Transferability of a coarse-grained atactic polystyrene model: Thermodynamics and structure

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ABSTRACT

In this paper, we construct a one-bead per monomer coarse grained (CG) model for atactic polystyrene (PS) via a combined structure-based and thermodynamic quantity-based CG method at 1 atm and 463 K by using the hard LJ 12–6 potential as the non-bonded interaction potential and applying iterative Boltzmann inversion method to derive the bonded potentials. Although the CG force field is built at one single thermodynamic state point without any temperature correction or pressure optimization terms, the CG model possesses a rather favorable transferability in a wide temperature of 100–600 K. More importantly, the CG model gives the glass transition temperature of 382 K, which is very close to the atomistic result of 360 K and the experimental value of 363 K. Additionally, the unique double-peak feature and the unusual temperature dependence of the polymerization peak in the experimental scattering spectrum of atactic PS are well captured by the systematic CG model.

1. Introduction

As one of the most prevalent commercial polymers, polystyrene (PS) has a rather wide use in industry and our daily life. However, polystyrene plastics are commonly applied under the circumstance below their glass transition temperature (T_g), where the equilibration of the system and the motion of chain segments are too slow to be investigated by traditional atomic-scale molecular dynamics simulations (MD). While coarse grained (CG) molecular models simplify the interaction sites by merging several neighboring atoms into a single CG particle, the irrelevant degrees of freedoms are thus largely reduced and the computational efficiency are tremendously improved [1–4]. So far, various kinds of useful CG models have been proposed according to different target properties that need to be reproduced [3,5–18], such as density, force and the radial distribution function (RDF). Among them, hybrid CG approaches or combined schemes [19–22], i.e. several target properties are simultaneously adopted for parameter fitting, possess

better prediction power than previous CG models. In a similar way, some previous works of our group [23–27] consider the bulk density, local conformation distributions and radial distribution function of the underlying atomistic model system as targets to build the CG force fields (FF) for the 4-cyano-4′-pentylbiphenyl (5CB) liquid crystal, trans-1,4-polybutadiene (PB) and atactic polystyrene (PS)polymers. As we see, apart from the target properties for the determination of CG FF at the state point, a stable nematic phase and its unique anti-parallel arrangement of the nearest neighboring molecules as well as the phase transition temperature from nematic to isotropic phase as observed in atomistic simulations are well replicated by the 5CB CG model. As for the tans-1,4-PB CG model systems the resulting local conformation statistic, chain size and local packing properties as well as density values closely match the atomistic simulated data whether in the amorphous phase at 500 K or the crystalline state at 300 K. Additionally, for atactic PS the target properties, the extracted chain size and thermal expansion coefficient are generally reproduced by the PS CG model in a wide range of temperatures 300–600 K. It thus appears that the hybrid schemes, i.e. the combined structure-based and thermodynamic quantity-based CG method, can indeed effectively improve the prediction power of CG model. Particularly, such derived CG model is both thermodynamically and structurally consistent with the underlying atomistic model across different

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thermodynamic states, which is not only essential for bridging between different levels of resolution in multi-scale modeling but also have important consequences when studying phase transitions in various soft matter materials. It can be anticipated that the combined structure-based and thermodynamic quantity-based CG method provides a possibility to explore the complicated properties or phenomena of polymer systems across the phase transition, *e.g.* the glass transition of polystyrene, which can give useful guidelines for the application and modification of polymeric materials.

Since T_g is one of the most important attributes of amorphous polymers and the amorphous polymer glasses have found countless applications, the reproducibility of T_g by CG models is not only a great challenge in the modeling community but also of high technological importance [28]. In addition to estimate T_g from the temperature dependence of mean squared displacement [29], its value is usually also determined from the inflection point of the high-temperature and low-temperature density data in molecular simulations [27,28,30]. At present, the construction of most CG FF is mainly based on a bottom-up strategy for reproducing the underlying atomistic target properties, which makes it necessary to carry out atomistic MD simulations at the parameterization temperature. However, considering of the fact that it is rather difficult to optimize CG FF at these state points, such as crystalline state or near the glass transition point, due to time- or length-scale limitations of the atomistic simulations, CG FF is usually built at high temperatures in the molten state. Thus, this requires CG force field to possess good temperature transferability at different thermodynamic states, which is still a significant challenge even nowadays in computational chemistry and physics [24,25,27,28,31−35]. Strictly speaking, the CG FF obtained at a given state point should be specific to the phase state and cannot be used for other state points [36]. But in fact, the resulting CG FF is still utilized when there is not a significantly change in the weight of the removed degrees of freedom at these different state point [36]. Take PS for example, several CG models [31,34,35,37−39] have been proposed in the past decades. Among them, the purely structure-based CG models have limited transferability due to their strong state dependence [32,35,37], where the best one derived by the pressure-corrected iterative Boltzmann inversion (IBI) method and a one-bead per monomer mapping scheme (i.e., 1:1) can be applied only in a narrow temperature range of ± 50 K around the parameterization temperature [35]. While the thermodynamic-structure combined MARTINI [38] potentials extend the transferable range of PS CG models with a four-bead-per-monomer (4:1) coarse-graining strategy to be applicable within 350−600 K [39], however is still in the melt region. Another novel combined coarse-graining strategy with a two-bead per monomer (2:1) resolution for taking the steric effects of phenyl rings into account and by using T_g as the target property (i.e. the densities at different temperatures are considered as the target quantity) exhibits good chain length transferability, i.e. the molecular weight dependent T_g is commensurate with all-atomistic results, and perfect transferability of elastic modulus from 150 to 750 K [40]. Judging from these pioneering researches, it is still lack of transferable CG models that are competent and convenient (i.e. a CG model built at a single thermodynamic state with a one-bead per monomer mapping scheme and without any temperature dependent LJ potential correction or pressure optimization terms) to be used to reproduce T_g and study the glass transition of PS even today.

As mentioned above, besides thermodynamics properties, a combined CG model also possesses the capacity of reproducing some structural properties of the underlying atomistic model, such as the conformational distributions, chain size, structure factor and RDF, of which structure factor (S_q) is often utilized to describe the structure features of polymeric systems at all distance either in experiments or simulations. Among non-crystalline polymers, PS is unusual since in addition to a higher wave vector (q) peak at 1.4 Å^{-1} associated with the ubiquitous "amorphous halo" as observed in many polymers, there exists the unusual "polymerization peak" at around $q = 0.75$ Å^{-1} in its experimental S_q measured by neutron diffraction or wide-angle X-ray scattering [41,42]. It is noteworthy that the polymerization peak is not observed in X-ray patterns of most polymer glasses, rubbers and melts, and is also absent in scattering patterns of the styrene monomer as well as liquid benzene. Moreover, in contrast with many glassy polymers in which the lowest q peak is the most intense, the polymerization peak is relatively weak. In addition, the temperature dependence of this polymerization peak exhibits anomalous behavior, i.e. the intensity of the peak increases with increasing temperature, while the amorphous peak is essentially temperature independent. A recent work via an all-atom molecular dynamics simulation by Chakravarthy et al. [41] indicates that the polymerization peak stems from the intermolecular backbone-backbone correlations and intermolecular backbone-phenyl correlations and the amorphous peak is derived from spatial correlations of the intermolecular and intramolecular phenyl-phenyl segments. Although Giulia et al. [39] replicate the experimental S_q of PS by CG simulations using a 4:1 model and a hybrid thermodynamic-structural CG method, until now, there is still a vacancy that CG model is carried out to reproduce the temperature dependence of the polymerization peak in S_q of PS.

Recently, our group investigate the effect of the different non-bonded potential, i.e. LJ potentials with different function forms and parameters, on the transferability of a CG model for atactic PS [27], and find that CG models with harder LJ potentials own better temperature transferability than the softer ones. Hence, in this work, for atactic PS system in order to construct a simple and efficient CG model with relevant structural and thermodynamic properties i.e., structure factor and Tg, consistent with atomistic reference model, we employ a one-bead per monomer mapping scheme and adopt thermodynamic-structure combined CG method at a single thermodynamic state of 463 K and 1 atm to obtain a CG FF for atactic PS. Particularly to extend the temperature transferability range of the CG model we utilize a harder LJ potential as the CG non-bonded potential and to more realistically consider the packing effect of intra-chain phenyl rings, especially at low temperature we apply the IBI approach to derive the CG bonded potentials Interestingly, the resulting CG model reproduces exactly the atomistic T_g, the unique double-peak feature and the unusual temperature dependence of the polymerization peak in S_q of atactic PS. The remainders of this paper is organized as follows. First, we present our CG model for atactic PS, *i.e.* the coarse-graining procedure, as well as the simulation details in the next section. Then, the simulation results and discussions are given in Section 3. Finally, we close with a summary of our findings in Section 4.

2. Models and simulation details

2.1. Atomistic simulation

For the determination of coarse-grained force field, atomistic MD simulations are firstly carried out in the parameterized condition. As is well known, the polystyrene sort of materials are mostly used as general-purpose plastics in industry, where the processing (injection or extrusion modeling) temperature of PS lies in the range of 170−220 °C (443−493 K) and the ambient pressure is 1 atm. Considering that experimental data in the processing condition are commonly available and conveniently taken as benchmarks for CGFF evaluation, we thus chose a middle