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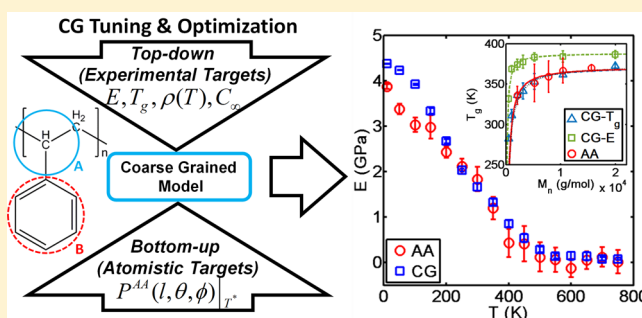
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Thermomechanically Consistent and Temperature Transferable Coarse-Graining of Atactic Polystyrene

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ABSTRACT: We present a systematic, two-bead per monomer coarse-graining strategy allowing for the prediction of the thermomechanical behavior of polystyrene. Analytical bonded potentials optimized to match atomistic bonded distributions for different stereochemistries emulate local structure. Alternatively, the backbone torsional potential is leveraged to match the chain stiffness in a direct approach. Nonbonded potentials using a temperature-dependent density correction term demonstrate transferability of the temperature-dependent modulus. Flory–Fox constants of the T_g -optimized CG model are commensurate with all-atomistic and experimental results. The thermomechanically consistent coarse-graining (TCCG) procedure is demonstrated using polystyrene as a benchmark system to be a robust and effective technique to extend the computational prediction of the thermomechanical behavior of polymers to the mesoscale.



1. INTRODUCTION

The defining characteristics of polymer materials are a result of different structural and dynamic behaviors occurring over a large range of length and time scales. Coarse-graining (CG) removes less essential atomistic features to probe attributes of interest occurring over larger spatiotemporal scales that would otherwise be inaccessible to more detailed models. This can be achieved by combining select groups of atoms into fewer interaction sites or “beads” using an appropriate atomistic-to-CG mapping scheme.^{1–3} Chemical specificity can then be inserted into the CG model through matching atomistic structural features (bottom-up) or directly tuning to match macroscopic properties (top-down).⁴ More recently, many CG studies have taken a hybrid approach, combining both bottom-up and top-down strategies. The increased efficiency of CG models enable studies of higher length and time scale behavior such as viscoelasticity,^{5–7} phase transformation,^{8–10} self-assembly,^{11–13} and interface effects.^{14,15}

Polystyrene (PS), is one of the most prevalent thermoplastic polymers in industrial applications and experimental properties for comparison are widely available. It is therefore often chosen as a benchmark system for polymer physics and molecular dynamics (MD) studies, and all-atomistic,¹⁶ united atom force fields,^{17,18} and CG models have been generated for PS.^{1–3,19–32} Each CG force field has been parametrized using a different procedure and bead mapping scheme, as the intended end-usage of the model and target properties are unique. Milano et al.,²⁰ Sun et al.,²⁵ and Qian et al.²³ used the inverse Boltzmann iterative (IBI) method^{2,30} for optimizing tabulated potentials and were able to reproduce well, the radius of gyration, R_g , and

characteristic ratio C_∞ of experimental PS. Harmandaris et al. used shifted Lennard-Jones (LJ) nonbonded potentials to demonstrate consistent chain structure, entanglement length, and pressure-dependent glass transition temperature in agreement with experiments.^{7,33} Fritz et al. further built upon the work of Harmandaris and co-workers by reparameterizing the model using the conditional reversible work³⁴ (CRW) method and accurately predicted the thermal expansion coefficient and glass transition temperature.^{14,21} Rossi et al. used MARTINI parameters originally developed for lipids and biomolecules to study polystyrene brushes in benzene solvent.^{15,24} More recently, Rosch et al.³² developed a PS CG model with the multiscale coarse-graining (MS-CG) procedure and utilized various methods, including shifting of the LJ pair potential to improve the stress-strain correlation.^{35–37}

CG models generally endure several main challenges. First, the many-body potential of mean force (PMF) concomitant with the atomistic system can only be feasibly approximated by effective pair potentials in the reduced order system.^{4,19} In addition, the balance between energetic and entropic contributions to the many-body PMF from the atomistic system are typically represented inaccurately by the effective pair potentials defined over the reduced CG configuration.^{4,19,38} This inherently reduces the ability for the CG model to simultaneously reproduce all properties accurately even at the thermodynamic state of calibration, known as the

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issue of *representability*.^{2,3,19} Therefore, the coarse-grain modeler must often be discriminatory in choosing the attributes to match according to the application in focus. Second, the target atomistic features used to define effective pair potentials in the CG model represent a thermodynamic state specific energy and entropy balance as well as a specific density. Consequently, the accuracy of the model to emulate properties is typically limited to only a small range of temperatures near the calibration state, which is known as the issue of *transferability*.^{3,4,19,23,39} Third, critical thermomechanical material properties such as the temperature-dependent elastic modulus have been difficult to emulate in the CG model due to reduced friction, altered dynamics, and inaccurate thermal expansion prediction resulting from loss of degrees of freedom and usage of softer, smoother potentials compared to the rough many-body PMF surface.^{8,19,32,40} We note that several CG models are able to predict dynamic quantities associated with the glass transition including the fundamental work performed by Tschöp and co-workers.^{10,14,33} However, thermomechanical properties such as the elastic modulus as a function of temperature and molecular weight have not been a primary focus.³ Still, direct prediction of these properties at the CG level is an increasing need for emerging mesoscopic applications such as copolymers, nanocomposites, and thin films. In these systems, relevant mechanical behavior occur over nanometer length scales, and a wide range of processing temperatures.^{41–44}

Therefore, the goal of the present study is to generate a computationally efficient CG model for PS, capable of directly predicting bulk thermomechanical properties while maintaining transferability of these predictions over temperature ranges at least 100 K above and below T_g and for various molecular weights above and below the entanglement length. We also aim to maintain chemical specificity by matching bonded target distributions from atomistic simulations and chain stiffness of the atactic system compared to experimental data.

In a recent study, we developed a systematic, thermomechanically consistent coarse-graining (TCCG) methodology for poly(methyl methacrylate) (PMMA) and four other methacrylate homopolymers.⁴⁵ We found that by tuning the nonbonded pairwise potential to match the glass transition behavior, we were able to replicate bulk properties such as molecular weight (M_n) dependent T_g and modulus in the elastic regime E for PMMA. In the context of this methodology, T_g is defined as the temperature at which the T -dependent molecular mobility of monomers within a polymer chain marks a distinct change in slope.⁴⁶ Building upon previous work, in the present study, a combination of bottom-up and top-down CG approaches are used. We correct the thermal expansion behavior by introducing a temperature-dependent density correction term into the pairwise potential and find that the resulting model is able to reproduce the elastic modulus compared to experiments over temperatures from 150 to 750 K. We also observe that T_g -optimized parameters replicate the molecular weight dependent T_g according to the Flory–Fox relation. We are able to demonstrate that coarse graining of polymers through a two-bead per monomer methodology with minimal parameters can be used to capture thermomechanical and structural behavior as a function of backbone and side-chain features. This methodology may provide a basis for an expanded CG parameter library of additional polymers in the future.

2. COARSE-GRAINING STRATEGY

Here we describe the general CG strategy followed in the present study. We optimize effective pair potentials to match target quantities using two overarching steps (see Figure 1).

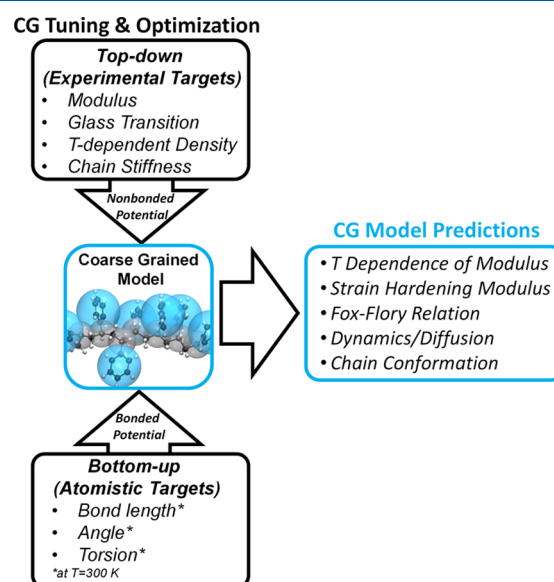


Figure 1. General coarse-graining strategy using a bottom-up and top-down framework.⁴ Top-down methods are used to directly tune the nonbonded parameters to match experimental and all-atomistic simulation material properties. A bottom-up strategy is used to optimize bonded interactions to reproduce local structure from atomistic simulation. The resulting CG model is tested to predict the transferable elastic modulus, strain hardening modulus, Flory–Fox parameters, chain conformation, and diffusion coefficients.

First, we use a bottom-up strategy to replicate the local structural characteristics of the atomistic system. This is done by optimizing CG bonded potentials to match the effective atomistic bonded distributions at a single temperature state point using the IBI method.^{2,30} Second, we use a top-down framework and perform a series of parametric studies to directly tune the nonbonded potential parameters to the elastic modulus E , glass transition temperature T_g , and density as a function of temperature $\rho(T)$. We also adjust the backbone dihedral potential to match the characteristic ratio C_∞ . The total CG potential is the sum of the bonded and nonbonded potentials.

$$U_{\text{total}}^{\text{CG}} = \sum U_{\text{bonded}}^{\text{CG}} + \sum U_{\text{nonbond}}^{\text{CG}} \quad (1)$$

We then measure the ability for the CG model to predict the following quantities compared to atomistically detailed simulations and experiments: (1) the temperature transferable elastic modulus $E(T)$, (2) stress–strain characteristics such as the strain hardening modulus G_R , (3) molecular weight dependent glass transition $T_g(M_n)$, (4) molecular weight dependent chain conformation, and (5) dynamic scaling.

2.1. Atomistic Target Distributions and Simulation Details. To perform bottom-up optimization of CG bonded structural terms, we begin by generating all-atomistic systems containing four chains, with a chain length of 75 monomers at 300 K. We justify the usage of relatively few and short chains as we find that bonded features in the glassy regime are largely independent of system size and chain length. Atactic, isotactic,

and syndiotactic systems are generated separately via a random-walk algorithm within Accelrys Materials Studio.⁴⁷ The initial structures are annealed until the experimental target density is achieved using the molecular dynamics package, LAMMPS⁴⁸ (release version April 12, 2013), with force field parameters consistent with DREIDING.⁴⁹ The energy of the system is minimized using the conjugate gradient algorithm,⁵⁰ followed by three annealing cycles, where the temperature is elevated from 300 to 750 K at a rate of 4.5 K/ps and then lowered back to 300 K at the same rate. We then apply the Nosé–Hoover barostat set at a high pressure of 10 000 atm for 2.5 ns. Temporary high pressures are used within the annealing step in order to increase the rate of convergence to experimental density. After removal of high-pressure conditions and performing dynamics at 300 K under the NPT ensemble for 2 ns, we do not observe any residual stresses. This cycle allows the system local structure and thermodynamic properties of interest in the final state to no longer be dependent upon the starting configuration. We use a time step $\Delta t = 1$ fs, temperature damping parameter $T_{\text{damp}} = 100$ fs, and the pressure damping parameter $P_{\text{damp}} = 1000$ fs.

2.2. Atomistic to Coarse-Grain Mapping Scheme.

Target averaged distributions for effective bond lengths, angles, and dihedrals are generated from the atomistic simulations according to the following mapping scheme. We utilize a two-bead-per-monomer, coarse-grain mapping for polystyrene corresponding to an 8 to 1 reduction in the total number of atomistic to CG beads. The mapping scheme is similar to the CG models of Harmandaris^{21,26} and Rosch;³² however, the choice of bead centers and bond structure is unique. We elect to use a mapping strategy similar to our CG modeling approach for methacrylates in order to later perform comparison studies between PS and PMMA and to retain compatibility for future styrene–methacrylate copolymer studies. Each PS monomer is reduced to a single backbone bead and a single side chain CG bead (see Figure 2). The backbone bead (type “A”) center is located at the backbone carbon immediately bonded to the phenyl ring and incorporates the mass of the CH group and half of the mass of each neighboring methylene CH₂ group. The side-chain bead (type “B”) center is located at the center of

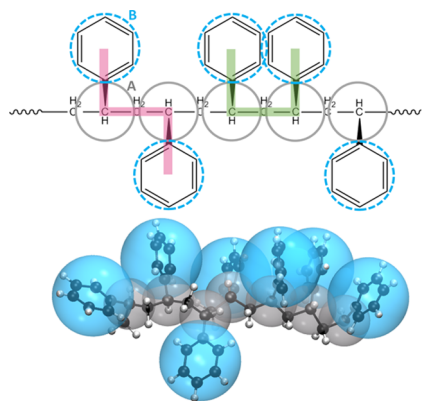


Figure 2. (top) Polystyrene atomistic to CG mapping showing coarse-grain bead center locations. Backbone type “A” beads are centered on the alkyl carbon bonded to phenyl ring. Side-chain type “B” beads are located at the center of mass of the phenyl ring. A random distribution of racemo (pink) and meso (green) diad torsional potentials are used to form the atactic system in the CG model. (bottom) The coarse grain model is shown superimposed over the atomistic model.

mass of the phenyl CH₅ moiety and incorporates the mass of the ring. The masses of beads A and B are 27.05 and 77.11 g/mol, respectively. All CG beads are taken to be spherical and therefore do not include phenyl ring orientation specific effects such as π – π stacking.⁵¹ This mapping choice allows for a well-defined, physically consistent bond structure and provides a relatively well-balanced mass ratio between the two bead types, 1:2.8.

2.3. Bonded Interaction Definition. We define bonded interactions to model an alkane backbone with branched pendant groups to be consistent with the general configuration of the atomistic chain (see Figure 2). Backbone A–A bonds are defined between two adjacent backbone type “A” beads. A–B bonds are defined between a backbone type “A” bead and its adjoining side chain type “B” bead. We also define a potential that describes the A–A–A bending angle along the backbone and the A–A–B bending angle. Finally, we define potentials for A–A–A–A and B–A–A–B torsions. A–A–A–B and B–A–A–A torsional and higher order bonded potentials beyond 1–4 interactions are not defined as we expect that the characteristic bonded features of the PS chain are captured by the aforementioned potentials.

2.4. Stereochemistry Definition. Asymmetric vinyl polymers such as polystyrene can be characterized by the stereoregular or stereoirregular orientation of the vinyl groups along the chain which significantly affects the resulting polymer behavior.^{21,52–54} Adjacent monomer pairs in the chain, called diads, are defined as meso if vinyl groups have the same orientation or racemo for vinyl groups having opposite orientation (see Figure 2). Atactic PS consists of a random distribution of meso and racemo diads along the chain. In our CG model, B–A–A–B dihedrals represent the torsional angle between consecutive pendant moieties in a diad which can be defined uniquely for meso and racemo diads. Dihedral distributions from isotactic atomistic simulations (containing all meso diads) are used as targets to optimize the set of CG meso dihedral potential parameters, while syndiotactic atomistic distributions (containing all racemo diads) are used as targets to optimize CG racemo dihedral parameters. Different stereoisomers can be defined in the CG model by assigning either all meso, racemo, or a random combination of each diad type. We use the latter combination for atactic PS. This two-bead CG methodology and mapping scheme can be adopted to represent tacticity in other asymmetric vinyl polymers as well.

2.5. Bonded Interaction Optimization Procedure. We use the inverse Boltzmann iterative (IBI) method to optimize all bonded potentials. These methods as well as many other coarse-graining techniques to develop CG effective pairwise potentials have been comprehensively investigated and we point the reader to several reviews for further details.^{1–4,6,19,27}

We choose to use analytically defined bonded potentials as they can provide certain advantages. For example, the use of simple functional forms can facilitate systematic variation of parameters for sensitivity analyses, physical interpretability can be obtained through spring constants from harmonic and Gaussian formulas,⁵⁵ and analytical potentials can also be more efficient to compute. We fit the inverted PDF with analytical formulas of the following forms:

$$U_{\text{bond}}(l) = k_{\text{bond}}(l - l_0)^2 \quad (2)$$

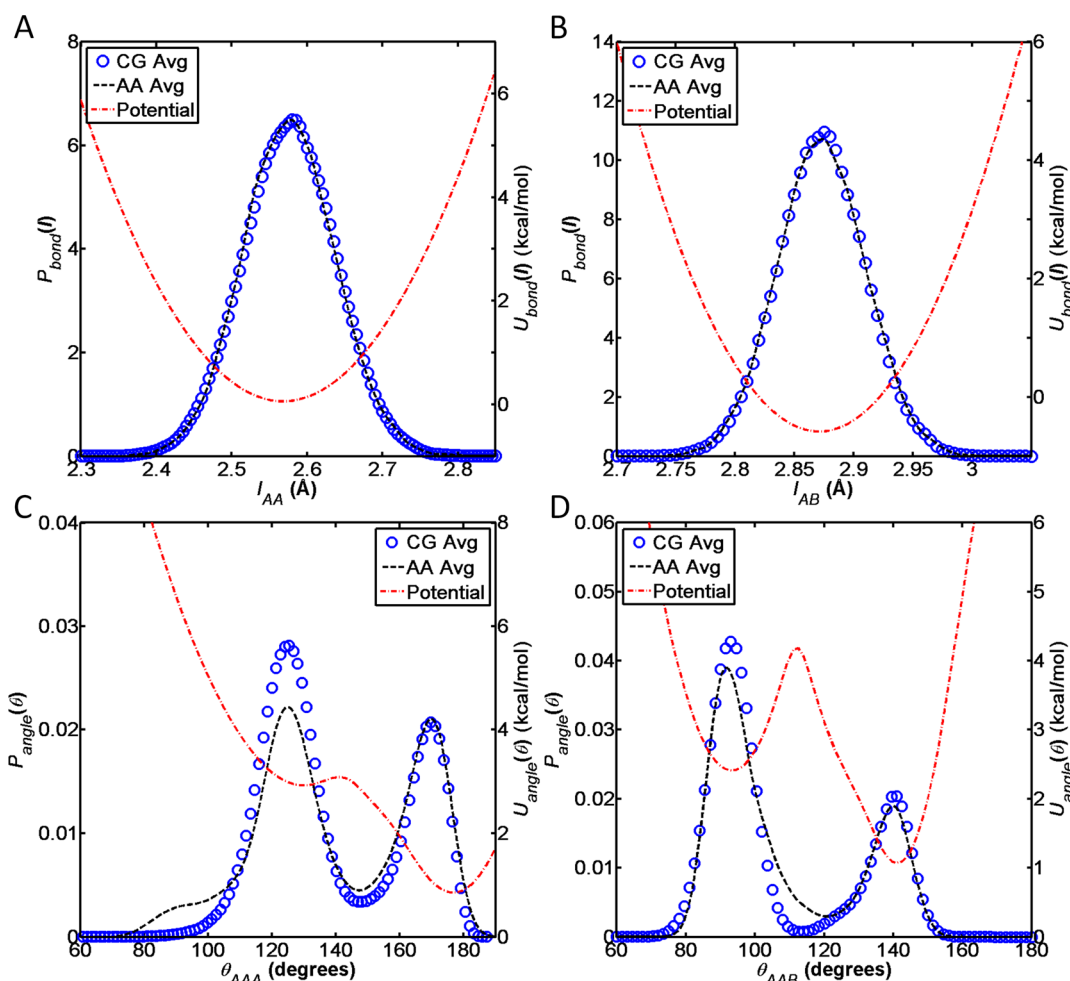


Figure 3. Bonded distributions and potentials for atactic polystyrene: (A) A–A bond length distribution, (B) A–B bond length distribution, (C) A–A–A angle distribution, and (D) A–A–B angle distribution.

$$U_{\text{angle}}(\theta) = -k_b T \ln \left[a_1 \exp \left(-\left(\frac{\theta - \theta_1}{b_1} \right)^2 \right) + a_2 \exp \left(-\left(\frac{\theta - \theta_2}{b_2} \right)^2 \right) + a_3 \exp \left(-\left(\frac{\theta - \theta_3}{b_3} \right)^2 \right) \right] \quad (3)$$

$$U_{\text{dihedral}}(\phi) = \sum_{k=1}^5 A_k \cos^{k-1}(\phi) \quad (4)$$

We use a simple harmonic equation (eq 2) to model the bond length potential, where k_{bond} is the energy constant and l_0 is the equilibrium bond length. The summation of three Gaussians is Boltzmann inverted (eq 3) to model the angle potential, where a_1 , a_2 , a_3 , b_1 , b_2 , and b_3 are fitting constants, and θ_1 , θ_2 , and θ_3 are the equilibrium angles. Finally, the dihedral angle is modeled using a multiharmonic equation (eq 4), where A_k are fitting constants in energy units.

Although the CG mapping is generally defined to maximize the independence of each interaction potential type, some degree of interdependence between potentials is unavoidable. Therefore, we sequentially introduce and optimize the potentials in the order of decreasing relative strength, starting with the strongest energy contributing interaction. This minimizes the amount of disruption to already-optimized

distributions and reduces the need for reoptimization. We use the sequence of optimization consistent with Reith et al.:²⁹

$$U_{\text{bond}} \rightarrow U_{\text{angle}} \rightarrow U_{\text{nonbond}} \rightarrow U_{\text{dihedral}}$$

In the case of the bond and angle potentials which are optimized before the nonbonded potential, only a smaller system of 5 chains, 100 monomers per chain is necessary since the bonded distributions depend mostly on local intrachain interactions. During each iteration of the bond and angle optimization, the CG bonded distribution is estimated from simulations in the NVT ensemble using a Nosé–Hoover thermostat at a condition of 300 K. We use a time step $\Delta t = 4$ fs and $T_{\text{damp}} = 400$ fs. Chains interact via a soft nonbonded potential during this step.

The CG mapping scheme used produces well-defined Gaussian peaks for both the A–A backbone bond length and A–B backbone–side chain bond length (see Figure 3A,B). The A–A–A and A–A–B angles both show distributions with two distinct peak values (see Figure 3C,D). Each A–A–A angle in the reduced model corresponds to two torsions between adjacent alkane carbons in the atomistic backbone. The various sequences of the two atomistic torsional values lead to the double peak structure in the A–A–A angles. For instance, the alkane backbone torsion in the atomistic system according to the DREIDING force field has a tendency toward $\sim 60^\circ$ synclinal and $\sim 180^\circ$ antiperiplanar (trans) conformations but

averts gauche conformations. We find that the $\sim 170^\circ$ peak in the effective A–A–A CG angle corresponds to two successive trans conformations and the $\sim 125^\circ$ peak corresponds to a synclinal followed by a trans torsion. Two synclinal dihedrals in succession lead to values near $\sim 100^\circ$, which can be observed in the atomistic distribution in Figure 3C; however, there is no appreciable peak. We neglect this feature in the CG model due to its relatively small size.

After bonds and angle parameters have been determined, the nonbonded potential is tuned through a parametric study which is described in the following two sections. Here we describe the procedure for developing A–A–A–A and B–A–A–B dihedral potentials which are optimized after the nonbonded potential and thus require a different relaxation procedure than the bonds and angles. We minimize a system containing 100 chains with 100 monomers each using the conjugate gradient algorithm, we perform a soft potential pushoff step, and then implement the full optimized potential. Next, we anneal the system by increasing the temperature from 300 to 750 K at a rate of 1.1 K/ps and then is decreased back to 300 K at the same rate. This cycle is repeated three times, and then a high-pressure condition (1000 atm) is applied in the NPT ensemble. We then remove the high-pressure condition and allow the system to return to its native density at 300 K and atmospheric pressure in the NPT ensemble. Note that all residual stresses that are removed during the final equilibration step in the glassy state are from finite compressibility within the elastic regime. Again, we have performed direct comparison tests and do not find that the temporarily applied high pressure affects the resulting structural distributions. The B–A–A–B dihedral shows similar features among different stereochemistries but each having distinct magnitudes. Isotactic meso diads show nearly equal preference for +anticlinal, –anticlinal, and synperiplanar angles ($+120^\circ$, -120° , and 0° , respectively) and a minimum for the antiperiplanar 180° angle (see Figure 4A). The propensity for 0° conformation is relatively high compared to the other tacticities, which is expected from meso diads that have side chain beads in the same orientation. The dihedral distribution for syndiotactic racemo diads show much higher preference for $+120^\circ$, -120° angles compared to 0° which is also expected (see Figure 4B). For the atactic system, no additional parametrization is performed. The optimized meso and racemo set of B–A–A–B parameters are randomly assigned to diads along the chain with an approximate 50–50 distribution. The resulting CG distribution, without any adjustment, matches very well with the all-atomistic system (see Figure 4C). Resulting peaks at $+120^\circ$, -120° , and 0° angles for the stereoirregular atactic system are approximate averages between the magnitude of the respective peaks for isotactic and syndiotactic systems (see Table 1 for bonded potential parameters).

The A–A–A–A dihedral angle formed by four consecutive backbone beads does not show any strong characteristic features and has a relatively flat unsymmetrical distribution with comparatively low-energy contribution. Therefore, we choose to leverage the A–A–A–A backbone dihedral potential to reproduce the chain stiffness. A similar chain-conformation-driven approach was also taken by Fritz et al., where they included bonded interactions beyond the 1–4 range to reproduce the proper stiffness for each PS tacticity.²¹ We implement a simple cosine potential of the form $U_{\text{dihedralAAAA}}(\phi) = A \cos(\phi)$ and tune the amplitude A to match the end-to-end length and characteristic ratio of the experimental system.

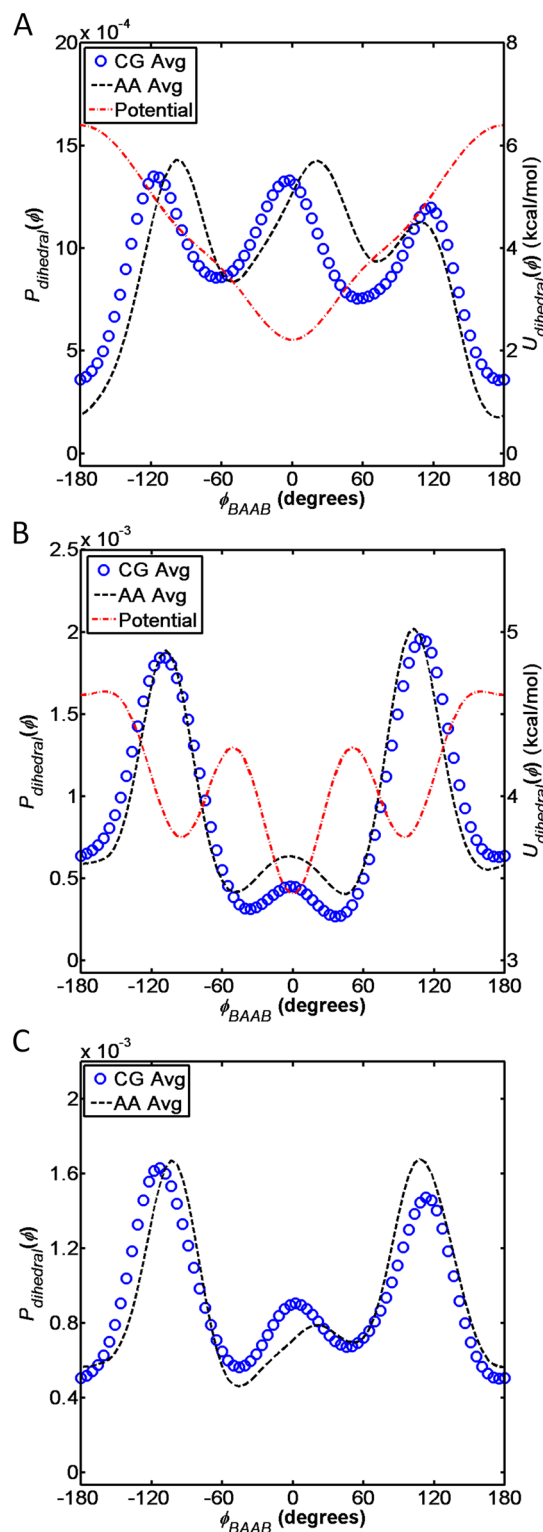


Figure 4. B–A–A–B dihedral distributions for atactic, isotactic, and syndiotactic PS: (A) B–A–A–B dihedral distribution for isotactic PS meso diad; (B) B–A–A–B dihedral distribution for syndiotactic PS racemo diad; (C) B–A–A–B dihedral distribution for atactic PS using a random distribution of meso and racemo torsional parameters.

The amplitude of the cosine potential is varied from 0.4 to 2.0 kcal/mol, and the resulting chain dimensional statistics are measured for 100 monomer chains at 450 K, which is below the entanglement length, using annealing and equilibration steps previously described. After performing the initial dihedral

Table 1. Functional Form of Force Field and Optimized Potential Parameters for PS

interaction	potential form	parameters		
A–A bond length	$U_{\text{bondAA}}(l) = k(l - l_0)^2$	$k = 80.69 \text{ kcal}/(\text{mol } \text{\AA}^2)$		
A–B bond length	$U_{\text{bondAB}}(l) = k(l - l_0)^2$	$l_0 = 2.568 \text{ \AA}$ $k = 224.6 \text{ kcal}/(\text{mol } \text{\AA}^2)$		
A–A–A angle	$U_{\text{angleAAA}}(\theta) = -k_b T \ln \left[a_1 \exp - \left(\frac{\theta - \theta_1}{b_1} \right)^2 + a_2 \exp - \left(\frac{\theta - \theta_2}{b_2} \right)^2 + a_3 \exp - \left(\frac{\theta - \theta_3}{b_3} \right)^2 \right]$	$a_1 = 2.277 \times 10^{-1}$ $b_1 = 10.76^\circ$ $\theta_1 = 177.1^\circ$	$a_2 = 5.588 \times 10^{-1}$ $b_2 = 19.27^\circ$ $\theta_2 = 148.8^\circ$	$a_3 = -5.497 \times 10^{-1}$ $b_3 = 18.78^\circ$ $\theta_3 = 148.5^\circ$
A–A–B angle	$U_{\text{angleAAB}}(\theta) = -k_b T \ln \left[a_1 \exp - \left(\frac{\theta - \theta_1}{b_1} \right)^2 + a_2 \exp - \left(\frac{\theta - \theta_2}{b_2} \right)^2 + a_3 \exp - \left(\frac{\theta - \theta_3}{b_3} \right)^2 \right]$	$a_1 = 1.451 \times 10^{-1}$ $b_1 = 6.762^\circ$ $\theta_1 = 141.5^\circ$	$a_2 = 1.767 \times 10^{-2}$ $b_2 = 9.745^\circ$ $\theta_2 = 93.22^\circ$	$a_3 = 3.199 \times 10^{-2}$ $b_3 = 11.01^\circ$ $\theta_3 = 134.7^\circ$
A–A–A–A dihedral angle	$U_{\text{dihedralAAAA}}(\phi) = A \cos(\phi)$	$A(\text{atactic}) = 0.5 \text{ (kcal/mol)}$		
B–A–A–B dihedral angle	$U_{\text{dihedralBAAB}}(\phi) = \sum_{k=1}^5 A_k \cos^{k-1}(\phi)$	<i>meso</i> $A_1 = 4.236 \text{ (kcal/mol)}$ $A_2 = -1.274 \text{ (kcal/mol)}$ $A_3 = 0.5337 \text{ (kcal/mol)}$ $A_4 = -0.8179 \text{ (kcal/mol)}$ $A_5 = -0.4622 \text{ (kcal/mol)}$ (see Table 2)	<i>racemo</i> $A_1 = 3.762 \text{ (kcal/mol)}$ $A_2 = 0.3631 \text{ (kcal/mol)}$ $A_3 = 2.128 \text{ (kcal/mol)}$ $A_4 = -0.9691 \text{ (kcal/mol)}$ $A_5 = -1.880 \text{ (kcal/mol)}$	
nonbonded	$U_{\text{nonbond}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + S_{\text{LJ}}(r)$			

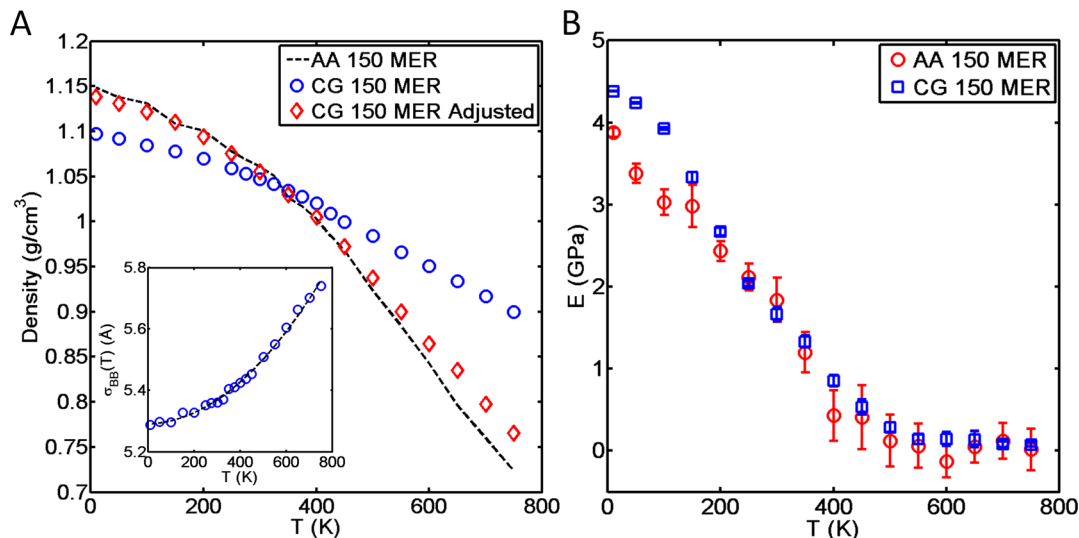


Figure 5. Density correction and all-atom vs CG temperature dependent modulus. (A) CG and all-atom density as a function of temperature before and after temperature dependent pairwise potential correction. The σ_{BB} value is adjusted as a function of temperature and fit with a polynomial function (inset). (B) E as a function of temperature for the CG 150 monomer system after density correction is compared to the all-atom modulus.

tuning step, a larger range of molecular weights are tested to ensure the chain stiffness converges to the experimental values. The resulting amplitude A used for the A–A–A–A dihedral cosine potential is 0.5 kcal/mol for the atactic system (see Table 1 and Figure 8A, inset).

2.6. Nonbonded Interaction Definition. Nonbonded interactions modeled using the LJ 12–6 potential are defined between backbone–backbone AA beads, backbone–side chain AB beads, and side chain–side chain BB beads. Along the chain, 1–2 and 1–3 nonbonded interactions are turned off and the full nonbonded potential is applied to 1–4 and higher bond order interactions. All beads are uncharged and no long-range Coulombic interaction is calculated in the CG model.

2.7. Nonbonded Interaction Optimization. Most previous CG models for PS optimize the nonbonded potential in a bottom-up manner to reproduce the radial distribution function (RDF) or potentials of mean force (PMF) of effective beads in the all-atomistic melt state.⁵ These methods usually do not demonstrate thermomechanical consistency for several reasons. First, although correct local distribution of beads is achieved, friction is reduced due to soft potentials and smoother potential energy landscape. In addition, temperature transferability of the system density currently cannot be guaranteed *a priori*,³⁸ and most models with RDF trained nonbonded potentials show deviation of the thermal expansion coefficient α obtained from experiments and atomistic simulations.^{21,23,39} Many studies use a linear perturbation

Table 2. Nonbonded 12–6 LJ Potential Parameters Tuned To Match T_g and Elastic Modulus E Separately

type	ϵ_{AA} (kcal/mol)	σ_{AA} (Å)	ϵ_{BB} (kcal/mol)	σ_{BB} (Å)	ϵ_{AB} (kcal/mol)	σ_{AB} (Å)
T_g optimization	0.285	4.421	0.812	5.421	0.481	4.921
E optimization	0.150	3.700	1.200	5.390 ^a	0.490	4.561

^aValue at $T = 300$ K; at other temperatures: $\sigma_{BB}(T) = 8.0 \times 10^{-7}T^2 + 2.4 \times 10^{-5}T + 5.3$.

correction step during IBI optimization of the nonbonded potential to effectively reproduce the pressure and density at a single temperature.²³ Previous results from methacrylate homopolymer coarse-graining using a two-bead per monomer resolution as well as results from Rosch et al. using both one- and two-bead resolutions for polystyrene showed that the elastic modulus cannot be effectively reproduced from purely bottom-up IBI optimization of the nonbonded potential to match atomistic RDF targets.^{32,45}

By increasing the pairwise potential energy well depth, we reintroduce a rough additive potential energy landscape which is necessary to both constrain segmental mobility associated with T_g and increase forces required to strain the material. We use the GROMACS style LJ nonbonded potential which has the form

$$U_{\text{nonbond}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + S_{\text{LJ}}(r) \quad (5)$$

where σ is a constant that defines the distance between two beads at which U_{nonbond} is zero and ϵ is the depth of the well in energy units. The polynomial term $S_{\text{LJ}}(r)$ shifts the full LJ potential at distances below an inner cutoff R_{inner} by a constant value and ensures a smooth transition to zero energy from the inner cutoff to the outer cutoff R_{outer} . We use $R_{\text{inner}} = 12$ Å and $R_{\text{outer}} = 15$ Å. In our two-bead per monomer model, we tune six different nonbonded parameters: σ_{AA} and ϵ_{AA} for backbone–backbone AA interactions, σ_{BB} and ϵ_{BB} LJ parameters for the side chain–side chain BB interaction, and σ_{AB} and ϵ_{AB} for cross-interactions. We perform a parametric full factorial Design of Experiments (DOE)⁵⁶ study to quantify the main effects of the respective parameters on the desired properties and optimize their values to concurrently match the experimental density (1.04 g/cm³),⁵⁸ experimental T_g from DSC measurements (~380 K),⁵⁷ and the elastic modulus (2.3–3.3 GPa) from uniaxial extension.⁵⁸

2.8. Density Transferability. Upon inspection of the temperature dependent density, shown in Figure 5A, we find that the CG model (blue circles) underpredicts the all-atom density (black dashed line) at temperatures lower than 300 K and overpredicts the density at temperatures higher than 300 K. The calculated thermal expansion coefficient α at 300 K is found to be $2.85 \times 10^{-4} \text{ K}^{-1}$, which is lower than the experimental⁵⁹ and all-atom systems, which are approximately 5.50×10^{-4} and $5.94 \times 10^{-4} \text{ K}^{-1}$, respectively. From parametric studies, we find that σ_{BB} has a strong linear effect on the density. We use this relationship to calculate the necessary value of σ_{BB} at each temperature to correct the density and subsequently fit the values with a continuous quadratic polynomial function of the form $\sigma_{BB}(T) = aT^2 + bT + c$, where $a = 8.0 \times 10^{-7} \text{ Å/K}^2$, $b = 2.4 \times 10^{-5} \text{ Å/K}$, and $c = 5.3 \text{ Å}$ (see Figure 5A, inset). This can be implemented into a temperature dependent form of the LJ potential for the side-chain nonbonded interaction:

$$U_{BB}(T) = 4\epsilon \left[\left(\frac{\sigma_{BB}(T)}{r} \right)^{12} - \left(\frac{\sigma_{BB}(T)}{r} \right)^6 \right] + S_{\text{LJ}}(r) \quad (6)$$

where $\sigma_{BB}(T)$ is the density corrected polynomial function also reported in Figure 5A inset and Table 2. We find that this methodology works well to correct the density (red diamonds in Figure 5A) over the full temperature range and predicts $\alpha = 5.30 \times 10^{-4} \text{ K}^{-1}$ over the range of 200–500 K, which is close to all-atom and experimental results. The resulting values of $\sigma_{BB}(T)$ range from 5.3 to 5.7 Å over an 800 K temperature range which are relatively close to the optimized value at 300 K. Note that the value of σ_{BB} has not changed at $T = 300$ K, and therefore modulus tuning results at 300 K remain unaltered. The elastic modulus at 300 K for the CG model is estimated around 1.7 GPa for the atactic system, which slightly underestimates the lower range of experimental results. However, this is consistent with the measured value for the atomistic model at 300 K, 1.7 GPa, as well as results from uniaxial deformation on a united atom model of PS reported by Lyulin et al., which was found to be approximately 1.9 GPa at 300 K for an 80 monomer per chain system.⁶⁰ We find also that the change in predicted T_g with and without density correction is within experimental error. Our final set of nonbonded parameters provide a $T_{g\infty}$ of about 386.5 K, which is within the range of experimental values^{68,69} (see Table 2 for nonbonded potential parameters). The method used for estimating T_g computationally is described in detail in section 3.2.

3. CG MODEL PREDICTIONS RESULTS AND DISCUSSION

3.1. Modulus vs Temperature Measurement. To measure the modulus of the all-atom or coarse-grain models at varying temperatures, we use the fix deform method implemented in LAMMPS. We start with relaxed systems at temperatures ranging from 750 to 10 K, which have been cooled at a rate of 0.1 K/ps. A uniaxial deformation is then applied to the simulation box according to a prescribed strain rate of $5 \times 10^8 \text{ s}^{-1}$. The same strain rate is used for the CG and all-atom resolution models, and the study is repeated for two chain lengths, 75 and 150 monomers per chain. The lateral sides are held under zero pressure in the NPT ensemble, allowing the axes orthogonal to the strain to deform without prescribing a Poisson's ratio. The system is deformed to 300% strain over a period of 2 ns. The E at each temperature is estimated by the linear fit of the stress–strain curve from 0 to 4%.

This is first performed on the CG model without the temperature-dependent density correction term to see how later addition of the term affects the transferability of thermomechanical properties. We find that below 300 K modulus is underpredicted by the CG model compared to all atom results due to lower predicted density, and modulus is overpredicted at temperatures above 300 K compared to all atom results due to higher predicted density in this temperature range. After applying the temperature dependent density

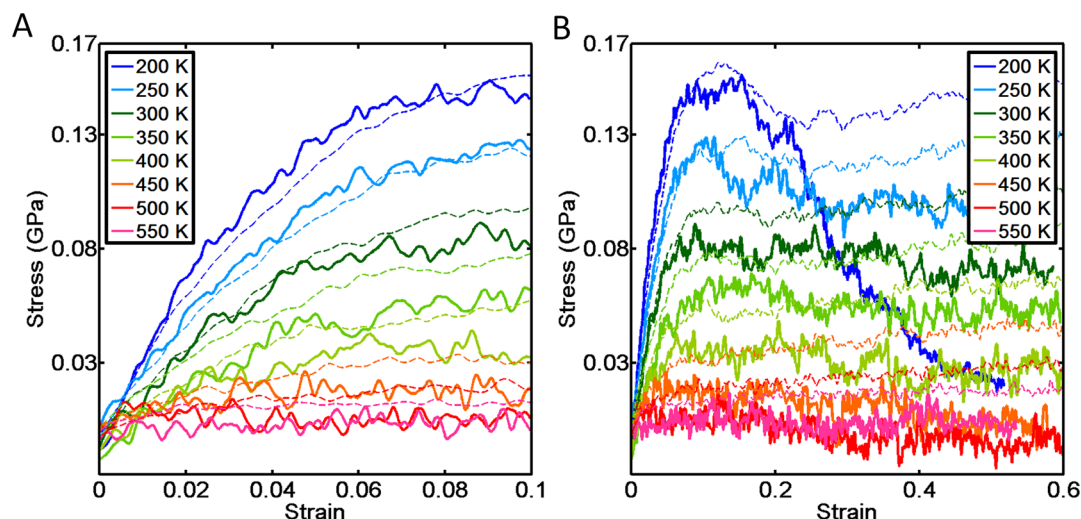


Figure 6. Stress vs strain curves for 75 monomers per chain CG and all atom systems from 200 to 550 K. CG curves shown as dotted lines, and all atom shown as solid lines. Refer to online version for color. (A) Stress–strain behavior from 0 to 10% strain. (B) Extended stress–strain curve from 0 to 60% strain.

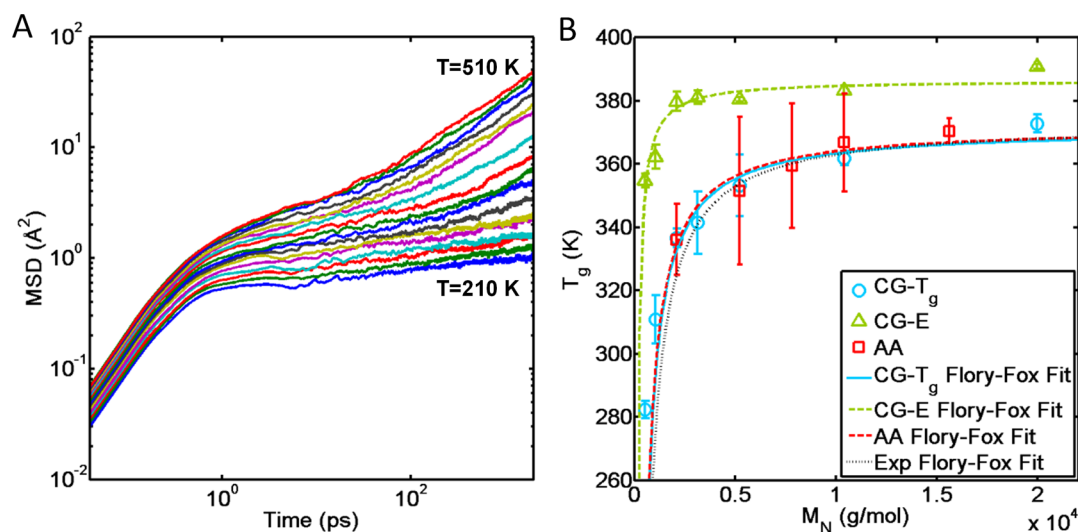


Figure 7. (A) Example of MSD for different temperatures from 210 to 510 K shown for T_g -tuned CG parameters. (B) The glass transition temperature T_g estimated using the MSD average method consistent with Tsige and Taylor.⁴⁶ T_g optimized parameters are shown as blue triangle markers, and the corresponding Flory–Fox fit is shown as a dash-dotted line. Elastic modulus optimized parameters after density correction are shown by green square markers, and the corresponding Flory–Fox fit is shown as a dashed line. All-atom results are shown as red circles, and the corresponding Flory–Fox fit is shown as a solid line. The experimental Flory–Fox fit is shown as a dotted line.

correction, we find that the E for CG and all-atom systems improve and match well at temperatures ranging from 150 to 750 K, with some deviation at low temperatures below 150 K (see Figure 5B). We also find that the broad downturn region corresponding to the glassy-to-rubbery transition is approximately from 300 to 400 K, which roughly supports our T_g predictions. We note that the T_g is more accurately estimated using the mean-squared displacement (MSD) described in the following section. In comparing the two chain lengths, significant difference in the E values between the 75 and 150 monomer systems is not observed.

The stress vs strain curves shown in Figure 6A show good correlation between CG and all-atom stress profiles below 10% strain; however, above 10% strain, we see some disparities, shown in Figure 6B. At high strain, the all-atom system undergoes strain softening behavior, whereas the CG system displays strain hardening up to 100% strain (60% strain shown

here). At temperatures just above the glass transition, the material is still in the rubbery plateau region and has not yet undergone complete flow. The strain hardening characteristic in the CG model is consistent with experimental uniaxial compression results from van Melick et al.⁶¹ as well as united-atom tensile simulation results from Lyulin et al.⁶⁰ We expect that the softening behavior of all-atom results at high strain may be due to greater localization of stress arising from the lower number of chains simulated. For the CG model, it is found that the true stress σ is linear with $\lambda^2 - \lambda^{-1}$ from the neo-Hookean description of the strain energy function derived by Mooney,⁶² where $\lambda = L/L_0$. The slope, G_R is defined to be the strain hardening modulus, which we measure in the range of 250–450 K, to be an average of 11 and 13 MPa for the 75 and 150 monomers per chain systems, respectively. These results are in good agreement with the results from simulation, (Lyulin et al.)

and experiments, (Melick et al.), which are found to be 13 ± 3 and 13 MPa, respectively.

3.2. Molecular Weight Dependent Glass Transition and Flory–Fox Comparison. In Fox and Flory's seminal work on the glass transition of polystyrene as a function of molecular weight, they hypothesize that the depression of T_g at shorter chain lengths is inversely proportional to the number of chain ends.⁶³ The developed Flory–Fox relationship has since been well established:⁶³

$$T_g(M_n) = T_{g\infty}(1 - K/M_n) \quad (7)$$

where $T_{g\infty}$ is the glass transition temperature for chains approaching infinite length and K is an empirical constant in g/mol units.

To estimate the T_g in the all-atom and coarse-grain models, we employ the method developed by Tsige and Taylor.⁴⁶ We generate chain lengths varying from 5 to 192 monomers per chain for the CG model and generally adjust the number of simulated chains to maintain the system size between 10 000 and 50 000 beads. Chains must first be generated using a random-walk algorithm with end-to-end distances close to the average value; otherwise, it is not feasible for chains above the entanglement length, (experimentally, ~ 125 monomers)²⁰ to achieve full relaxation within coarse-grain time scales due to topological constraints.^{7,21,64} For all-atomistic systems, we generate systems ranging from 20 to 150 monomers per chain and adjust the number of chains to maintain a system size around 5000 beads. We use the NPT ensemble to equilibrate the system to 300 K at atmospheric conditions for 8 ns using $\Delta t = 4$ fs. The system is heated to 530 K in the NVT ensemble and then gradually cooled down to 210 K in 20 K increments at an effective rate of 10 K/ns, which are much faster than experimental rates but slower than cooling rates found in other computational studies measuring T_g .⁶⁵ At each temperature point during cooling, the mean-squared displacement (MSD) for all beads is measured for 2 ns, which is defined as

$$\text{MSD}(t) = \langle |r_i(t) - r_i(0)|^2 \rangle \quad (8)$$

where $r_i(t)$ is the position of the i th bead at time t (see Figure 7A). The subdiffusive regime encompasses times at which the MSD scales with t^α with $\alpha < 1.0$. This includes times after the ballistic regime ($t > 1.0$ ps) and up to times before the diffusive regime. We take the average of the MSD in the subdiffusive regime and plot it against the temperature. The resulting plot gives a bilinear dependence of the average MSD versus the temperature which feature an intersection at the estimated T_g .

The atomistic system predictions for T_g are found to be in good agreement with experimental studies. For the CG system, we use the NPT ensemble rather than NVT to accommodate the σ -corrected potential. $T_{g\infty}$ for the modulus tuned CG model (386.5 K) is within experimental estimates ranging from 373–388 K,^{68,69} and therefore we consider the model to be “thermomechanically consistent” to predict modulus between 150 and 750 K and to predict T_g at chain lengths above 100 monomers⁵⁷ (see Figure 7B). We find, however, stronger deviation compared to atomistic results at lower molecular weights. We therefore conclude that the incremental well depth used to match modulus values can adversely affect chain end mobility. We note that this is a distinction between the PS model and the previous PMMA model which exhibited $T_g(M_n)$ and correlation with experimental E with one set of parameters.⁴⁵ This may reveal a fundamental difference

between PS and PMMA which cannot be completely captured by the two-bead per monomer method. Note that we do not see significant difference in T_g predictions as a result of density correction.

We provide an additional set of nonbonded potential parameters that have been optimized to refine the correlation of atomistic and experimental T_g results for a wider range of molecular weights. These T_g -optimized parameters may be used for studies focusing on T_g and that are not as concerned with modulus prediction. This is done through a parametric study in which the elastic modulus is neglected and only T_g and ρ is considered. We find that the T_g -optimized CG model matches very well with the atomistic predicted $T_{g\infty}$ values, (371.4 K vs 371.9 K, respectively.) The Flory–Fox K constants for the T_g -optimized CG model and atomistic systems vary by approximately 3% and show similar good agreement with experimental results⁶³ (see Figure 7B and Table 3). The T_g -

Table 3. Flory–Fox Parameters for All-Atom, CG, and Experimental Atactic PS

	$T_{g\infty}$ (K)	K (g/mol)
experimental ⁶⁸	373	268.1
all-atom (DREIDING)	371.9	210.2
CG (T_g optimized)	371.4	216.0
CG (E optimized)	386.5	46.7

optimized parameters, however, underestimate the lower range of the experimental elastic modulus by approximately 50%. The modulus is measured to be about 1.15 GPa at 300 K.

Table 4. Chain Structure Conditions

M_n (kDa)	monomers per chain	chains	M_n (kDa)	monomers per chain	chains
0.5	5	1000	10	100	50
1	10	500	20	192	50
2	20	250	30	288	50
3	30	160	50	481	50
5	50	100			

3.3. Chain Statistics and Structural Comparison. Chain statistics are evaluated to see whether the chain conformation has been preserved in the bulk despite strong nonbonded potentials. We use the relaxation procedure similar to the standard procedure for preparing polymer melts outlined by Auhl et al.⁶⁴ CG systems of varying molecular weight from 5 to 481 monomers per chain are generated (see Table 4). Next, a soft potential push-off step is gradually ramped up to remove close contacts and overlaps. The full potential is turned on and the system is allowed to equilibrate for up to 500 ns to allow for relaxation and to monitor the chain dimensions.

We calculate the chain length specific characteristic ratio $C_N = \langle R^2 \rangle / (N - 1)l^2$ from the end-to-end distance for each molecular weight (see Figure 8A). N is calculated as 2 times the number of monomers and represents the number of backbone carbons in the chain. $l = 1.53$ Å is the length of the carbon–carbon bond. Flory's characteristic ratio at infinite chain length C_∞ is estimated to be 8.6 for the atactic system at 450 K using the relation $d \ln C_\infty / dT = -0.9 \times 10^{-3}$ (C_∞ is 9.85 at 300 K).⁶⁶ We find that as the chain length increases, C_N saturates to ~ 8.0 , which is near the experimental C_∞ . To assess the degree of relaxation along the chain, we also plot the mean-squared

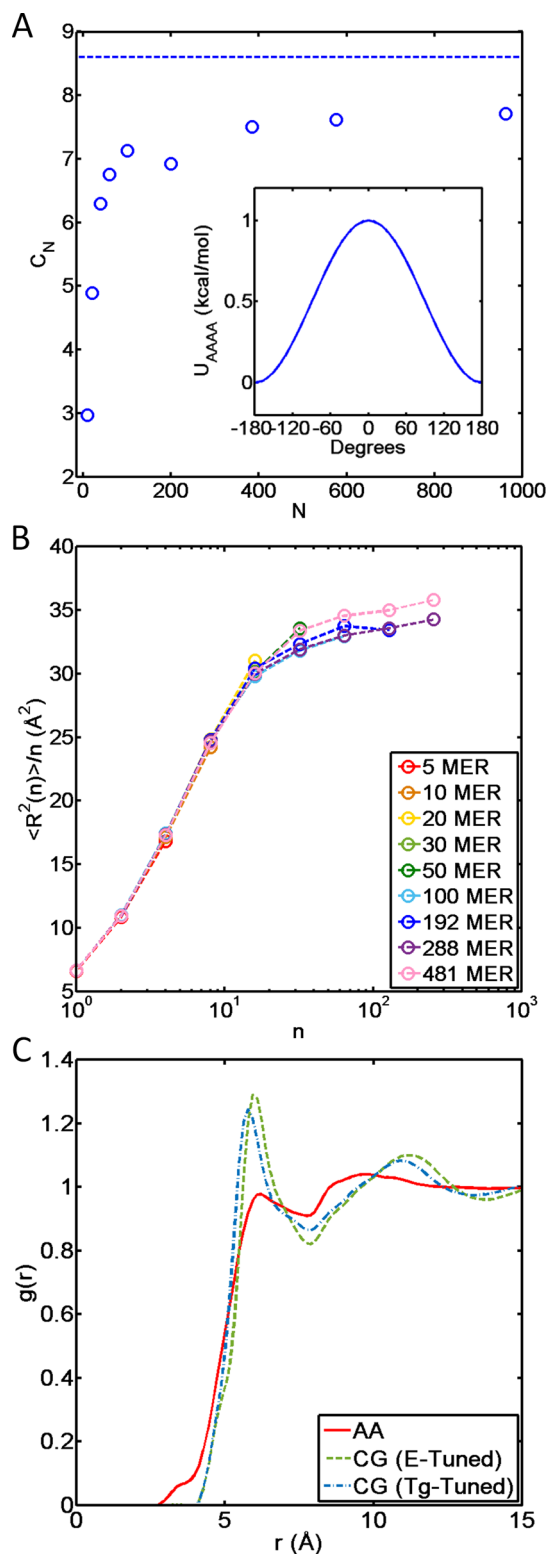


Figure 8. (A) Resulting characteristic ratio C_N as a function of molecular weight for the atactic system at 450 K. N represents the total number of carbons in the alkane backbone. Experimental $C_\infty = 8.6$ for the atactic system is shown as the blue dashed line. Inset shows the A–A–A–A dihedral potential which is used to tune chain stiffness. (B) Normalized mean-squared internal distances calculated for subchain distances are shown for chains from 5 to 481 monomers after 500 ns relaxation. (C) Radial distribution function comparison for the all atomistic, E -tuned CG, and T_g -tuned CG systems.

internal distances at 450 K, defined as $\langle R^2(n) \rangle / n$ where the subchain end-to-end length $\langle R^2(n) \rangle$ is normalized by the number of monomers n in the subchain.⁶⁴ We find that curves up to 481 monomers are almost fully collapsed together after 500 ns, which denotes relaxation at subchain lengths (see Figure 8B). Note that full chain relaxation for chain lengths above 481 is difficult to achieve as can be observed by slightly higher internal distances for the 481 system even after 500 ns. Double-bridging Monte Carlo moves, which can be used to efficiently accelerate chain relaxation, can be implemented for the two-bead model in future studies.^{64,67}

The radial distribution function $g(r)$ of the all atomistic and CG E -tuned and T_g -tuned models is shown in Figure 8C which are calculated at 450 K for all CG force centers starting from the third nearest bonded neighbors. The initial peak for both atomistic and CG systems is found to correspond to the same radial distance; however, the CG peak value is much higher relative to the atomistic system. This is a direct result of the increased well depth used in the CG model and demonstrates that the modulus and glass transition cannot be reproduced if nonbonded potentials are developed only through bottom-up IBI optimization. Although the CG model may be used to predict thermomechanical quantities, one must take caution that some functionalities of the model, such as CG to atomistic back-mapping may produce inaccuracies.

3.4. Dynamic Scaling and Diffusion Comparison.

To estimate the relative friction and scaling of dynamic quantities, the CG and all-atom self-diffusion coefficient D of liquid monomers at high temperatures is compared at both 450 and 750 K. The MSD curves at 450 K have been shifted down for

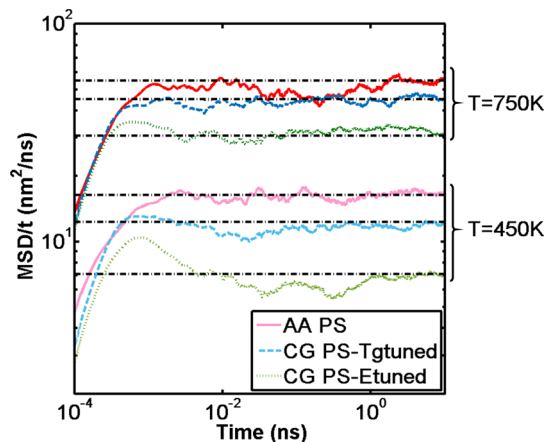


Figure 9. Dynamic scaling and diffusion comparison. The MSD/t is plotted versus time for liquid monomers from all-atom system, T_g -tuned CG system, and the E -tuned CG system at 450 and 750 K. Horizontal lines show scaling with $t^{1.0}$. The MSD curves for 450 K have been shifted vertically down for clarity.

visual clarity (see Figure 9). D can be calculated from the MSD by the Einstein relation:

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r_j(t) - r_j(0)|^2 \rangle \quad (9)$$

where $r_j(t)$ is the position of the j th monomer at time t . Harmandaris et al. proposed a dynamic scaling factor, S_{AA-CG} , which is chain length (M_n) dependent and is defined by the ratio of effective friction ζ in each system, $S_{AA-CG}(M_n) = \zeta^{AA} /$

ζ^{CG^7} . This factor is equivalent to the ratio of diffusion coefficients for the all-atom and CG systems, $D_{\text{CG}}/D_{\text{AA}}$. We find that $S_{\text{AA-CG}}$ for the E -tuned parameters and T_g -optimized parameters are 0.82 and 0.56, respectively, at 750 K and 0.75 and 0.43, respectively, at 450 K, which indicate that the friction in both CG systems are slightly higher than the all-atom system and are on the same order of magnitude. The computational speed-up of the CG system compared to the all-atom system is still over 100 times faster on the basis of a 600 monomer system due to lower degrees of freedom and larger time step.

3.5. Discussion for Two-Bead Parameter–Physical Property Relationships. We can make several conclusions about the effect of individual two-bead model parameters on the resulting physical properties through sensitivity analysis. Increasing the depth of the side chain LJ pair potential well has a stronger ability to enhance the modulus of the bulk system than either the backbone pair potential well depth, bonded parameters, or molecular weight. This reveals that the side chain to side chain cohesive interaction between neighboring chains may be the strongest determining factor for the modulus at small strains. Increasing either the size of side chain beads or the well depth has an augmenting effect on the T_g . Increasing the well depth raises the energy required for the particle to escape its confining cage associated with glass transition. The augmenting effect of increased side chain size on T_g can be explained by backbone rotation hindrance, which reduces the segmental mobility of the chain. Increasing the size of side groups concurrently has a negative effect on modulus due to the strong dependence of density on the side chain volume. Finally, we note that the pair potential well depth of beads do not significantly affect the system density in the glassy state likely because high packing efficiency is already achieved.

4. CONCLUSIONS

We have demonstrated the versatility of the present method for coarse-graining asymmetric vinyl polymers such as polystyrene. By using a simple two-bead mapping scheme, introducing analytical bonded interactions consistent with the structure of the polymer, and performing IBI optimization to match all-atomistic target bonded distributions, we are able to reproduce “local” structural properties of the system. In addition, using top-down tuning of backbone dihedral parameters allows us to match the chain length characteristic ratio. We also demonstrate that tuning the nonbonded parameters of the model to match the T_g and elastic modulus of the atomistic system at a single state point provides transferability of E from 150 to 750 K after applying temperature-dependent density correction. This may be a versatile method to improve transferability of certain density-dependent properties in CG systems. We also find that the strain hardening modulus G_R correlates with experimental and simulation results. The molecular weight dependent T_g can be further improved using T_g -optimized parameters that allow the Flory–Fox parameters to match with simulation and experiments. Including dynamic scaling results calculated through comparison of the CG and all-atom diffusion coefficients, we find that the CG model provides a speed-up of over 100 times faster on the basis of a 600 monomer PS system size.

We have established several advantages of using the TCCG method for polymer coarse-graining and extending the capabilities to computationally predict their behavior in mesoscopic contexts. First, we are able to demonstrate simultaneous prediction of structural, dynamic, glass transition,

and mechanical strength characteristics, which has previously been elusive to achieve in CG models. Second, we control the transferability of thermomechanical predictive capabilities to temperatures well beyond the point of calibration through a density corrected nonbonded potential. Third, using a two-bead mapping scheme with separate backbone and side chain terms enables compatibility with our previously developed two-bead models for simulations of copolymers and blends. Finally, we express that the methodology has been shown to be robust, having been applied to five methacrylate homopolymers as well as polystyrene and could be further extended to additional polymeric systems.

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Notes

The authors declare no competing financial interest.

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