}}^{\text{Melt}}$. Thus, the vitrification-reheating procedure is to obtain sufficiently long chains to study how polydispersity affects diffusion, as in Section 3.3. As the long chains formed during the vitrification process may break up, parameter $\epsilon_{\alpha\beta}^b$ was increased to six times the original value listed in Table 1 during the reheating process, as well as in the subsequent simulations for diffusion.

In addition, monodisperse linear polymer models (Table 2), with chain lengths from 11 to 235, were constructed for comparison purposes. The ends of all chains, regardless of lengths, were chosen to be type A, in order to avoid the combination reaction of two chains. Moreover, to prevent chain breaking (similar to the reheating to obtain $\text{Sample}_{\text{Reheat}}^{\text{Melt-1,2,3}}$), $\epsilon_{\alpha\beta}^b$ was increased to six times the original value. Thus, the initial monodisperse chain length distribution can be preserved during MD simulations. Monodisperse linear polymer melts were first generated and equilibrated at $T_{\text{intermediate}}$,

while monodisperse linear polymeric glasses were obtained using the same procedure as

$$Sample_{FromCooling}^{Glass-2} \cdot$$

Table 2. Properties of polydisperse and monodisperse polymer melt samples for diffusion studies. All samples were equilibrated at $T_{intermediate}$. $\bar{L}_n$ and $\bar{L}_w$ are the number-averaged and weight average chain lengths by counting particles, respectively. $\bar{D}$ is the dispersity. n is the number density. D is the self-diffusivity.

Sample	Extent of Reaction	Number of Particles	Chain Length		$\bar{D}$ $(\bar{L}_w/\bar{L}_n)$	$n (\sigma_{AB}^{-3})$	$D (10^{-2} \sigma_{AB}^2 t_0^{-1})$
			$\bar{L}_n$	$\bar{L}_w$			
$Sample_{FromCooling}^{Melt}$	0.900	27436	10.0	18.7	1.870	0.180	0.728 ($\epsilon_{\alpha\beta}^b / \epsilon_{AB} = 0.45$)
$Sample_{Reheat}^{Melt-1}$	0.904	27436	10.4	20.1	1.932	0.118	1.75
$Sample_{Reheat}^{Melt-2}$	0.942	27436	17.4	33.7	1.938	0.121	0.97
$Sample_{Reheat}^{Melt-3}$	0.965	27436	28.8	55.6	1.931	0.123	0.55
$Sample_{Monodisperse}^{Melt-11}$		28160	11			0.116	2.69
$Sample_{Monodisperse}^{Melt-17}$		26112	17			0.119	1.73
$Sample_{Monodisperse}^{Melt-21}$		28350	21			0.120	1.25
$Sample_{Monodisperse}^{Melt-29}$		26100	29			0.122	0.770
$Sample_{Monodisperse}^{Melt-33}$		25344	33			0.123	0.700
$Sample_{Monodisperse}^{Melt-55}$		28160	55			0.124	0.310
$Sample_{Monodisperse}^{Melt-87}$		28188	87			0.124	0.159
$Sample_{Monodisperse}^{Melt-111}$		28416	111			0.125	0.0845
$Sample_{Monodisperse}^{Melt-145}$		28420	145			0.125	0.0592
$Sample_{Monodisperse}^{Melt-195}$		28080	195			0.125	0.0272
$Sample_{Monodisperse}^{Melt-235}$		28435	235			0.125	0.0215

Except the polymeric glasses with an aspect ratio of 3:1 (sample dimensions are detailed in Table 3) along the Z-direction, all other samples are cubic in shape (with a dimension close to $60 \sigma_{AB}$).

Table 3. Properties of polydisperse and monodisperse polymeric glasses for mechanical tests, respectively.

Sample	Extent of Reaction	Dimensions (σ_{AB}^3)	Number of Particles	Chain Length		n (σ_{AB}^{-3})
				$\bar{L}_n$	$\bar{L}_w$	
<i>Sample</i> ^{Glass-2} _{FromCooling}	0.942	$42.6 \times 42.6 \times 127.8$	32928	17.4	33.7	0.142
<i>Sample</i> ^{Glass-7} _{Monodisperse}		$40.8 \times 40.8 \times 122.4$	28812	7		0.141
<i>Sample</i> ^{Glass-17} _{Monodisperse}		$40.9 \times 40.9 \times 122.6$	29376	17		0.144
<i>Sample</i> ^{Glass-55} _{Monodisperse}		$41.8 \times 41.8 \times 125.4$	31680	55		0.145
<i>Sample</i> ^{Glass-115} _{Monodisperse}		$42.4 \times 42.4 \times 127.2$	33235	115		0.145
<i>Sample</i> ^{Glass-235} _{Monodisperse}		$42.7 \times 42.7 \times 128.1$	33840	235		0.145
<i>Sample</i> ^{Glass-335} _{Monodisperse}		$42.5 \times 42.5 \times 127.5$	33500	335		0.145
<i>Sample</i> ^{Glass-445} _{Monodisperse}		$43.6 \times 43.6 \times 130.8$	36045	445		0.145
<i>Sample</i> ^{Glass-555} _{Monodisperse}		$43.4 \times 43.4 \times 130.2$	35520	555		0.145

2.3. Coarse-grained models for branched, cross-linked and network polymers

The coarse-grained model described above, intended for linear polymers, can be easily modified to describe branched, cross-linked or network polymers. To model branched polymers, the repulsion range for the homobonds are slightly reduced to allow some three-coordinated particles. Thus, $\sigma_{\alpha\beta}/\sigma_{AB}$ is set to be 2.0 while keeping all other parameters identical to the linear polymer system (Section 2.1). To model cross-linked polymers, two additional species of particles (C and D) are introduced. The interactions between C-C, D-D and C-D are identical to A-A, B-B and A-B, respectively. Therefore, linear polymer chains with alternating C and D form spontaneously during the polymerization process. In addition, both C and D particles attract A particles, but repel B particles, thus the polymer chains made of C and D particles will serve as the linker chains between polymer chains made of A and B particles. For A-C and A-D interactions, $\sigma_{\alpha\beta}/\sigma_{AB}$ is set to be 1.0, and $\varepsilon_{\alpha\beta}/\varepsilon_{AB}$ is set to be 2.0 to facilitate linking; for B-C and B-D interactions, $\sigma_{\alpha\beta}/\sigma_{AB}$ is set to be 1.45, cutoff is set to be 1.63, and $\varepsilon_{\alpha\beta}/\varepsilon_{AB}$ is set to be 1.0. To model network polymers, similar to the branched polymers, the homobonds repulsion is reduced to allow high coordination number. For network polymers, $\sigma_{\alpha\beta}/\sigma_{AB}$ is further reduced to 1.87. Figure 4 shows the morphology of the different polymer types with the above specified force parameters, demonstrating the flexibility of the coarse-grained polymeric model.

Figure 4. Configurations of both linear, branched, crosslinked and network amorphous polymer chains after polymerization. Most chains were hidden for the first three cases for clarity. Note that all of them are dense polymer systems, the monomer size is shown small in order clearly demonstrate the bonds and structure of different polymers.

3. RESULTS AND DISCUSSIONS

3.1. Kinetics of polymerization reactions

The polymerization reaction is essentially the formation of heterobonds between A and B particles: the kinetic energy of the collision between A particles and B particles overcomes the repulsive energy barrier of A-B pair interaction. To understand the kinetics of the polymeric reaction, an initial system of isolated monomers with different number densities were simulated at the same temperature of $0.15 \epsilon_{AB}/k_B$. We chose the total number of functional groups (F) to characterize the polymeric reaction, consistent with Ref. [55]. As all monomer particles are bi-functional (Section 2.1), thus,

$$F = 2N_{particles} - 2N_{A-B} \quad (4)$$

N_{A-B} is the number of heterobonds (A-B bonds). Throughout this work, the heterobonds were counted once the separation of an A-B pair is within $1.45\sigma_{AB}$ (roughly the upper-limit of the nearest neighbor separation). $N_{particles}$ is the total number of particles in the system. The conversion fraction of the reactants (p) can be written as [56],

$$p = \frac{N_{A-B}}{N_{particles}} \quad (5)$$

$[F]$, the functional group concentration, is monitored as a function of time, shown in Figure 5(a). The polymerization rates can be easily calculated from the slopes, which were then plotted in Figure 5(b) as a function of the functional group concentration in a log-log plot. The slope in Figure 5(b) was found to be $10/3 \pm 0.12$ using a linear fitting, thus,

$$\frac{d[F]}{dt} = -k[F]^{10/3} \quad (6)$$

Here k is the reaction rate constant. It should be noted that as the conversion of the reaction is low, the total number of functional groups is almost a constant during the polymeric reactions described in Figure 5. The high order of reaction is due to the fact that the reactant system is a liquid (the average spacing is close to the particle size), much denser than a reactive gas in which a binary-collision-picture (thus second-order reaction) is expected.

Figure 5. (a) Change of the functional group concentration ($\Delta[F]=[F]_0-[F]$) as a function of time for systems with different initial concentrations ($[F]_0$) at $T_{intermediate}$. As the extent of reaction is negligible, the reaction rate $[\dot{F}]$ can be extracted. (b) The corresponding log-log plot of reaction rate versus the initial functional group concentration. The order of reaction is around 10/3.

We also investigated the temperature effect on the polymeric reaction rate. Figure 6(a) shows the number of A-B bonds formed as a function of time at different temperatures. Figure 6(b) shows the reaction rate according to Eq. (6) at different temperatures in an Arrhenius plot. It should be noted that $[\dot{F}]$ is plotted in place of the

reaction rate constant k , since the functional group concentration is a constant at $0.09 \sigma_{AB}^{-3}$. The slope of the linear fitting in Figure 6(b) indicates an activation energy of $0.39 \pm 0.02 e_{AB}$, which is consistent with the actual “bump” height of $0.38 \varepsilon_{AB}$ set in the A-B pair interaction (Figure 2).

Figure 6. (a) Change of the functional group concentration ($\Delta[F]=[F]_0-[F]$) as a function of time for systems with an initial $[F]_0 = 0.09 \sigma_{AB}^{-3}$ at different temperatures. (b) The corresponding log-log plot of reaction constant k (according to Eq. 6) versus temperature, the slope indicates an activation energy of approximately $0.39 \pm 0.02 e_{AB}$, which agrees very well with the actual barrier for $\varepsilon_{\alpha\beta}^b / \varepsilon_{AB} = 0.45$ (Table 1).

3.2. Structural characterization of polydisperse linear polymers

The polydisperse linear polymeric glass $Sample_{FromCooling}^{Glass-2}$, which was equilibrated at T_{low} , was subject to the following structural characterizations: two-body correlation function, three-body correlation function (angular distribution), and chain length distribution analysis. The radial distribution function (RDF) of $Sample_{FromCooling}^{Glass-2}$ is shown in Figure 7(a). The first peak corresponds to heterobond separation (i.e., A-B bonds) at about $1.14 \sigma_{AB}$, while the second peak corresponds to the homobond separation (i.e., A-A or B-B bonds). The radial integration of the first peak gives an average coordination number of 1.93 in this sample, consistent with the intended structure for a linear polymer. The RDF curve gradually decays to unity at large distances, as expected for a glassy system.

Figure 7. Structural characterization of *Sample^{Glass-2}_{FromCooling}* in terms of two-body RDF curve (a), and three-body ADF curve (b).

Next, the angles of all bonded triplets (A-B-A or B-A-B) were calculated, with the angular distribution function (ADF) shown in Figure 7(b). The peak is located around 153 degrees with an apparent asymmetric distribution, similar to other simulation work [57–59]. From this angular distribution, together with the bond length obtained from Figure 7(a), one can calculate the persistence length to be about $9.6 \sigma_{AB}$, according to Ref. [60],

$$l_p = \frac{b}{\ln|\langle \cos \gamma \rangle|} \quad (7)$$

Here l_p is the persistence length, b is the bond length, and γ is the angle between two bonds. Also according to Ref. [39], Flory’s characteristic ratio C_∞ can be estimated to be about 17.2 using the following equation,

$$C_\infty = \frac{1 + |\langle \cos \gamma \rangle|}{1 - |\langle \cos \gamma \rangle|} \quad (8)$$

The third structural characterization of the linear polymer is the chain length distribution. In Figure 8, we show the molar and weight fraction of chain length distribution after polymerization for this system. There are more short chains than long chains in terms of the number fraction. Yet, the intermediate chains have the highest weight fraction. In addition, it is worthy to note that some long chains form closed loops as expected, their effect, however, could be neglected since they only account for about 0.1% of the total chain population. The polymeric reaction, characterized in Section 3.1,

occurs for any pair of A particle and B particle are zero- or single-coordinated (CN=0 or 1). In other words, two chains can join if the end particles have only single neighbors. Therefore, the polymerization process can be characterized as a step-growth polymerization. Therefore, the Flory-Schulz [56] chain-length distribution is applicable to describe our coarse-grained polymer,

$$y_i = (1-p)p^{i-1} \quad (9)$$

$$w_i = i(1-p)^2 p^{i-1} \quad (10)$$

Here y_i and w_i are the molar and weight fraction for chains with a length of i , respectively, and p is the conversion fraction of reaction sites (Eq. 5).

Figure 8. Mole fraction (a) and weight fraction (b) of chain length distributions for *Sample_{FromCooling}^{Glass-2}*. (c) A representative linear polymeric sample with polydisperse chains, colored with different colors.

As shown in Figure 8, the molar- and weight-based chain length distribution can be very well described by the Eq. (9) and (10), without any fitting parameters. The

dispersity of these linear polymers is close to 2 (Table 2), in agreement with $1+p$ from Eq. (9, 10) as the polymerization reaction is nearly complete. Polymers with chain length distributions from different growth mechanisms other than step-growth can in principle be obtained by customizing the polymerization reaction pathways via adjusting the reactive force fields.

3.3. The effects of reaction and polydispersity on self-diffusion of polymer melts

In this section, we focused on how chemical reaction and chain length distribution affect the transport properties of polymer melts. The self-diffusivity (D), as one representative transport property, was measured under equilibrium via the Einstein equation from the time-dependent mean-square displacements (MSD) analysis. In a number of earlier simulation works, the MSD data was calculated based on the chain mass center [18,61,62]. In this study, since tracking the center of mass of a chain is apparently impossible for polymer melts with reaction (i.e., chains are breaking apart and joining at equilibrium), the MSD was calculated based on every particle in the polymer melts. Figure 9 compares the MSD curves of a non-reactive (by increasing the bump height by six times, thus minimizing the effect of chemical reactions) monodisperse polymer melt sample (*Sample^{Glass-55}_{FromCooling}*) based on the center of mass, chain center (the center most three particles), chain ends (two end particles) and all particles. It can be seen that the MSD curves converge in the diffusive limit, validating our choice of calculating MSD based on all particles in the polymer melts. The MSD based on individual particles $g(t)$ is defined as,

$$g(t) = \frac{1}{N} \left\langle \left| r_i(t+t_0) - r_i(t_0) \right|^2 \right\rangle \quad (11)$$

Where $r_i(t)$ is the position of particle i at time t and the average is taken over all the particles. According to the Einstein equation, D can be evaluated according to,

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} g(t) \quad (12)$$

Figure 9. Log-log plot of the MSD based on the chain centers (black), chain center of mass (green), chain ends (red), and all particles (blue), respectively, for a monodisperse polymer melt system with chain length 55 ($Sample_{Monodisperse}^{Melt-55}$) at $T_{intermediate}$. All curves collapse in the long time limit, validating the choice of all-particle-based MSD analysis. The broken line has a slope of one as a guide to the eye.

Since chemical reactions can potentially affect chain length distribution, particularly for monodisperse polymer melts, our strategy here is to isolate the effects of reaction and the effect of polydispersity on diffusion. We first investigated how reaction affects diffusion in polymer melts with identical chain length distribution. To accomplish this, we focused on $Sample_{FromCooling}^{Melt}$ and then systematically varied the bump height $\varepsilon_{\alpha\beta}^b$ of the force field. A higher bump height reduces the chemical reaction (both combination

and dissociation reactions). As the extent of reaction only varies with the bond strength and temperature, the chain length distribution of the polymer melt stays the same. In this way, the effect of chemical reaction on self-diffusivity of the polymer melts can be obtained. Figure 10(a) shows the log-log plot of MSD as a function of time for polymer melts with various bump heights (thus various reaction rates). Figure 10(b) shows that the self-diffusivity decreases as the bump height increases (or as the reaction rate decreases), approaching a constant diffusivity in the limit of zero reaction rate. In other words, diffusivity is sensitive to the reaction rate, in addition to the chain length distribution of the polymer melts (almost identical). This result qualitatively echoes the theoretical work [63] by Cates for “living” polymers. Instead of relaxing solely by reptation motion for non-reactive polymers, reaction for “living” polymers allows chains to cut through each other and relax on a much shorter time scale. Further detailed theoretical treatment on how the reaction rate affects diffusion of “living” polymers will be conducted in a follow-up paper.

Figure 10 (a) Log-log plot of the MSD as a function of time for a polydisperse polymer melts system ($Sample_{FromCooling}^{Melt}$) with different reaction rates. $\epsilon_{\alpha\beta}^b / \epsilon_{AB}$ in the legend indicates the actual bump height (Table 4). The broken line has a slope of one as a guide to the eye. (b) Self-diffusion coefficient D decreases as the actual bump heights increases (reaction reduces) to a value corresponding to the diffusivity in the zero-reaction limit.

Table 4. Self-diffusion coefficient D for $Sample_{FromCooling}^{Melt}$ with different bump heights. The number average chain length is around 10.0, and weight average chain length is around 18.7. The particle density is $0.18 \sigma_{AB}^{-3}$.

$\varepsilon_{\alpha\beta}^b / \varepsilon_{AB}$	0.3	0.45	0.6	0.9	1.35	1.8	2.85
Actual barrier (ε_{AB})	0.22	0.38	0.51	0.81	1.26	1.71	2.75
D ($10^{-2} \sigma_{AB}^2 t_0^{-1}$)	1.198	0.728	0.496	0.270	0.155	0.116	0.097

Next, we aimed to investigate how polydispersity affects self-diffusivity by a comparison study of monodisperse and polydisperse polymer melts, without the complication from chemical reaction. This is because the chemical reaction not only affects diffusion directly, but also affects the chain length distribution. To accomplish this goal, we increased the bump height to six times the original value. For comparison purposes, both monodisperse and polydisperse polymer melts are subjected to the same magnified bump height. It should be noted that, in order to explore polydisperse polymer melts with longer chains (or higher degree of polymerization), the polydisperse polymer melts were obtained by re-heating the polymeric glass to $T_{intermediate}$. The chain length distribution was maintained by increasing bump height without any depolymerization (more details in Section 2.2). In order to be comparable to existing literature on diffusion of non-reactive polymer melt, these samples (Table 2) were equilibrated at $T_{intermediate}$ with a pressure of $0.03 \varepsilon_{AB} / \sigma_{AB}^3$. This pressure was chosen such that the volume fraction of the polymer melt is roughly 40%, similar to Ref. [18]. The number densities for all non-reactive polymer melts are listed in Table 2, at which the MSD data is acquired. Figure 11(a) shows the log-log plot of the MSD as a function of time for both

monodisperse and polydisperse polymer melts. It is clear that all polymer melts reach the diffusive regime. Diffusion coefficients can be straightforwardly calculated from the MSD data (Table 2 and Table 4).

Figure 11 (a) Log-log plot of MSD as a function of time for various monodisperse and polydisperse polymer melts at $T_{intermediate}$. (b) Log-log plot of self-diffusivity D versus chain length. It should be noted that both number average and weight average chain length were used to characterize the polydisperse polymer melts.

The self-diffusivity as a function of chain length up to 55 is shown in Figure 11(b) for both monodisperse and polydisperse polymer melts. Regardless of the chain length distribution, the diffusivity decreases as the chain length increases. Specifically, the

diffusivity for monodisperse polymer melts exhibits a power-law dependency with respect to the chain length,

$$D = D_0 N^\alpha \quad (13)$$

From linear fitting in Figure 11(b), D_0 and α were found to be $0.75 \pm 0.14 \sigma_{AB}^2 t_0^{-1}$ and -1.35 ± 0.05 , respectively. This exponent α differs from -1.0 as predicted by the Rose model [64], yet is consistent with other simulation results [37,65]. For the polydisperse polymer melts, the diffusivity is plotted against both the number-averaged and weight-averaged chain length in Figure 11(b). It is clear that neither the number-averaged, nor the weight-averaged chain length can be used in place of the chain length in Eq. (13). In order to utilize Eq. (13) to predict the self-diffusivity of polydisperse polymer melts, a new definition of average chain length must be used. We defer a full investigation on an analytical formula for self-diffusivity as a function of chain length distribution in a later study.

We also extended the investigations to a wider range of monodisperse polymer chain lengths to estimate the entanglement chain length for polymer melts generated by this model. It has been widely accepted that the diffusivity of long, entangled polymer chains follow the reptation model [66,67], which predicts $D \propto N^{-2}$. As seen in Figure 12, the reptation model describes the long-chain polymer melts very well. The breakdown of the reptation model occurs around chain length of 50, which is the estimated entanglement chain length.

Figure 12. Log-log plot of self-diffusivity D of monodisperse polymer melts for chain lengths from 11 to 235. The red straight line has a slope of two denoting the reptation regime. The entanglement length for this polymer model is around 50.

3.4. Polydispersity effect on mechanical properties of glassy polymers

Uniaxial tensile tests were carried out for monodisperse and polydisperse glassy polymer samples (Table 3), with sample preparation detailed in Section 2.2. In order to preserve the chain length distribution, the bump height is magnified to six times the original value during vitrification for the monodisperse glasses, similar to diffusion study of monodisperse polymer melts. Note that in the glassy state at low temperatures, the chemical reaction rate is essentially zero. Therefore, for subsequent mechanical tests detailed here, the bump height is set at the original value for all monodisperse and polydisperse samples.

A constant strain rate loading was applied along the Z-direction, while zero stress was maintained for the two other transverse directions. The temperature was maintained at T_{low} . First, a polydisperse polymeric glass ($Sample_{FromCooling}^{Glass-2}$) was used to examine the

general mechanical response of our model polymer, particularly the strain rate dependency. Three strain rates were used: $5 \times 10^{-5} t_0^{-1}$, $5 \times 10^{-4} t_0^{-1}$ and $5 \times 10^{-3} t_0^{-1}$. The stress-strain curves are shown in Figure 13(a). For the high strain rate test, the sample exhibits a typical elastic response, followed by a distinctive yield point, and then strain softening and strain hardening regimes. The stress overshoot at the yield point and the subsequent strain-softening regime disappear as the strain rate decreases. Both the Young's modulus and the peak yield strength decrease with the decreasing strain rate. These observations agree reasonably well with the experimental and simulation results [16,68].

Figure 13. (a) Stress-strain curves of uniaxial tensile test for a polydisperse polymeric glass ($Sample_{FromCooling}^{Glass-2}$) under three different strain rates (indicated in the legend) at T_{low} . (b) The corresponding alignment parameter evolution during the uniaxial tensile test. Higher strain rate leads to enhanced chain alignment, thus higher strength.

To further investigate the microstructure response of polymer chain segments during deformation, we introduced a chain alignment parameter, χ , to quantify the degree of orientation along the applied stress direction. χ is essentially the average of the absolute value of the dot product of the bond vector and the loading direction (cosine of the angle), which can be written as,

$$\chi = \left\langle \frac{|\vec{r}_{ij} \cdot \hat{z}|}{|\vec{r}_{ij}| |\hat{z}|} \right\rangle \quad (14)$$

Here $\vec{r}_{ij}$ loops over all heterobonds in the system. $\hat{z}$ is the unit vector along the loading direction. χ ranges from 0.5 (ideally random distribution) to 1.0 (perfectly aligned along the loading direction). Figure 13(b) shows the evolution of the alignment parameter, χ , as a function of strain. For all the strain rates, it keeps increasing up to the point where the samples start to break. Interestingly, higher strain rate leads to higher saturated value for χ . This is quite reasonable since the polymer chains cannot relax as much under higher strain rate as that under lower strain rate. Higher degree of chain alignment leads to higher structural anisotropy, which can be viewed as the structural origin of strain hardening of linear polymeric glasses.

Snapshots of uniaxial tension tests under the intermediate strain rate are shown in Figure 14. As the deformation progresses, the initially highly entangled polymer chains try to follow the macroscopic strain by aligning themselves along the loading direction. The chain-alignment is believed to correlate with strain hardening at high tensile strains. Although bond breaking is allowed during mechanical tests, no A-B bond breakage was observed during our simulations. Therefore, chain sliding and pull-out, instead of chain scission, lead to the eventual fracture of the sample.

Figure 14. Deformation morphology of uniaxial tensile test for a polydisperse sample (*Sample^{Glass-2}_{FromCooling}*) under strain rate $5 \times 10^{-4} t_0^{-1}$ at T_{low} . Zoomed-in figures (A-D) show the apparent chain alignment, cavity formation and chain pull-out.

We now moved to investigate the effect of polydispersity on the mechanical response of polymeric glasses. Figure 15(a, b, c) shows the stress-strain curves for both monodisperse and polydisperse polymeric glasses with the three different strain rates, respectively. As the strain rate decreases, similar to that of the polydisperse sample, all monodisperse samples exhibit lower Young's moduli and peak yield strengths (Figure 15(e, f)), as well as diminished yield point behaviors. For a given strain rate, samples with longer chain lengths exhibit more pronounced strain hardening behaviors, and have considerably higher fracture strains. Figure 15(d) shows the alignment parameter evolution for the intermediate strain rate of $5 \times 10^{-4} t_0^{-1}$. Similar to polydisperse samples in Figure 13(b), χ increases with strain then saturates. The saturated highest degree of

chain alignment increases with the chain length, which leads to stronger strain hardening behaviors in Figure 15(b). The correlation between chain alignment and strain hardening behavior is evident. For the polydisperse sample, the χ evolution almost overlaps with the value of chain length 55, indicating the longer chains in the polydisperse samples, with a number average chain length of only 17.4 (see Table 3, $Sample_{FromCooling}^{Glass-2}$), contribute significantly to the overall chain alignment.

Figure 15. Stress-strain curves for both monodisperse polymeric glasses ($Sample_{FromCooling}^{Glass-7}$, $Sample_{FromCooling}^{Glass-17}$ and $Sample_{FromCooling}^{Glass-55}$) and the corresponding polydisperse polymeric glass ($Sample_{FromCooling}^{Glass-2}$) under three different strain rates (a), $5 \times 10^{-4} t_0^{-1}$ (b) and $5 \times 10^{-3} t_0^{-1}$ (c) at T_{low} . (d) The alignment parameter analysis for all samples under the intermediate strain rate of $5 \times 10^{-4} t_0^{-1}$. The fracture points were marked by the crosses. (e) The corresponding Young's moduli for all the samples under the three

strain rates. (f) The corresponding ultimate tensile strength (UTS) for all the samples under the three strain rates.

It should be noted that there is no bond breaking in the above uniaxial tensile tests, since the polymeric samples have rather short chains (up to 55) compared to the entanglement chain length of 50 estimated from the diffusion studies (Section 3.3). In other words, the entanglement density of the polymer is too low for chain breaking. Instead, chain pull-out occurs. To examine the effect of chain length on the competition between chain breaking and chain pull-out, monodisperse polymer glasses with chain length up to 555 were tested. Figure 16 shows the fraction of broken bonds with respect to initial overall number of bonds as a function of the polymer chain length. It is clearly seen that a transition from simple chain pull-out to chain scission occurs at about chain length of 335, which is roughly seven times the entanglement length from diffusion. This observation is somewhat similar to the disentanglement-to-scission transition, at a chain length ten times the entanglement length, in polymers using a coarse-grained bead-spring model in Ref. [69].

Figure 16. Number of broken bonds after fracture normalized by initial total number of bonds before uniaxial tensile test over a wide range of polymer chain length. All the samples were tested under the strain rate of $5 \times 10^{-3} t_0^{-1}$.

4. CONCLUSIONS

In this work, we developed a reactive and versatile particle-based polymeric model to understand how polydispersity affects polymer properties. The most significant advantage of this model over the existing coarse-grained polymer models is its ability to describe the polymerization reaction. This enables generating mimetic polymeric models via *in silico* synthesis, including linear, branched, cross-linked and network polymers. Particularly, the linear polymer samples exhibit Flory-Schulz chain length distribution due to the step-wise growth mechanism, which can be conveniently used to study the effect of polydispersity. It was found that diffusion of a polymer melt is affected by both the chemical reaction and polydispersity. The polydisperse polymer melt has a lower diffusivity than its monodisperse counterpart in terms of its number average chain length, while it has a higher diffusivity than its monodisperse counterpart in terms of its weight average chain length. On the other hand, the mechanical responses of linear polymeric glasses vary with both the strain rate and polydispersity. Low strain rate and short chains reduce strain hardening, due to decreased degree of chain alignment. The Young's modulus of polydisperse polymeric glass is lower than its monodisperse counterpart, while the ultimate tensile strength (UTS) is higher than its monodisperse counterpart with either the number average or the weight average chain length, especially at the lowest strain rate. It is our hope that this new reactive polymer model will be able to open doors

to future research to delineate the precise structure-property relations in polydisperse polymers.

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Graphical abstract: