Coarse-Grained Molecular Dynamics Modeling of A Branched Polyetherimide

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(Dated: June 17, 2020)

A coarse-grained model is developed to allow large-scale molecular dynamics simulations of a branched polyetherimide derived from two backbone monomers [4,4’-bisphenol A dianhydride (BPADA) and m-phenylenediamine (MPD)], a chain terminator [phthalic anhydride (PA)], and a branching agent [tris[4-(4-aminophenoxy)phenyl]ethane (TAPE)]. An atomistic model is first built for the branched polyetherimide. A systematic protocol based on chemistry-informed grouping of atoms, derivation of bond and angle interaction by fitting bond and angle distributions to Gaussian functions, and parameterization of nonbonded interactions by potential of mean force (PMF) calculations, is used to construct the coarse-grained model. A six-pair geometry, with one atomic group fixed at center and six replicates of another atomic group placed surrounding the central group in a NaCl structure, has been demonstrated to significantly speed up the PMF calculations. Furthermore, we propose a universal entropic correction term to the PMFs that can make the resulting coarse-grained model transferable temperature-wise, by enabling the model to capture the thermal expansion property of the polymer. The coarse-grained model has been applied to explore the mechanical, structural, and rheological properties of the branched polyetherimide.

I. INTRODUCTION

Polyetherimides, as a special class of polyimide polymers, are the products of condensation reactions among bifunctional carboxylic anhydrides containing ether linkages and primary diamines.[1] They are an important type of engineering thermoplastics with broad applications in industry, agriculture, transport, and healthcare because of their high heat resistance and stability, high mechanical strength, excellent electrical properties over a wide range of temperature and frequencies, improved melt processability, good adhesive properties, and good chemical and environmental stability.[1–6] For example, Ultem is a family of polyetherimide products derived from the BPADA dianhydride and MPD diamine that has superior heat, solvent, and flame resistance and has been widely used in automotive industry, medical and chemical instrumentation, and aerospace engineering.[2, 8, 9] To simplify the discussion, all abbreviations and acronyms of chemical formulae used in this paper are summarized in Ref. [7]. Since the development of Ultem, there has been a strong interest in discovering and synthesizing new polyetherimides that possess improved existing or desirable new properties and functions.[10–17] A laboratory trial and error, Edisonian approach is of course possible but becomes expensive and time-consuming when there is a need to scan a wide range of potential chemical formulae. To expedite materials discovery, computational approaches including molecular dynamics (MD) simulations have evolved into indispensable tools.[18]

Over the past several decades, all-atom MD simulations with various force fields have been applied to investigate polyetherimides.[19–48] Young et al. computed the dielectric relaxation strength of polyetherimides based on the ODPA dianhydride and APB diamine or its nitrile substituted version using atomistic MD simulations.[19] Qi et al. simulated a composite of carbon nanotubes (CNTs) and the LARC-SI polyimide, which is a copolymer based on two dianhydrides (ODPA and BPDA) and the 3,4’-ODA diamine, and computed its glass transition temperature, and stress-strain curves, Young’s moduli, densities, and Poisson ratios at various temperatures.[20] Eichinger et al. computed the solubility parameter of Ultem and evaluated the interfacial interactions between Ultem and a variety of low molecular liquids.[21] In a series of papers, Lyulin and collaborators have performed all-atom MD simulations on a range of polyetherimides, including those based on the dianhydride R and various diamines (e.g., BAPS, BAPO, and BAPB),[22–25, 28–30] Ultem and Extem (a polyetherimide based on the BPADA dianhydride and DDS diamine)[26, 27], and the ODPA-P3 polyetherimide and BPDA-P3 and aBPDA-P3 polyimides based on the P3 diamine.[31] They have demonstrated a two-step protocol that allows microsecond all-atom MD simulations for the equilibration of polyimides.[22, 23] computed the thermal properties of bulk R-BAPS and Extem,[24] and identified the ordering behavior of R-BAPS and R-BAPB at the surface of a single-walled CNT[25] and a graphene sheet.[28] They also investigated the influence of electrostatic interactions on the thermophysical properties of Ultem and Extem,[26, 27] and R-BAPS.[29] Furthermore, they simulated the mechanical deformation and computed the elasticity modulus of various polyimides.[30, 31]

Minelli combined MD simulations and the perturbed
chain statistical associating fluid theory to predict the solubility of various gases in Ultem and Kapton (a PMDA-ODA polyimide).[32] Lim et al. simulated the diffusion and sorption of CO₂ and CH₄ in amorphous Ultem and a CNT-Ultem composite.[33, 34] Luchinsky et al. computed the vibrational and infrared spectra and the thermodynamic and rheological properties of a mixture of Ultem and polycarbonate via all-atom MD simulations.[35] They also investigated the diffusion and reptation dynamics of polymer chains at a polymer-polymer interface in the mixture.[36] Pinel, Brown, Neyertz et al. used MD simulations to probe the effect of the rigidity of the dianhydride monomer (ODPA versus BCDA) and the addition of trifluoromethyl or methoxy substituents to the diamine monomer on the structure of the ODPA-ODA-b-BCDA-ODA copolymides.[37] Subsequently, Neyertz, Brown, and collaborators simulated the permeation and sorption of various gases, including helium and oxygen, in polyimides and copolyimides based on the ODPA and/or BCDA dianhydride and ODA diamine.[38–41] Pan et al. simulated the ODPA-MPD-b-ODPA-ODA copolymides with biphenyl side chains, which contains different numbers of methylene spacing groups, attached to the MPD monomers.[42] They further applied a similar simulation model to investigate how the length of the alkyl side chains tethered to the MPD monomers influences the properties of Ultem.[43] Xia et al. computed the fractional accessible volume of Extem, Ultem, and polysulfone.[44] Zhang et al. used MD simulations to study the miscibility of Ultem and polycarbonate.[45] Zhao et al. employed MD simulations to reveal the effects of various silane coupling agents on the interface between silica and a ODPA-ODA polyetherimide.[46] Wen et al. computed the glass transition temperature of various polyetherimides based on the BPADA dianhydride and different diamines with all-atom MD simulations and derived a predictive model of their glass transition temperature using machine-learning algorithms.[47] Additionally, Hamm et al. used the ReaxFF reactive force field to model the pyrolysis process of Ultem.[48]

All-atom MD simulations have significantly deepened our understanding of polyimides and polyetherimides at the molecular level. However, they are still limited to relatively small systems and short time scales.[22, 49] To access larger size and longer time scales, we have to resort to other computational techniques. One approach is to employ a coarse-grained description of a polymer system to get rid of fast degrees of freedom that play a less important role in the physical properties and processes of interest.[50, 51] The typical practice, called “coarse-graining”, is to group atoms into coarse-grained beads and parameterize the interactions between the coarse-grained beads on the basis of all-atom simulations or available experimental data on material properties.[50, 51]

Several methods of deriving coarse-grained potentials, including bottom-up approaches such as iterative Boltzmann inversion (IBI),[52–54] inverse Monte Carlo,[55, 56] force matching,[57–59], the relative entropy,[60, 61] and the reversible work,[62] and various top-down or mixed approaches,[63–66] have been developed. Several groups have applied these methods to construct coarse-grained MD models of polyimides[67–73] and polyetherimides.[74–76] Clancy et al. coarse-grained polyimides based on the BPDA dianhydride and three different APB diamine isomers into chains of linked vectors and used such linked-vector chains to quickly obtain relaxed configurations of the polymers that can be reverse-mapped to atomistic systems.[67, 68] Odgaard et al. used this technique to build all-atom configurations for the representative volume elements of the silica nanoparticle/BPDA-APB polyimide composites with various interfacial treatments.[69] Pandiyan et al. used the IBI method to construct coarse-grained models of a high-temperature polyimide (HFPE-30) based on the 6FDA dianhydride and PPD diamine, terminated by the 4-PEPA anhydride, at different levels of detail.[70] Kumar et al. constructed a coarse-grained model of PMR-15, which is a polyimide based on the BTDA dianhydride and MDA diamine with the NA anhydride as the chain terminator, and studied its adhesion property on a rutile surface.[71] Sudarkodi et al. further used these types of coarse-grained models to simulate the uniaxial tensile deformation of PMR-15 and HFPE-52 polyimides.[72]

A few coarse-graining attempts are also reported on polyetherimides. Chakrabarty and Cagin developed an atomistically informed coarse-grained model of a piezoelectric polyetherimide based on the (β-CN)APB diamine and ODPA dianhydride and used this model to study the thermal, mechanical, and electrical properties of the polymer.[74] Markina et al. developed coarse-grained models of two polyetherimides based on the dianhydride R and BAPS or BPAB diamine using the dissipative particle dynamics method and showed that the chain stiffness has a profound influence on their crystallization behavior.[75] Volgin et al. developed two coarse-grained models of a polyetherimide based on the dianhydride R and BAPS diamine using the IBI method and studied the effects of coarse-graining level on the diffusion of a C₆₀ nanoparticle in the polymer matrix.[76]

A typical challenge faced by most coarse-grained models of molecular systems is that the models are usually thermodynamic state-dependent and not transferable.[50] Recently, Hu et al. constructed a transferable coarse-grained MD model based on the IBI approach combined with the density correction method to predict the thermodynamic, structural, and mechanical properties of Kapton.[73] Clearly, more efforts are needed along this direction for polyimide and polyetherimide polymers. In this paper, we aim to develop a coarse-grained model for a branched polyetherimide that is not only transferable but also expandable. Being transferable means that the model can be used at different thermodynamic state points, such as different temperatures. The expandability requirement indicates that when a new
functional group (e.g., a side group, an ionic group, etc.) is added to a polyetherimide for which a coarse-grained model is already available, we just need to expand the existing coarse-grained model by adding new beads corresponding to the newly added groups. The task then becomes parameterizing the interactions between these new beads and the existing beads. We demonstrate in this paper that by combining a chemistry-informed grouping method, potential of mean force calculations, and an entropic correction of the resulting coarse-grained force field, it is possible to construct a transferable and expandable coarse-grained model of a branched polyetherimide based on the BPADA dianhydride and MPD diamine, with the PA anhydride as chain terminators and TAPE as branching agents.

This paper is organized as follows. The general theory of coarse-graining, first systematically discussed by Noid and coworkers,[77, 78] and how it can be practically approximated and implemented, are introduced in Sec. II. Then we apply this theory to develop a coarse-grained model of the branched polyetherimide, as detailed in Sec. III. In Sec. IV, the coarse-grained model is applied to compute mechanical, structural, and rheological properties of the branched polyetherimide and the results are compared to those from all-atom MD simulations and experiments. Finally, conclusions are included in Sec. V.

II. GENERAL THEORY OF COARSE-GRAINING

In this paper, the term “coarse-graining” refers to the process of deriving a coarse-grained description of a polymeric system from a fine-grained, atomistic model of the same system. In other words, atoms in the detailed description are grouped into coarse-grained beads (i.e., pseudo-atoms) with some fine details smoothed over. The coarse-graining procedure thus involves two key steps: the mapping from groups of atoms to coarse-grained beads and the determination of interactions between the coarse-grained beads. We are motivated by the consideration that the final coarse-grained model being developed for the prototypical branched polyetherimide should be transferable, reusable, and expandable when a new formula of polyetherimide is the target of modeling.

We will delay the discussion on the coarse-graining mapping to Sec.III A, where our coarse-grained model of the branched polyetherimide is introduced. In this section, we introduce the general theory underlying the coarse-graining approach adopted here to determine the coarse-grained force field (i.e., the interaction potentials between the coarse-grained beads), which was originally proposed by Noid and coworkers.[77, 78] We then discuss the implementation of this theory through potential of mean force (PMF) calculations for a pair of atomic groups. Technical issues in the implementation, including many-body effects on the coarse-grained potentials and how to fix the center of mass of a group of atoms in the PMF calculations, are discussed in detail. Finally, we present a test case with a pair of benzene molecules to validate the coarse-graining approach.

A. Theory of Noid and Coworkers

We first briefly summarize the theory of coarse-graining formulated by Noid and coworkers.[77] Our goal is to map an atomistic system with \( n \) atoms to a system of \( N \) coarse-grained beads through a mapping function \( R_i(r^n) \) for coordinates and \( M_{P_i}(p^n) \) for momenta, where \( R_i \) and \( P_i \) are coordinates and momenta of the \( I \)-th coarse-grained beads while \( r_i \) and \( p_i \) are atomistic coordinates and momenta. Usually, linear mappings are used as

\[
M_{R_i}(r^n) = \sum_{i=1}^{n} c_i r_i, \quad (1)
\]

and

\[
M_{P_i}(p^n) = M_I \sum_{i=1}^{n} c_i p_i / m_i, \quad (2)
\]

where \( I \) runs from 1 to \( N \), the notation \( r^n \) (\( p^n \)) represents the collection of atomistic coordinates (momenta), \( c_i \) are coefficients in the linear mapping, \( m_i \) is the mass of the \( i \)-th atom, and \( M_I \) is the mass of the \( I \)-th coarse-grained bead.

The Hamiltonian of the atomistic system is

\[
h(r^n, p^n) = \sum_{i=1}^{n} \frac{1}{2m_i} p_i^2 + u(r^n), \quad (3)
\]

where \( u(r^n) \) is the potential energy of the atomistic system. The coarse-grained Hamiltonian is

\[
H(R^N, P^N) = \sum_{I=1}^{N} \frac{1}{2M_I} P_i^2 + U(R^N), \quad (4)
\]

where \( R^N \) (\( P^N \)) represents the collection of coarse-grained coordinates (momenta) and \( U(R^N) \) is the potential energy of the coarse-grained system. The main task of coarse-graining is therefore to determine \( U(R^N) \).

For a perfect coarse-grained model, which yields identical equilibrium properties as the atomistic model, the coarse-grained potential can be written as \[77\]

\[
U(R^N) = -k_B T \ln z(R^N) + \text{const}, \quad (5)
\]

where

\[
z(R^N) \equiv \int dr^n \exp \left(-\frac{u(r^n)}{k_B T}\right) \delta \left(M_{R_i}^N(r^n) - R^N\right). \quad (6)
\]
The coarse-grained force field, \( F_I(R^N) \equiv -\frac{\partial U(R^N)}{\partial R_I} \), is then given by

\[
F_I(R^N) = \frac{k_BT}{z(R^N)} \int dr^n \exp \left( \frac{-u(r^n)}{k_BT} \right) \prod_{j \neq I} \delta (M_{RJ}(r^n) - R_J) \frac{\partial \delta}{\partial R_I} \left( \sum_{i \in I} c_{iI}r_i - R_I \right), \tag{7}
\]

where the set \( I_I \) consists of the indices of a group of atoms that are mapped into the \( I \)-th coarse-grained bead. For the partial derivative, the following identity holds,

\[
\frac{\partial}{\partial R_I} \left( \sum_{i \in I_I} c_{iI}r_i - R_I \right) = -\frac{\partial}{\partial r_k} \left( \sum_{i \in I_I} c_{iI}r_i - R_I \right), \tag{8}
\]

where \( k \in I_I \). After this transformation, we can do the integral on the right side of Eq. (7) by parts and the following partial derivative will emerge,

\[
\frac{\partial}{\partial r_k} \left( \exp \left( \frac{-u(r^n)}{k_BT} \right) \prod_{j \neq I} \delta (M_{RJ}(r^n) - R_J) \right).
\]

This partial derivative can be greatly simplified if we focus on atoms that are only mapped to the \( I \)-th coarse-grained bead but not other beads. That is, the index \( k \) is limited to all \( k \in I_I \) but \( k \notin I_J \) for \( J \neq I \). For such indices, we can introduce a nonzero factor \( d_{Ik} \) such that

\[
\sum_{k \in S_I} d_{Ik} = 1 \quad \text{for all } I, \tag{9}
\]

where \( S_I \) is the set of indices for the atoms that only belong to the \( I \)-th coarse-grained bead in the coarse-graining mapping. The combination of Eq. (8) and Eq. (9) yields the following identity,

\[
\frac{\partial}{\partial R_I} \left( \sum_{i \in I_I} c_{iI}r_i - R_I \right) = \sum_{k \in S_I} d_{Ik} \frac{\partial}{\partial r_k} \left( \sum_{i \in I_I} c_{iI}r_i - R_I \right). \tag{10}
\]

Using Eq. (10), we can rewrite Eq. (7) as

\[
F_I(R^N) = -\sum_{k \in S_I} d_{Ik} \frac{k_BT}{z(R^n)} \int dr^{n-1} \prod_{j \neq I} \delta (M_{RJ}(r^n) - R_J) \int dr_k \exp \left( \frac{-u(r^n)}{k_BT} \right) \frac{\partial}{\partial r_k} \left( \sum_{i \in I_I} c_{iI}r_i - R_I \right), \tag{11}
\]

where \( dr^{n-1}_k \equiv \prod_{j=1,j \neq k}^n dr_j \). An integration by parts yields

\[
F_I(R^N) = \frac{1}{z(R^N)} \int dr^n \exp \left( \frac{-u(r^n)}{k_BT} \right) \delta \left( M_{R}(r^n) - R^N \right) \sum_{k \in S_I} \left( -\frac{d_{Ik}}{c_{Ik}} \right) \frac{\partial u(r^n)}{\partial r_k} 
\]

\[= \sum_{k \in S_I} \frac{d_{Ik}}{c_{Ik}} f_k(r^n) R^N, \tag{12}
\]

where \( f_k(r^n) \equiv \frac{\partial u(r^n)}{\partial r_k} \) representing the force on the \( k \)-th atom from all other atoms in the system and \( \langle \cdots \rangle_{R^N} \) indicates an ensemble average performed under the coarse-graining mapping summarized in Eq. (1).

Equation (12) is the theoretical foundation of computing the coarse-grained force field. In the mapping adopted here, all atoms are separated into nonoverlapping groups, each of which is mapped to one and only one coarse-grained bead. Furthermore, the coarse-grained bead is placed at the center of mass of the group of atoms that it represents. In this case, \( c_{Ik} = \frac{m_k}{\sum_{k \in S_I} m_k} \) and if \( k \in S_I \), then \( k \notin S_J \) for all \( J \neq I \). A natural choice is \( d_{Ik} = c_{Ik} \), which indicates that the force on the \( I \)-th coarse-grained bead is the ensemble average of the forces on atoms with indices in \( S_I \) from all other atoms in the system, subjected to the mapping from atoms to beads. Noid et al. further proved that this scheme also guarantees that the momentum part of the phase-space probability distribution function in the coarse-grained model matches that in the atomistic model.[77]

To summarize, the derivation in this section shows that the coarse-grained model and the atomistic model have consistent probability distribution functions of thermodynamic states in the phase space as long as

- One group of atoms is mapped to one coarse-grained bead.
- No atom is shared by more than one group.
- A coarse-grained bead is placed at the center of mass of the group of atoms that the bead represents.
- The force on a coarse-grained bead is the ensemble average of the forces exerted on all atoms in the group, which the bead represents, by all other atoms in the atomistic system.

The coarse-graining method on the basis of these constraints is called force matching coarse-graining.[57–59]

**B. Pairwise Nonbonded Coarse-Grained Force Field**

The general theory of coarse-graining presented in the previous section is valid for any molecular system. However, the resulting coarse-grained force field is a
many-body force field, which is very difficult to compute in general. Furthermore, the coarse-grained model is state-dependent as the coarse-grained force field is computed for a given thermodynamic state, as indicated by Eq. (12). Therefore, the coarse-grained model developed using the general theory is actually not transferable, though it is proved to be self-consistent and rigorous from the perspective of thermodynamics.[58, 59, 77]

One approximate coarse-graining scheme was proposed by Wang and collaborators.[79] Their effective-force coarse-graining (EF-CG) method results in a pairwise coarse-grained force field. In EF-CG, an atomic system is divided into groups of atoms, with each group mapped to a coarse-grained bead. The interaction between a pair of beads is computed from the average force between the corresponding atomic groups, under the presence of all other atoms in the atomistic system. The advantage of this scheme is that the many-body nature of the coarse-grained force field is naturally captured. However, the implementation of EF-CG requires MD simulations of the entire atomistic system and nontrivial constraints on the pair of atomic groups under consideration. As a result, the resulting coarse-grained model is still not transferable.

In this paper, we aim to develop a coarse-grained model for a branched polyetherimide that is transferable and expandable. In particular, the former feature indicates that the model can be used to simulate the polyetherimide under different temperatures and the latter means that when a new polyetherimide containing one or several new functional groups is dealt with, the same number of new coarse-grained beads will be added to the coarse-grained model. The only parameterization that is needed to update the coarse-grained model is to compute the interactions between the new beads and all the existing beads. In this sense, the coarse-grained force field is expanded with the newly added beads. We term this method a library-like approach, which is obviously appealing as it avoids the need to construct a new coarse-grained model every time when the polymer of interest is updated. However, the theoretical foundation of such an approach is not well understood at the moment.[50] In this paper we provide evidences demonstrating that such an approach may be viable.

The simplest system is one that can be divided into two groups of atoms and can be coarse-grained into two beads. The force on one bead is then the sum of the forces on all atoms in the group this bead represents by all atoms in the other group. If the center of mass of each group is chosen as the location of the corresponding coarse-grained bead, then the coarse-grained model with a pairwise interaction is fully consistent with the general theory of coarse-graining discussed by Noid et al.[77] This is easy to understand as in such a simplified system, there is no many-body effect since there are only two coarse-grained beads anyway. In a more general case, there are of course more than two beads in the coarse-grained model. Then parameterizing the coarse-grained force field in a pairwise fashion assumes the force field is additive and automatically neglects its intrinsic many-body nature as required by the thermodynamic consistency between the atomistic and coarse-grained models. In this paper we show that an entropic correction term can be added to the pairwise coarse-grained force field derived with PMF calculations to not only make the model transferable but also effectively compensate for the error introduced by neglecting the many-body effects.

C. Fixing the Center of Mass of a Group of Atoms

When computing the force between two groups of atoms, one technical key is to fix the center of mass of each group, which will then allow the separation between the two centers of mass to be used as a coarse-grained coordinate. Fritz et al. used the LINCS constraint algorithm to fix the center of mass of a group of atoms and compute the coarse-grained force field between atomic groups.[80] Here we adopt a different approach implemented in LAMMPS. In the starting configuration, the velocity of the center of mass of each group of atoms is set to zero (i.e., the total momentum of the group is set to zero). When a group of atoms interact with atoms from other groups, all atoms first move according to the Newtonian equation of motion. After one time step in MD simulations, the atomic coordinates are updated and the new location of the center of mass of each group is computed. The displacement vector, \( \vec{d}_c \), of a group’s center of mass from its original location to the new one is determined as well as its velocity, \( \vec{v}_c \). Then all atoms in that group are displaced by \( -\vec{d}_c \) such that the center of mass of the group is shifted back to its original location. At the same time, \( \vec{v}_c \) is subtracted from the velocity of each atom in the group to ensure that the velocity of the group’s center of mass is restored to zero. To justify this “recentering” approach, in the Supporting Information we prove that it is equivalent to the method where a constraint force is added to each atom in a group such that the group’s center of mass does not move (i.e., the total force on the group, including the constraint forces applied to all the atoms in the group, is always zero) and the group does not exhibit any artificial rotation (i.e., the net torque from the constraint forces on the group is zero but there can be torques from interactions with other groups). Herein we employ the “recentering” approach to constrain the center of mass of a group of atoms.

D. Sampling Configurations at a Fixed Center-to-Center Distance: Test

To demonstrate the method of using PMF calculations to approximate the ensemble average in Eq. (12) that connects a coarse-grained force field to an atomistic one, we utilize a model system that consists of one benzene molecule and one oxygen atom, as shown in Fig. 1(a). A
configuration of this model system can be approximately characterized by three parameters, the magnitude of the vector $\vec{r}$ pointing from the benzene’s center of mass to the oxygen and two angles that describe the orientation of $\vec{r}$ relative to the benzene molecule. A Cartesian coordinate system can be set up using the benzene’s center of mass as its origin and three orthonormal vectors, $\vec{v}_1$, $\vec{v}_2$, and $\vec{v}_3$ as the axes. Among these, $\vec{v}_1$ and $\vec{v}_2$ define the plane in which the benzene molecule lies in and $\vec{v}_3$ is normal to this plane. At a finite temperature, the six carbon atoms and six hydrogen atoms in the benzene molecule actually have a three-dimensional conformation. However, we can always define a plane that captures the planar nature of the benzene molecule. For example, a plane that minimizes the sum of square distances or has zero average distance for all the carbon atoms from this plane can be used. The location of the oxygen atom in this coordinate system is therefore given by the vector $\vec{r}$, i.e., its length $r \equiv |\vec{r}|$ as well as two angles: the polar angle $\omega$ and the azimuthal angle $\phi$, as shown in Fig. 1(a).

We computed $P(\omega, \phi)$ for a series of static configurations of the benzene-oxygen system. Noting the symmetry of the system, the polar angle $\omega$ is varied from 0 to $\pi/2$ in steps of $\pi/90$. For each $\omega$, the azimuthal angle $\phi$ is varied from 0 to $\pi$ in increments of $\pi/90$. For each configuration, the benzene molecule is in its ground-state conformation (i.e., a planar hexagonal configuration) and the interaction energy between the benzene molecule and the oxygen atom, $\epsilon(\omega, \phi)$, is computed. The canonical distribution is then used to determine $P(\omega)$. Additionally, $P(\omega)$ is determined with the trajectory or energy generated from a MD simulation of a model system that consists of one benzene molecule at the origin of a Cartesian coordinate system and six oxygen atoms surrounding it at the same separation in the positive and negative directions of the three axes, as shown in Fig. 1(b). This system is designed to speed up the sampling of various configurations, in particular, rare configurations that may have significant contributions to an ensemble average when $r$ is small. In this case, extremely long MD simulations are needed if a single pair of benzene and oxygen is used. Later in this paper we show that this strategy of using six pairs simultaneously is practically useful when PMF calculations are performed for groups of atoms of which the conformations deviate significantly from a sphere, such as aromatic rings.

The results of $P(\omega)$ at $r = 5$ Å are shown in Fig. 2. For both one benzene-oxygen pair and one benzene/six oxygen system, the results based on the MD trajectory (circles and triangles in Fig. 2) and the corresponding energy (squares and pluses in Fig. 2) are close but differ slightly around $\omega = 60^\circ$, $90^\circ$, and $120^\circ$. This difference is likely due to the limited number of configurations sampled in the MD simulation as it can be noted that the difference between the two (circles and pluses in Fig. 2) is much smaller for the one benzene/six oxygen system in Fig. 1(b), which can sample more configurations in the same number of MD time steps. The results computed using the energies of uniformly-scanned static configurations (solid line in Fig. 2), on the other hand, show a very good agreement with those based on the MD trajectory of one benzene-oxygen pair. However, this agreement may just be a coincidence as the energy of a static configuration is essentially the energy of the system in that configuration at 0 K and it is unclear why it seems to produce reasonable results when that energy is used to compute the Boltzmann factor at 300 K. The results of the system with six benzene-oxygen pairs are in rea-
FIG. 2. Comparison of the probability density, \( P(\omega) \), calculated in five different ways for a benzene-oxygen system at \( r = 5 \, \text{Å} \). The data are based on MD trajectory (○) and energy (□) of one benzene-oxygen pair at \( T = 300 \, \text{K} \), MD trajectory (△) and energy (+) of the one benzene/six oxygen system at \( T = 300 \, \text{K} \), and static configuration energy (solid line) of one benzene-oxygen pair (effectively at \( T = 0 \, \text{K} \)).

reasonable agreement with those from one pair, though the former seem to slightly overestimate (oversample) configurations for \( 30^\circ \lesssim \omega \lesssim 60^\circ \) and \( 120^\circ \lesssim \omega \lesssim 150^\circ \), while underestimate (undersample) configurations in the other ranges of \( \omega \). Although the discrepancy is noted, we will utilize the six-pair setup in Fig. 1(b) to speed up the calculation of pairwise nonbonded interactions between coarse-grained beads when developing the coarse-grained model of the branched polyetherimide below. The error introduced by this choice will be balanced out when entropic corrections are included in the coarse-grained force field, as discussed later.

III. DEVELOPMENT OF A COARSE-GRAINED MODEL OF A BRANCHED POLYETHERIMIDE

We employ the methodology discussed in the previous section to develop a coarse-grained model of a branched polyetherimide and use this model to compute its mechanical, structural, and rheological properties. The protocol of developing such a model is outlined in Fig. 3, which mainly includes three steps: the grouping of atoms into coarse-grained beads, the parameterization of bonded (i.e., bond, angle, dihedral, etc.) interactions, and the parameterization of nonbonded interactions between the coarse-grained beads. In the following sections we describe each step in detail.

A. Mapping Groups of Atoms into Coarse-Grained Beads

The branched polyetherimide dealt with in this paper is polymerized from two backbone monomers, BPADA and MPD, a chain terminator, PA, and a tri-functional branching agent, TAPE. One short branch, terminated on one end with PA and connected to TAPE on its other end, is shown in Fig. 4. After several attempts, we settle with using 5 types of coarse-grained beads for such a system: type-A beads for the phthalimide groups, type-B beads for the oxygen atoms in the flexible ether linkages, type-C beads for the bisphenol A groups, type-D beads for the aromatic rings in the phenylenediamine groups, and type-E beads for the core parts of TAPEs. The groupings are shown schematically in Fig. 4. In total there are 10 atomic groups in this short branch. Group 1 is chemically almost the same as groups 3 and 7 except that there is one extra hydrogen atom in group 1 since it is at the end of the branch. The mass and charge of group 1 are therefore slightly different from those of groups 3 and 7. However, we map all three groups to type-A beads (with slightly different masses and charges) to simplify the non-Coulombic part of their nonbonded interactions with other coarse-grained beads. The error of this treatment is partially compensated for by the entropic correction of the coarse-grained force field introduced later. Groups 2 and 8 are chemically almost identical except for the location of one hydrogen atom. As a result, they have the same mass but their charges are somewhat different. For simplicity, we map these groups into type-D beads with different charges. The charges and masses of all atomic groups are summarized in Table I.

We adopt the chemistry-informed mapping scheme in Fig. 4 because it leads to unimodal distributions for all the bonds and angles between the coarse-grained beads and therefore a Gaussian approximation can be used to derive the stiffness constants of bonds and angles, as discussed below. Other mapping schemes, including those more coarsened, usually cause the angle potential to have two or more local minima, which is not desirable for the parameterization of the bond and angle interactions between the coarse-grained beads. We also notice that it is necessary to keep the oxygen atoms in the ether link-
FIG. 3. The coarse-graining flowchart.

FIG. 4. Mapping atomic groups into five types of coarse-grained beads. For clarity, only one short branch connected to TAPE and terminated with PA is shown.

ages as a distinct type of coarse-grained beads. This observation is consistent with the understanding that the inclusion of ether groups in polyetherimides is responsible for their enhanced chain flexibility and improved melt processability compared to other polyimides.[1]

B. Parameterization of Coarse-Grained Bonded Interactions

The second step of coarse-graining is to parameterize the bond and angle interactions in the coarse-grained chain using results from all-atom MD simulations. For two neighboring groups of atoms, each mapped to a coarse-grained bead, we compute the distance between their centers of mass and examine the probability distribution of the distances. For three consecutive groups of atoms, we compute the angle formed by the corresponding centers of mass and examine the probability distribution of the angles. All probability distributions based on the grouping scheme in Fig. 4 are well approximated by Gaussian distributions, indicating that the bonds and angles can be described by a harmonic potential,

\[ U(x) = \frac{1}{2}k_x(x - x_0)^2, \]

and the corresponding probability density is

\[ p(x) = \frac{k_x}{2\pi k_B T} e^{-\frac{U(x)}{k_B T}}, \]

where \( x \) is the length for a bond or the angle \( \theta \) for an angle, \( x_0 \) the equilibrium bond length or angle, \( k_x \) the corresponding stiffness, and \( U(x) \) the harmonic bond or angle potential.

Figure 5 shows the probability distributions of the 2-3-4 angle and the 6-7-8 angle (see Fig. 4 for the definition of bead types and atomic group indices), which are both D-A-B type angles and are well fit by Gaussian distributions. The fitting allows us to extract a spring constant and an equilibrium angle for the harmonic angle potential. The spring constants and equilibrium values for the same type angles are very close, as shown in the example in Fig. 5. Similar results are obtained for all bonds and angles. The spring constants, equilibrium bond lengths, and equilibrium angles for all bonds and angles are summarized in Table II and Table III. The results validate the usage of harmonic potentials for the bond and angle interactions in the coarse-grained force field. For the same type bonds and angles appearing more than once even in one branched chain, they all have similar stiffnesses and equilibrium values. This finding justifies the simplification of mapping 10 atomic groups into 5 types of coarse-grained beads. We further confirm that the parameters of the coarse-grained bond and angle potentials are insensitive to temperature for the range of temperatures of interest here.
FIG. 5. The probability distribution of the 2-3-4 angle at $T = 450$ K: all-atom MD data (circles) and a Gaussian fit (solid line) with $k_\theta = 427$ kcal/mol/rad$^2$ and $\theta_0 = 2.62$ rad; the probability distribution of the 6-7-8 angle at the same $T$: all-atom MD data (squares) and a Gaussian fit (dashed line) with $k_\theta = 425$ kcal/mol/rad$^2$ and $\theta_0 = 2.61$ rad.

TABLE II. Coarse-grained bond parameters.

| Bond Type | Bonds | $k_r$ (kcal/mol/Å$^2$) | $r_0$ (Å) | $k_\theta$ (kcal/mol/rad$^2$) | $\theta_0$ (rad) |
|-----------|-------|------------------------|-----------|-------------------------------|----------------|
| A-D       | 1-2   | 267                    | 4.86      | 270                           | 4.88           |
|           | 2-3   | 255                    | 4.87      |                               |                |
|           | 7-8   | 286                    | 4.91      |                               |                |
| A-B       | 3-4   | 381                    | 4.09      | 391                           | 4.08           |
|           | 6-7   | 400                    | 4.07      |                               |                |
| A-C       | 4-5   | 88                     | 4.99      | 86                            | 5.02           |
|           | 5-6   | 83                     | 5.04      |                               |                |
| B-D       | 8-9   | 505                    | 2.80      | 505                           | 2.80           |
| B-E       | 9-10  | 80                     | 5.58      | 80                            | 5.58           |

C. Parameterization of Coarse-Grained Nonbonded Interactions

1. Potential of Mean Force Calculations

The next step of constructing the coarse-grained model is to parameterize the nonbonded interaction between a pair of beads that belong to the same chain but are separated by at least three bonds or that belong to different chains. In each PMF calculation, the center of mass of each group of atoms is fixed but the atoms in the group are still mobile, causing the group to rotate and vibrate around its center of mass. A Langevin thermostat is used to keep the system at a target temperature. By sufficiently sampling the relative configurations and orientations of the two groups with their centers of mass separated at a given distance, we calculate the average force between them as a function of the separation. The results show that the average force is along the vector connecting the two centers of mass. Therefore the separation between the centers of mass can be used as a coarse-graining coordinate. Integrating the average force over separation, we obtain the coarse-grained potential for each pair of coarse-grained beads.

Since atoms carry charges in an all-atom model, we split the coarse-grained potential into two parts: the Coulomb component and the van der Waals component. The Coulomb interaction between two atomic groups is included in the coarse-grained force field using the total charge of a group as the charge of the corresponding coarse-grained bead. The charges of all atomic groups for the branched polyetherimide can be found in Table I. If one or two groups from the pair being parameterized are charged, the Coulomb force is subtracted from the mean force between the two groups and the remaining part is designated as the van der Waals component, which is still along the vector connecting the centers of mass. The integration of this component over separation is called the nonbonded, van der Waals PMF. Its mathematical expression is

$$U(r) = -\int_{r_m}^{r} \langle f_c \rangle_s ds,$$

(15)

where $r_m$ is a large separation at which $U(r_m) \approx 0$, and $\langle f_c \rangle_s$ is the force between the two groups at separation $s$ with the Coulomb force between them subtracted. Hereafter we reserve PMF specifically for the van der Waals component of the nonbonded interactions between two atomic groups. Other researchers have also used Equation (15) to compute the mean potentials between ions,[84, 85] molecules,[86] and nanoparticles.[87–89]

As an example, Fig. 6 shows the PMF for a pair of benzene molecules. Two sets of results are included. One is computed from all-atom MD simulations with a single pair of atomic groups, similar to the setup shown in Fig. 1(a). The data show the typical feature of intermolecular interactions, i.e., the force is attractive at large
and repulsive at short separations, with a well-defined minimum at an equilibrium separation around 5 to 6 Å.

FIG. 6. The van der Waals PMF, \( U(r) \), as a function of separation \( r \) for a pair of benzene molecules. The results are from all-atom MD simulations with a single pair (○) and a system with one molecule at center and six surrounding molecules (□, see Fig. 1(b) for the setup). The lines are guides to the eye.

Using the setup in Fig. 1(a), we have parameterized the PMFs for all 15 pairs of atomic groups for the branched polyetherimide. For atomic groups carrying different charges but mapped to the same type of coarse-grained beads (with the corresponding different charges), the results show that after the subtraction of Coulomb interactions, the van der Waals PMFs are similar. This is the reason that only 15 PMFs are included in the coarse-grained force field. However, a large discrepancy is observed between the coarse-grained model and the all-atom model. Under standard conditions for temperature and pressure, the mass density of the branched polyetherimide is 1.209 g/cm\(^3\) but the density from the coarse-grained model, without any modification as discussed below, is much higher at 1.622 g/cm\(^3\). This difference reflects a generic “softness” issue of a coarse-grained model constructed via a bottom-up approach on the basis of PMF calculations,[90] i.e., the coarse-grained potentials are usually much softer than the atomistic ones, making the coarse-grained system denser than the atomistic system.

We can illustrate the “softness” issue more clearly with benzene. Under standard conditions, the mass density of benzene at 300 K is 0.795 g/cm\(^3\) from all-atom MD simulations, which is only slightly lower than the experimental value of 0.876 g/cm\(^3\). During coarse-graining, each benzene is grouped into a bead and the van der Waals PMF between two beads serves as the coarse-grained force field. If this PMF is computed with a setup similar to Fig. 1(a) where only a single pair of benzene molecules is utilized, we find that the mass density from the coarse-grained model is much higher at 1.579 g/cm\(^3\). This soft PMF is shown as circles in Fig. 6.

The “softness” issue is related to the insufficient sampling of relative configurations in a PMF calculation. For a benzene pair at large separations, their conformations are not strongly correlated and an all-atom MD simulation can sufficiently sample all possible configurations. However, when they get close, the two benzene molecules prefer to be in the T-shaped or parallel-displaced configurations, which are energetically favored.[91] In the PMF calculation of benzene-benzene interactions with a benzene pair, the contributions of these configurations dominate, where the two benzene molecules are close to each other. However, in a real benzene system, the local packing of two benzene molecules is affected by other surrounding molecules and cannot all assume the lowest-energy configurations. As a result, the average separation between adjacent benzene molecules is larger than the separation at which the PMF calculated with a single pair reaches a minimum. Furthermore, in a polymeric material containing aromatic rings, the rings are connected to other atomic groups. The T-shaped or parallel-displaced configurations are still favored by the aromatic rings but are subjected to the constraints set by the presence of other groups. As a result, a pair of aromatic rings cannot be as close as in the situation where only the two rings are present. In this sense, the “softness” issue is the outcome of using pairwise nonbonded interactions between coarse-grained beads to approximate the many-body interactions among atomistic groups.

To overcome the “softness” problem, we resort to the setup illustrated in Fig. 1(b). To compute the PMF between a pair of atomic groups, we place the center of mass of one group at the origin of a Cartesian coordinate system (\(xyz\)), replicate the other group six times, and place the six groups around the central group on the \(x\), \(-x\), \(y\), \(-y\), \(z\), and \(-z\) axes with their centers of mass at equal distance from the origin. In each snapshot, there are therefore six possible configurations between the central group and the surrounding groups, i.e., there are six pairs simultaneously but all in different configurations. In this approach, the sampling of unfavorable and rare configurations of the pair is enhanced and the system is more suitable to capture the many-body nature of nonbonded interactions between atomic groups in the full-atom model being coarse-grained. For the benzene-benzene pair, the PMF calculated with this six-pair geometry is included in Fig. 6, which is obviously more repulsive at short distances compared to the PMF calculated with only one pair. The location where the potential reaches its minimum from the six-pair setup has also shifted to a larger value. As a result, the density of benzene from the coarse-grained model based on nonbonded PMFs calculated with the six-pair geometry is reduced to 0.914 g/cm\(^3\), much closer to the result of the atomistic model.

If more simultaneous pairs are used in a PMF calculation, we expect the resulting coarse-grained nonbonded potentials to become even more repulsive at short sepa-
rations and the corresponding polymer density from the coarse-grained model to be reduced further. We have tested a setup in which twelve groups of atoms, all being replicates of the same group, are placed around one central group. The placement is similar to the arrangement of twelve nearest neighbors around one atom in a face-centered-cubic crystal. Indeed, the resulting PMF is more repulsive at small distances. For benzene, the density from the corresponding PMF is reduced to 0.692 g/cm$^3$, which is smaller than the density from the atomistic model. Later on, we will show that the twelve-pair setup makes it harder to introduce a uniform entropic-correction term to the coarse-grained force field for the branched polyetherimide. Therefore, we settle with the six-pair setup for PMF calculations. It should also be pointed out that with atomic groups that have shapes resembling spheres, the results from the one-pair and six-pair setup are very close. In this regard, benzene molecules, which are almost planar, are an ideal model system illustrating the difficulty of developing coarse-grained models for molecular and polymeric systems.

For the 5 types of coarse-grained beads defined in Fig. 4 for the branched polyetherimide, we have performed PMF calculations for all the 15 pairs. Two examples, for the D-D and A-D pair, are shown in Fig. 7. As expected, the results for the D-D pair are quite similar to those for the benzene pair since the D bead represents an aromatic ring. The PMF from the six-pair setup is slightly more repulsive than that from the one-pair setup at short separations. However, for the A-D pair, the correction introduced by the six-pair setup is quite significant. The location of the PMF minimum shifts from about 4 Å to about 6 Å, which indicates that the PMF from the six-pair setup is much more repulsive than that from the one-pair setup when the two corresponding atomic groups approach each other. The PMFs for other pairs also show shifts comparable to those shown in Figs. 7(a) and (b).

2. Entropic Corrections of Coarse-Grained Nonbonded Interactions

The six-pair setup discussed above has improved the PMF calculations and enabled the resulting coarse-grained force field to better capture the many-body nature of nonbonded interactions between atomic groups. However, the coarse-grained force field is still too attractive, leading to a polymer density higher than that from the atomistic model. An entropic correction can be introduced to the nonbonded, van der Waals PMF.[80, 92] 

\[
U(r) = -\int_{r_m}^{r} \left( \langle f_c \rangle_s + \frac{2k_B T}{s} \right) ds
\]

\[
= -\int_{r_m}^{r} \langle f_c \rangle_s ds - 2k_B T \ln \left( \frac{r}{r_m} \right) , \tag{16}
\]

where the term $2k_B T \ln \left( \frac{r}{r_m} \right)$ is included to account for the entropic volume contribution. This contribution can be written as $2k_B \ln r$ as the volume sampled by the two atomic groups, which have a fixed center-to-center separation, $r$, and can rotate around each other, scales as $r^2$.[80, 92] Correspondingly, an entropic correction term, 

\[
\delta \langle f_c \rangle = k_B T_2 \frac{2}{r} , \tag{17}
\]

should be added to the force between the two groups from the directly computed PMF. Note that the factor 2 in the above expression only reflects the fact that the sampled volume scales with $r^2$. In practice there is a prefactor in the expression of the sampled volume and therefore the entropic correction term in the force can be more generally written as

\[
\delta \langle f_c \rangle = k_B T_{\alpha} \frac{\alpha}{r} , \tag{18}
\]

where $\alpha$ is treated as a fitting parameter that can be tuned to render the coarse-grained force field to better
match the atomistic one. In this paper, a coarse-grained force field including an entropic correction term as shown in Eq. (18) is termed a CG\(\alpha\) model.

To find the optimized value of \(\alpha\), we built an atomistic system consisting of 64 branched polyetherimide chains using MAPs.[81] The system was first heated to 800K and relaxed at that temperature for 5 ns. Then the system was cooled down to 300K within 5 ns. During these steps, the pressure of the system was kept to be one atmosphere. The configuration of the system during the cooling process at a given temperature (between 300 K and 800 K) was taken as a starting state for computing the density of the branched polyetherimide. At each temperature, the system was first relaxed for 3 ns and its density was calculated in the subsequent 2 ns using an NPT ensemble. For the coarse-grained system, the same density was calculated in the subsequent 2 ns using an NPT ensemble. For the coarse-grained system, the same density was calculated in the subsequent 2 ns using an NPT ensemble. For the coarse-grained system, the same density was calculated in the subsequent 2 ns using an NPT ensemble.

We find that a single value of \(\alpha\) is sufficient to cause the density of the branched polyetherimide from the CG\(\alpha\) model to match that from all-atom MD simulations at a given \(T\). For example, \(\alpha = 1.97\) for \(T = 300\) K, as shown in Fig. 8. However, when temperature is raised, the CG\(\alpha\) model predicts a more compressible polymer system than the atomistic model. For example, at \(T = 600\) K, the CG\(\alpha\) model gives a density 1.031 g/cm\(^3\) for the branched polyetherimide, while the density from the atomistic model at this temperature is higher at 1.150 g/cm\(^3\).

![FIG. 8. Density (\(\rho\)) of the branched polyetherimide as a function of temperature (\(T\)) from all-atom MD simulations (\(\bigcirc\)), the CG\(\alpha\) model (\(\square\)), and the CG\(\alpha\)\(^n\) model (\(\triangle\)).](image)

Later we will discuss the results on the mechanical properties of the branched polyetherimide from the CG\(\alpha\) model, which are significantly different from those from the all-atom model as well as experimental values. In order to improve the coarse-grained model, we find out that the entropic correction term in the force should be modified as

\[
\delta(f_r) = k_B T^\alpha n r_0 \left(\frac{r_0}{r}\right)^n ,
\]

where \(n\) is an additional fitting parameter and \(r_0\) is the separation between a pair of atomic groups at which their mutual force from the PMF calculation reaches minimum (i.e., where the force is most attractive). The rationale behind this modification is that the entropic correction should be more significant at small separations between a pair of atomic groups, where all-atom MD simulations are limited in terms of efficiently and sufficiently sampling all possible configurations of the pair. The form of the entropic correction term in Eq. (19) guarantees that it is negligible if \(r \gg r_0\) and its importance grows in a power law for \(r < r_0\). The coarse-grained force field with Eq. (18) as the entropic correction term is designated as the CG\(\alpha\)\(^n\) model.

Since the CG\(\alpha\)\(^n\) model has two fitting parameters, \(\alpha\) and \(n\), we can tune the model to have a density match with the atomistic model at two temperatures. As shown in Fig. 8, with \(\alpha = 0.395\) and \(n = 15\), the density of the branched polyetherimide from the CG\(\alpha\)\(^n\) model matches that from the all-atom model at both \(T = 300\) K and 600 K. Furthermore, without further tuning the densities at other intermediate temperatures also match between the CG\(\alpha\)\(^n\) and all-atom model. That is, the CG\(\alpha\)\(^n\) model captures the thermal expansion property of the branched polyetherimide from the atomistic model. This turns out to be a key point of making the coarse-grained model to better capture the mechanical properties of the branched polyetherimide, as discussed below.

It should be clarified that the six-pair setup for PMF calculations and the entropic correction in either Eq. (18) or Eq. (19) are both needed as complementary steps to improve a coarse-grained model. If the six-pair setup was not used, then we would need to have a separate \(\alpha\) or \((\alpha, n)\) combination for each pair of atomic groups (i.e., for each PMF) in order to achieve a density match at one temperature for the CG\(\alpha\) model or a range of temperatures for the CG\(\alpha\)\(^n\) model. The number of fitting parameters would be too many for an optimization process to quickly converge. With the six-pair setup, just one \(\alpha\) or one \((\alpha, n)\) combination is needed for all the PMFs in the CG\(\alpha\) model or the CG\(\alpha\)\(^n\) model, respectively. The data for all the 15 PMFs based on the CG\(\alpha\) model are included in the Supporting Information.

**IV. APPLICATIONS OF THE COARSE-GRAINED MODEL OF THE BRANCHED POLYETHERIMIDE**

In this section we apply the coarse-grained models developed previously to study the mechanical, structural, and rheological properties of the branched polyetherimide. We show that the CG\(\alpha\)\(^n\) model reasonably captures
these properties. More applications of this model to other polyetherimides will be reported in the future.

A. Mechanical Moduli

We compute the mechanical moduli of the branched polyetherimide with both atomistic and coarse-grained models. The setup of such simulations is shown in Fig. 9. A system of polyetherimide chains (64 atomistic chains or 1000 coarse-grained chains; each chain contains 3 branches with one branch shown in Fig. 4) is first equilibrated in a NPT ensemble at 300 K and 1 atmosphere. Periodic boundary conditions are used in all directions. After equilibration, the simulation box size is 62.2 Å × 62.2 Å × 62.2 Å for the atomistic system and 155.7 Å × 155.7 Å × 155.7 Å for the coarse-grained system. A NVT ensemble is used from this point forward and the stress tensor of the equilibrated system is computed as a reference. Then either a tensile or shear strain is applied to deform the simulation box, as shown in Fig. 9. After deformation, the system is relaxed to remove transient effects and the stress tensor under the given strain is computed. The change of the stress tensor is analyzed as a function of the applied strain, which yields the mechanical moduli as well as Poisson’s ratio of the materials.

![Figure 9. Setup of simulations used to compute the mechanical moduli of the branched polyetherimide. The polymer domain undergoes either a tensile deformation [(a)→(b)] and a simple shear [(a)→(c)].](image)

For an isotropic material, its mechanical moduli are determined by only two independent parameters, $\lambda$ and $\mu$, where $\lambda$ is Lamé’s first parameter and $\mu$ is Lamé’s second parameter or the shear modulus of the material. The mechanical moduli are then given by

$$K = \lambda + \frac{2\mu}{3}$$,

$$G = \mu$$,

$$E = \mu \left( \frac{3\lambda + 2\mu}{\lambda + \mu} \right)$$,

$$\nu = \frac{\lambda}{2(\lambda + \mu)}$$,  \hspace{1cm} (20)

where $K$ is the bulk modulus, $G$ is the shear modulus, $E$ is Young’s modulus, and $\nu$ is Poisson’s ratio.

Lamé’s parameters can be determined by computing the stiffness tensor,

$$C = \begin{bmatrix}
\lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu
\end{bmatrix}.$$  \hspace{1cm} (21)

The matrix element $C_{ij}$ can be computed from $C_{ij} = \sigma_i / \epsilon_j$, where $\epsilon_j$ is a component of the strain tensor and $\sigma_i$ is a component of the corresponding stress tensor with both tensors expressed in a vector form. The subindices, $i$ and $j$, each running from 1 to 6, denote the $xx$, $yy$, $zz$, $yz$, $xz$, and $xy$ components, respectively, of the stress or strain tensor expressed in a $3 \times 3$ matrix form in a three-dimensional Cartesian system. In particular, $\sigma_1 = \sigma_{xx}$, $\sigma_2 = \sigma_{yy}$, $\sigma_3 = \sigma_{zz}$, $\sigma_4 = \sigma_{yz}$, $\sigma_5 = \sigma_{xz}$, and $\sigma_6 = \sigma_{xy}$ for the stress tensor. For the strain tensor, $\epsilon_1 = \epsilon_{xx}$, $\epsilon_2 = \epsilon_{yy}$, $\epsilon_3 = \epsilon_{zz}$, $\epsilon_4 = 2\epsilon_{yz}$, $\epsilon_5 = 2\epsilon_{xz}$, and $\epsilon_6 = 2\epsilon_{xy}$. Therefore, $\epsilon_1$ is a tensile strain along the $x$-axis while $\epsilon_4$ is twice the shear strain applied along the $y$-axis on a surface perpendicular to the $z$-axis, and so on.

We first use tensile deformations to compute the top-left block of the stiffness tensor. Then Lamé’s parameters are computed via

$$\lambda = \frac{1}{6} (C_{12} + C_{13} + C_{21} + C_{23} + C_{31} + C_{32})$$  \hspace{1cm} (22)

$$\mu = \frac{1}{6} (C_{11} + C_{22} + C_{33} - 3\lambda).$$  \hspace{1cm} (23)

Shear deformations are also simulated to determine $\mu$ and the results are consistent with those from tensile deformations.

![Table IV. Mechanical moduli and Poisson’s ratio of the branched polyetherimide at 300 K. The unit of $K$, $G$, $E$, and $\lambda$ is GPa. The row of $\nu$ and the column for the parameter $w$ are dimensionless.](image)

| Atomistic CGa | CGa n | Experimental | $w$ |
|--------------|-------|--------------|-----|
| $K$ | 4.185 | 0.727 | 2.110 | 4.297–4.942 | 0.50 |
| $G$ | 0.770 | 0.120 | 0.469 | 1.059–1.070 | 0.61 |
| $E$ | 2.178 | 0.342 | 1.311 | 2.965 | 0.60 |
| $\lambda$ | 3.671 | 0.647 | 1.797 | 3.584–4.236 | 0.49 |
| $\nu$ | 0.413 | 0.422 | 0.397 | 0.385–0.400 | |

The results on the mechanical moduli of the branched polyetherimide are computed with the atomistic, CGa, and CGa n models and are summarized in Table IV for $T = 300$ K and in Table V for $T = 400$ K. The experimental values at $T = 300$ K are also included in Table IV. All models yield very good results on Poisson’s ratio that match with the experimental value. Regarding the mechanical moduli, the data further show that the results
FIG. 10. Comparison of pair correlation functions, \( g(r) \), from the atomistic model (black solid line) and the \( \text{CG}^n \) model (blue dashed line) for all pairs of atomic groups or corresponding coarse-grained beads. The types of coarse-grained beads are defined in Fig. 4.

TABLE V. Mechanical moduli and Poisson’s ratio of the branched polyetherimide at 400 K. The unit of \( K, G, E, \) and \( \lambda \) is GPa. The row of \( \nu \) and the column for the parameter \( w \) are dimensionless.

|        | Atomistic | \( \text{CG}_\alpha \) | \( \text{CG}^n_\alpha \) | \( w \) |
|--------|-----------|------------------------|------------------------|-----|
| \( K \) | 3.754     | 0.345                  | 1.724                  | 0.46|
| \( G \) | 0.653     | 0.0167                 | 0.310                  | 0.47|
| \( E \) | 1.852     | 0.0491                 | 0.879                  | 0.47|
| \( \lambda \) | 3.319   | 0.334                  | 1.517                  | 0.46|
| \( \nu \) | 0.418     | 0.476                  | 0.415                  | 0.415|

from the atomistic model are close to the experimental ones and the \( \text{CG}^n_\alpha \) model is significantly improved from the \( \text{CG}_\alpha \) model in terms of matching the atomistic model. It is also interesting to notice that if we define \( w \) as the ratio between the value of a mechanical modulus from the \( \text{CG}^n_\alpha \) model and that from the atomistic model, then its value is around 0.5 for all mechanical moduli at either \( T = 300 \text{ K} \) or 400 K. This comparison indicates that the \( \text{CG}^n_\alpha \) model developed in this paper is able to capture the mechanical properties of the branched polyetherimide with an almost constant scaling factor about 0.5 and is transferable temperature-wise.

The much improved performance, including temperature transferability, of the \( \text{CG}^n_\alpha \) model is due to the fact that it captures the thermal expansion property of the branched polyetherimide when compared to the atomistic model. This behavior can be explained with the Grüneisen law that uses a parameter, \( \gamma \), to describe the effect of a changing temperature on the size and dynamics of a crystal lattice. One expression of \( \gamma \) is

\[
\gamma = \frac{\alpha_V K}{C_V \rho},
\]

where \( \alpha_V \) is the volume thermal expansion coefficient and \( C_V \) is the constant-volume heat capacity of the crystal. The physical implication of the Grüneisen law is that the thermal expansion behavior of a crystal, or more generally a solid, is intrinsically connected to its mechanical properties.[93–97] If we assume the Grüneisen law also applies to polyetherimides, then the law indicates that the ratio \( \gamma C_V / K \) should be the same for the atomistic and the \( \text{CG}_\alpha \) model as they yield matching polymer densities as well as volume thermal expansion coefficients. The fact that the value of \( K \) from the \( \text{CG}^n_\alpha \) model is about 50% of that from the atomistic model thus indicates that \( \gamma C_V \) should scale similarly between the two models.

### B. Pair Correlation Functions

We have computed the pair correlation functions, \( g(r) \), of all the 15 pairs of the atomic groups defined in Fig. 4 with all-atom MD simulations and the corresponding coarse-grained beads with the \( \text{CG}^n_\alpha \) model. The comparison is shown in Fig. 10. The locations of peaks in \( g(r) \) generally match well but their heights differ signifi-
cantly. The results of \( g(r) \) from the atomistic model indicates that the arrangement of the atomic groups in the branched polyetherimide are rather structureless, particularly beyond the first peak of \( g(r) \). On the other hand, the coarse-grained beads show more local ordering as evidenced by a strong first peak in \( g(r) \) for almost all the pairs. Beyond the first peak, the pair correlation functions of the coarse-grained beads match reasonably well with those of the corresponding atomic groups. The results in Fig. 10 are not surprising as \( g(r) \) never enters the process when the coarse-grained model is constructed. The discrepancy, which is acceptable from our perspective, is the price that has to be paid since our goal is to make the coarse-grained model transferable and expandable.

### C. Shear Rheology

![Graph showing shear viscosity as a function of shear rate](image)

**FIG. 11.** Shear viscosity as a function of shear rate from experiments (\( \triangle \) for a branched polyetherimide with \( M_n = 18.8 \text{ kDa} \) and \( \square \) for a linear polyetherimide with \( M_n = 20 \text{ kDa} \), by courtesy of Long and Wolfgang) and MD simulations (\( \bigcirc \) for a branched polyetherimide with \( M_n = 2.74 \text{ kDa} \)). For all systems, \( T = 563 \text{ K} \).

Finally, we apply the CG\(_n\) model discussed above to study the rheological properties of the branched polyetherimide. The simple-shear setup shown in Fig. 9 was used to compute the viscosity of the polymer in a triclinic simulation box under a given shear rate. The system consisted of 8000 branched polyetherimide chains with \( M_n = 2.74 \text{ kDa} \) initially in a cubic simulation box with side length 315.38 Å. The temperature was fixed at \( T = 563 \text{ K} \), at which the branched polyetherimide formed a melt. This was also the temperature at which the experimental data on viscosity were obtained. At a fixed shear rate, the shear stress in the melt was computed in MD simulations with the CG\(_n\) force field and used to determine the viscosity. The MD data for shear rates ranging from \( 10^6 \text{ s}^{-1} \) to \( 10^1 \text{ s}^{-1} \) are shown in Fig. 11, together with the experimental data for a branched polyetherimide with \( M_n = 18.8 \text{ kDa} \) and a linear polyetherimide with \( M_n = 20 \text{ kDa} \). The shear thinning behavior is obvious from both MD and experimental results. Furthermore, the upper range of the experimentally-probed shear rates is about \( 10^4 \text{ s}^{-1} \) to \( 10^5 \text{ s}^{-1} \). The CG\(_n\) model enables us to approach the experimental range of shear rates as well as the range of low shear rates where the Newtonian plateau occurs.

### V. Conclusions

We have developed a coarse-grained model of a branched polyetherimide on the basis of chemistry-informed grouping of atoms, parameterization of bond and angle interactions by fitting the distributions of bond lengths and angles to Gaussian functions, and parameterization of nonbonded interactions via potential of mean force calculations. Our results show that a six-pair setup, in which one atomic group is placed at the origin and six replicates of another atomic group are placed around the central group in a NaCl structure, can be used to improve configuration sampling in the potential of mean force calculations and an entropic correction term can be introduced to make the coarse-grained model to capture the thermal expansion property of the polymer. This latter strategy turns out to be the key to making the coarse-grained model transferable temperature-wise and a physical argument is provided to explain this observation. As a result, the coarse-grained model has captured the mechanical moduli of the branched polyetherimide within a (temperature-independent) constant scaling factor, which is around 0.5 here. The coarse-grained model further enables us to approach the range of shear rates accessible to rheology experiments and probe the polymer’s rheological behavior such as shear thinning. The coarse-grained model only fairly captures the structural property of the polymer and future improvements are still needed in this respect.

### Acknowledgments

This article is based on the results from work supported by SABIC. The authors gratefully acknowledge many stimulating discussions with Dr. Timothy E. Long and Dr. Guoliang (Greg) Liu. The authors thank Dr. Timothy E. Long and Mr. Josh Wolfgang for providing the experimental data in Fig. 11. The authors acknowledge Advanced Research Computing at Virginia Tech (URL: http://www.arc.vt.edu) for providing computational resources and technical support that have contributed to the results reported within this article. The authors also gratefully acknowledge the support of NVIDIA Corporation with the donation of the Tesla K40.
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[7] Summary of abbreviations and acronyms of chemical formulae. BPA: 4,4'-isophenol A dianhydride; MPD: m-phenylenediamine; PA: phthalic anhydride; TAPE: tris[4-(4-aminophenoxy)phenyl]ethane; ODPA: 4,4'-oxydipthalic anhydride; APB: bis-aminophenoxybenzene; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; aBPA: 2,3',4,4'-biphenyltetracarboxylic dianhydride; ODA: oxydianiline; R dianhydride: 1,3-bis(3',4-dicarboxyphenoxy)benzene dianhydride; BAPB: 4,4'-bis-(4'-aminophenoxy)-diphenyl; BAPS: 4,4'-bis-(4'-aminophenoxy)-diphenyloxide; P3 diamine: 1,4-bis(4-(4-aminophenoxy)phenoxy)benzene; PMDA: pyromellitic dianhydride; 6FDA: 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride; PFD: p-phenylenediamine; 4-PEPA: 4-Phenylethynylphthalic anhydride; BTDA: benzophenone-3,3',4,4'-tetracarboxylic dianhydride; MDA: 4,4'-methyleneedianiline; NA: 5-norbornene-2,3-dicarboxylic anhydride; BCDA: bicyclo[2.2.2]octylene-2,3,5,6-tetrahydrophthalic dianhydride; CF3ODA: 2-trifluoro-4,4'-oxydianiline; MeOODA: 2-methoxy-4,4'-oxydianiline; DDS: diamino diphenylsulfone.

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S1. Equivalence between the “Recentering” and Constraint-Force Schemes of Fixing a Center of Mass

Here we prove the equivalence between the “recentering” and constraint-force schemes of fixing the center of mass of a group of atoms. We first examine the movement of each atom in the “recentering” approach. We use \( \vec{f}_i \) to denote the total force on the \( i \)-th atom in a group from its interactions with all other atoms in the system. Then after an infinitesimal time \( dt \), the velocity of this atom becomes

\[
\vec{v}_i(t + dt) = \vec{v}_i + \frac{\vec{f}_i}{m_i} dt ,
\]

and the displacement of this atom is

\[
d\vec{r}_i = \vec{v}_i dt + \frac{1}{2} \vec{f}_i (dt)^2 ,
\]

where \( \vec{v}_i \) is the velocity of the \( i \)-th atom at time \( t \), and \( m_i \) is its mass. To fix the center of mass, we require \( \vec{v}_i \) to satisfy \( \sum_i m_i \vec{v}_i = 0 \), where the summation is over all atoms in the group under consideration. The displacement of the group’s center of mass before “recentering” is therefore

\[
d\vec{R} = \sum_i m_i \vec{r}_i dt = \sum_i m_i \vec{v}_i dt + \frac{1}{2} \sum_i m_i (dt)^2 .
\]

During “recentering”, each atom in the group is displaced by \(-d\vec{R}\) to move the group’s center of mass back to its starting location and the renormalized displacement of the \( i \)-th atom becomes

\[
d\vec{r}_{i,R} = d\vec{r}_i - d\vec{R} = \vec{v}_i dt + \frac{1}{2} \vec{f}_i (dt)^2 - \frac{1}{2} \sum_i m_i (dt)^2 .
\]

It is easy to prove that \( \sum_i (m_i \times d\vec{r}_{i,R}) = 0 \), indicating that the center of mass is fixed. The velocity of the center of mass, \( \vec{v}_c \), before “recentering” is

\[
\vec{v}_c = \frac{\sum_i \vec{f}_i}{\sum_i m_i} dt .
\]

When this velocity is subtracted from the velocity of each atom in the group, the renormalized velocity of the \( i \)-th atom becomes

\[
\vec{v}_{i,R}(t + dt) = \vec{v}_i(t + dt) - \vec{v}_c = \vec{v}_i + \frac{\vec{f}_i}{m_i} dt - \frac{\sum_i \vec{f}_i}{\sum_i m_i} dt .
\]

The velocity of the group’s center of mass after “recentering” is reduced to zero, i.e., \( \sum_i [m_i \times \vec{v}_{i,R}(t + dt)] = 0 \). As expected, “recentering” renders the center of mass of the group fixed.

Next, we consider the constraint-force approach by applying an extra constraining force, \( \vec{f}_{i,C} \), to the \( i \)-th atom in the group. The velocity of the \( i \)-th atom after an infinitesimal time \( dt \) is

\[
\vec{v}_{i,C}(t + dt) = \vec{v}_i + \vec{f}_{i,C} m_i dt ,
\]

and its corresponding displacement is

\[
d\vec{r}_{i,C} = \vec{v}_i dt + \frac{1}{2} \vec{f}_{i,C} m_i (dt)^2 .
\]
It is easy to show that if
\[ \vec{f}_{i,C} \equiv -m_i \sum_j \vec{f}_j \sum_j m_j, \tag{33} \]
then
\[ d\vec{r}_{i,C} = d\vec{r}_{i,R} \quad \text{and} \quad \vec{v}_{i,C}(t + dt) = \vec{v}_{i,R}(t + dt). \tag{34} \]
This proves that the “recentering” and constraint-force schemes are equivalent. Furthermore, it can be noted that
\[ \sum_i \vec{f}_{i,C} = -\sum_i \vec{f}_i, \tag{35} \]
and
\[ \sum_i \vec{r}_i \times \vec{f}_{i,C} = 0, \tag{36} \]
where \( \vec{r}_i \) is the position vector of the \( i \)-th atom relative to the group’s center of mass. Eqs. (35) and (36) are two natural requirements of the constraint-force scheme of fixing a center of mass. That is, the total force from the constraints should balance the total force exerted on all atoms in the group by other atoms in the system, which makes the acceleration of the center of mass to be zero. When the initial velocity of the center of mass is zero, it is naturally fixed. Furthermore, the constraint forces should have zero torque on the group to which they are applied. The rotation of the group around its center of mass is purely determined by the interactions with atoms in other groups.

S2. Additional Results on the Potential of Mean Force
Here we include additional results on the potential of mean force (PMF) among atomic groups mapped to the same coarse-grained beads in terms of van der Waals interactions but carrying different charges. As discussed in the main text, atomic group 1 is mapped to the same coarse-grained bead as groups 3 and 7 in terms of pairwise van der Waals interactions but the former carries a different charge from the latter two and a slightly higher mass (by ~ 0.7%) as well. Similarly, atomic groups 2 and 8, mapped to the same coarse-grained beads, have the same mass but different charges. In Fig. S1, the van der Waals PMF between a pair of #1 atomic groups is compared to that between a pair of #8 atomic groups. The PMF between #1 atomic group and #8 atomic group is compared to that between #3 atomic group and #2 atomic group. The results show that after the subtraction of the Coulombic part, the resulting van der Waals PMF is almost the same among the atomic groups mapped to the same coarse-grained beads, justifying the usage of only 5 types of coarse-grained beads for the nonbonded van der Waals interactions as discussed in the main text.

S3: Coarse-Grained Force Field of the Branched Polyetherimide
The following two files are available upon request: (1) The final coarse-grained force field of the branched polyetherimide, which can be read directly by LAMMPS; (2) A sample input script, which can be added to a LAMMPS script to read in this coarse-grained force field.
FIG. S1. The van der Waals PMF, $U(r)$, as a function of separation $r$, (a) for a pair of #1 atomic groups (circles) and a pair of #3 atomic groups (squares); (b) for a pair of #2 atomic groups (circles) and a pair of #8 atomic groups (squares); (c) between #1 atomic group and #8 atomic group (circles) and between #3 atomic group and #2 atomic group (squares). In (d), the mean force, $F(r)$, between #1 atomic group and #8 atomic group (circles) and between #3 atomic group and #2 atomic group (squares) is plotted against $r$. The atomic groups are defined in Table I of the main text.