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Thermodynamic properties of poly(vinyl alcohol) with different tacticities estimated from molecular dynamics simulation

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We used molecular dynamics simulation together with the OPLS-AA force field along with a high temperature equilibration protocol proposed by Belmares et al. to calculate selected thermodynamic properties of poly(vinyl alcohol) (PVA) with different tacticities. The results showed that the OPLS-AA force field was able to reproduce specific volumes, thermal expansion coefficients, glass transition temperatures and solubility parameters of the PVAs over a wide range of temperatures (200–550 K). PVA with different tacticities in the amorphous phase showed different solubility parameters but possessed similar specific volumes, thermal expansion coefficients and glass transition temperatures. For heat capacities, 300% overestimations were obtained. Such overestimations were reduced significantly to about 30% by applying the quantum correction method of Berens et al. We have also applied the newly developed two-phase thermodynamic (2 PT) approach in an attempt to further improve the results but failed.

1. Introduction

Owing to its film-forming property, barrier properties, hydrophilicity and excellent chemical stability [1], poly(vinyl alcohol) (PVA) has been gradually used in a variety of applications such as drug encapsulation and delivery, composite materials, metal nanoparticles stabilization [2] and active separation layers of pervaporation membranes [3], to name a few.

Like many other vinyl polymers, PVA exists in three possible stereomers (i.e., atactic, syndiotactic and isotactic). Due to its manufacturing process, commercial PVA is usually in the atactic form [4–7]. However, detailed information about the tacticity of a PVA sample can be established by nuclear magnetic resonance (NMR) spectroscopy [4]. It is well known that physical properties of vinyl polymers (e.g., glass transition temperature) depend on their tacticity [8]. It is expected that PVA has no exception [4]. However, results reported in this work seem not to support such an expectation. It has also been reported that PVA, even in its atactic form, is a semicrystalline polymer with a moderate level of crystallinity but its crystal structure has not yet been completely established because of its complicated structure and hydrogen bonding capability [9].

There exist quite a few reports on the use of molecular dynamics (MD) simulation to study PVA. These include its chain dynamics, interactions between PVA and various solvents and other polymers, PVA hydrogels and so on [2,6,10–12]. The force field used in majority of these studies was developed by Muller-Plathe et al. [7]. The COMPASS force field was also used [13–15]. Although most of these authors have been able to obtain good agreement with experiment for pure PVA, it is inconvenient to study new systems of interest involving both PVA and molecules of different types as re-parameterization is required. Obviously, using a force field that is optimized for PVA and a wide variety of compounds would be beneficial. Another issue of the aforementioned works is that small system size and/or short chains, as probably constrained by the computer resources available at the time, were used. In some cases, chains contained only up to 10 monomers [2] were used. While this is acceptable for the calculation of certain thermodynamic properties (e.g., specific volume), it is not the case for conformational sensitive properties (e.g., solubility parameter). In such cases, longer chains are needed. However, when longer chains are used, proper equilibration before MD simulation becomes an issue.

In light of the previous simulation works and taking the advantage of the computer resources available to the authors, we carried out a comprehensive set of MD simulations on PVA with different tacticities using the OPLS-AA force field to calculate a few key thermodynamic properties over a wide temperature range (200–550 K) encompassing both the glass transition and melting

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temperatures of PVA. The OPLS-AA force field was chosen as it is optimized for a variety of biomolecules and organic solvents. To address the equilibration issue, we used a relaxation strategy proposed by Belmares et al. [16]. The tacticity is of interest in the present work as its effect on properties of PVA has not been fully addressed in the simulation literature yet although Fossheim [8] did some work in this area.

2. Molecular dynamics simulation

In this work, Gromacs 4.5.5 [17–21] was used to perform all MD simulations using the OPLS-AA force field [22] as implemented in Gromacs. For PVA atomic type assignment in the OPLS-AA force field, please refer to Appendix A. However, in one simulation, we used OPLS-AA parameters with the partial atomic charges taken from the COMPASS force field [13] in order to compare our results with those of Wu [23]. In the preliminary work, we used other force fields including Amber [24] and force field parameters derived by Muller-Plathe et al. [7] and found that the OPLS-AA [22] yielded results that are most comparable to those of experiments. Also the comparison between the present work and that of Wu [23] suggests that the OPLS-AA results are comparable to those of using the COMPASS [13] force field if it is not better. We are confident in the force field we chose. We used Nose–Hoover thermostat [25] with a time constant of 0.2 ps and Parrinello–Rahman barostat [26] with a time constant of 2 ps to control the temperature and pressure of the model systems, respectively. In all simulations, the time step used was 1 fs and the sampling time was 1 ps unless otherwise stated. A cut-off distance of 1 nm was used for all non-bonded interactions except for those simulations using a single short chain where a cut-off distance of 0.6 nm was used to prevent the violation of minimum image convention. We used Particle Mesh Ewald (PME) for the long range Coulombic interactions [19]. We also applied the pressure correction to retrieve the correct density of the system as pointed out by Wu [23]. For detail of the pressure correction method readers can refer to Gromacs manual [27]. All properties were calculated over the temperature range of 200–550 K with an interval of 10 K and the simulation time used was 100 ns excluding equilibration phase, which varied between 60 and 100 ns. To decide whether a system has been equilibrated or not, we compared the energy, specific volume and solubility parameter of the system in 10 ns intervals. When the difference was less than recommended margins, it was concluded that equilibration was achieved. Since simulation of polymeric systems is usually non-ergodic [28], average on several different initial configurations was used to generate better estimate of properties. At totally 21 different temperatures ranging from 300 to 510 K (7 temperatures randomly selected from each stereomers), simulations were extended to 500 ns and beyond to check if system properties underwent further changes. Once again, we compared the specific volume, solubility parameter and conformational properties of the systems in the first and last 100 ns and no significant differences were found, suggesting that production simulations would generate reliable statistics after equilibration (60–100 ns simulations).

2.1. High temperature equilibration

It is well known that polymer relaxation is a slow process relative to small molecules and usually occurs in time scales beyond the capability of the MD simulation. Accordingly, MD simulation of polymeric systems is not ergodic and only a portion of the phase space close to the initial configuration is sampled [28]. In general, using well-relaxed chains as the initial structures for the corresponding MD simulations is crucial for accurate prediction of the equilibrium properties of polymers. To generate well-relaxed chains, we have followed the protocol proposed by Belmares et al. [16] with some modifications as follows:

1. All PVA chains (atactic, syndiotactic and isotactic) were generated using the polymer builder toolbox in Materials Studio 4.0 [29]. For all atactic chains, tacticity has been assigned randomly with chiral inversion probability of 50% (i.e., the ratio of meso diads to racemo diads is 50%). This random assignment of the tacticity, as mentioned by Rossinsky et al. [2], is consistent with commercial PVA chains formed by free radical polymerization. The connections for all isotactic and syndiotactic chains were head-to-tail. This is justified by the experimental findings of Flory et al. [30] in which they showed that depending on the temperature of the polymerization, the percentage of the head-to-head connection of the PVA monomers varies between 1% (at 298 K) to 2% (at 385 K). End groups for all chains were CH_3. Chains generated were then assembled in a cubic simulation cell subjected to three dimensional periodic boundary conditions at half of the target density (maximum experimental value reported at 300 K) using the Monte Carlo method developed by Theodorou and Suter [31] as implemented in the amorphous builder module of Materials Studio. A short energy minimization was done to remove all close contacts within the cell afterwards.
2. In the next step, all simulation cells were annealed according to the protocol proposed by Belmares et al. [16]. During annealing, the target density was chosen to be 1310 kg/m^3 [4,32–36]. Starting with cells generated in Materials Studio with density of 655 kg/m^3, we compressed each cell to 125% of the target density and then expanded them toward the target density. Both compression and expansion were stage wise processes in which each stage consisted of a 5000 steps of energy minimization followed by a 100 ps of MD simulation in NVT ensemble at 800 K. The expansion/compression process was performed in a stepwise fashion by imposing a sudden change in volume on the system in each step. Equilibration on the expanded/compressed system was done using the NVT ensemble. Starting from 50% of the target density, we compressed each simulation cell 15% of the target density in five steps until the density was 125% of the target density. Afterward, we expanded the simulation cell in five steps with each step with 5% reduction in density till the target density was reached.
3. After annealing, each cell was cooled in a stepwise process. Starting from 800 K, each cell was cooled down by 10 K and MD simulation was carried out for 100 ps in an NVT ensemble. At the final step of each simulation, a snapshot has been saved as relaxed chain at that temperature. This stepwise process repeated down to 200 K. As the goal of this section is to produce an initial structure at each temperature, the system was cooled as slowly as possible where the time constant of thermostat (which controls the velocity of cooling) was chosen to be 5 ps which is higher than normal 0.2 ps used in production simulations.
4. Upon generation of the relaxed structures at each temperature, each simulation cell went through a compression, in an NPT ensemble, to reach equilibrium. We considered several properties of the system (energy, specific volume and solubility parameter) as criteria for equilibrium. The equilibration time for different temperatures varied between 60 and 100 ns.

3. Results and discussion

3.1. Effect of equilibration

To demonstrate the effect of the high temperature annealing on the simulation results, we also simulated the same atactic PVA