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Multi-scale models for cross-linked sulfonated poly (1, 3-cyclohexadiene) polymer

Qifei Wang [a], David J. Keffer [a,*], Suxiang Deng [b], Jimmy Mays [b]

[a] Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA
[b] Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

Atomistic and coarse-grained (CG) models of cross-linked sulfonated Poly (1, 3-cyclohexadiene) (xsPCHD) were developed and implemented in Molecular Dynamics (MD) simulations of PCHD chains with different architectures. In the atomistic model, PCHD chains are cross linked by a sulfur–sulfur bond. Sulfonic acid groups are evenly distributed along the chain. The architecture is specifically aimed for application as a proton exchange membrane used in fuel cells. An atomistic force field for this architecture was tested and applied in the atomistic MD simulation of xsPCHD for the first time. The atomistic simulations generate the density and cross-linker separation distribution. To further study the structural properties of longer chain systems, a CG model was proposed. The bonded structural probability distribution functions (PDFs) and non-bonded pair correlation function (PCF) of the CG beads were obtained from the atomistic simulation results. The bonded CG potentials are obtained by simple inversion of the corresponding PDFs. The CG non-bonded potential is parameterized to the PCF using the Iterative Boltzmann Inversion (IBI) method. The CGMD simulations of xsPCHD chains using potentials from above method satisfactorily reproduce the structural properties from atomistic MD simulation of the same system. The transferability of the CG potentials has been further tested through CGMD simulation of xsPCHD homopolymer with different architectures.

1. Introduction

Poly (1,3-Cyclohexdiene) (PCHD) polymers and their derivatives are of interest due to their unique chemical structure: the six-member rings and the isolated double bond in the main chain. The PCHD homopolymer has better thermal and chemical stability, mechanical strength and photochemical properties as compared to other common vinyl polymers [1–5]. PCHD block copolymers have shown unusual phase separation behavior [6]. This unique property has been further investigated through the recent development of cross-linked sulfonated PCHD (xsPCHD)-based proton exchange membranes [7–9]. The unique phase separation behavior of the xsPCHD homopolymer, xsPCHD/PEG (polyethylene glycol) blend and xsPCHD-PEG block copolymer membranes generate higher proton conductivity than that of the common Nafion membrane at high temperatures [9]. Such phase behavior and many other properties strongly depend on the conformation of the polymer in solution or bulk [2,10]. The experimental study of the conformation of PCHD is rare probably due to the lack of well-defined and well-characterized samples [2]. Computational studies can focus on well-defined and perhaps idealized chains, even when they are composed of many different components, as is the case with xsPCHD. Due to the occurrence of phenomena across a broad range of time and length scales, the appropriate computational technique to investigate the behavior of cross-linked polymers is a multi-scale algorithm that incorporates a combination of molecular simulation and coarse-grained modeling.

Molecular simulation has proved to be useful in the study of chain conformation when the length scale is less that 10 nm roughly [11,12]. In molecular simulation (either Molecular Dynamics or Monte Carlo simulation), an important input into the simulation is a reliable force field. Some transferable force fields [13–17] have been developed and validated for various hydrocarbon compounds. For common vinyl polymers, different force fields have been successfully applied in molecular simulation study of structure and dynamics of polymeric materials [18–21]. For xsPCHD, a literature survey shows no atomistic simulation study has been reported. This is probably due to the complexity of the chain architecture and novelty of this polymer. In this work, the PCHD chains are cross-linked and sulfonated. This unique

* Corresponding author.
E-mail address: dkeffer@utk.edu (D.J. Keffer).

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molecular structure requires a combined use of elements from several previously parameterized transferable force fields.

An atomistic-level force field provides accurate simulation results but impairs the computational efficiency due to the large number of degrees of freedom in the model. For example, many local interactions like bond stretching, bending and torsion have to be calculated to obtain the total potential energy in an atomistic force field. Meanwhile, a small step size has to be used for these high frequency modes. On the other hand, the relaxation time of a polymer has a strong chain length dependence. When chain length is small, atomistic simulation is still tractable if the relaxation time is generally less than 100 ns. When chain length increases, the relaxation time increases nonlinearly [22]. The relaxation time of a long chain polymeric system could be on the order of 1000 ns or longer. As a consequence, the atomistic simulation of long chain polymeric systems is no longer computationally feasible. Therefore, the application of classic molecular simulation techniques is limited and integration with a more coarsely-grained model is needed to overcome these limitations.

The coarse-grained (CG) technique removes computational limitations by eliminating some degrees of freedom in the atomistic model. This is done by grouping atoms in the atomistic model together to form "super atoms". These super atoms interact with their own potentials. Since the degrees of freedom are greatly reduced in the CG model, structural and transport properties of long chain polymers can be calculated directly by CG simulation for much longer times and for much larger systems. In the CG procedure, normally a fully atomistic (or united atom (UA)) simulation of short chains are conducted first. From the atomistic simulation, the CG structural distribution functions for different interactions modes assigned in the CG model are obtained. The CG potentials are then generated based on these distribution functions. The generation of CG potentials is challenging since they are of no particular functional form. For bonded CG potentials, typically a simple Boltzmann inversion has proven sufficient to generate potentials that reproduce the atomistic description of local intra-chain structure [23,24]. For non-bonded CG interactions, different methods have been proposed to obtain the CG potentials. For example, adjusting power law type potential parameters (Lennard-Jones 12-6, 7-6, 7-4, 7-5, 8-6) [19,23,24], Ornstein–Zernike integral equation (IE) theory [12,25–28], reversible work calculation [29–31] and iterative Boltzmann inversion (IBI) method [32–36] are reported in the literature for CG modeling of polymeric systems. Different methods have their advantages in the systems to which they are applied.

Here, the aim of this work is to develop an atomistic and coarse-grained model of the xsPCHD homopolymer. The molecular model of xsPCHD polymer is explained in detail in the following section. This structure is designed for potential application as a fuel cell membrane. In the CG model, four CG beads are assigned to include two different types of sulfonation as well as cross-linking. The multi-scale modeling procedure is summarized as follows: first, atomistic MD simulations of a short-chain xsPCHD system are performed. From these simulations, bonded probability distribution functions (PDFs) and non-bonded pair correlation functions (PCFs) of the center-of-mass of atom fragments corresponding to CG beads were obtained. Second, these structural results from the atomistic simulations were used to generate CG potentials, using simple Boltzmann inversion for bonded modes and the IBI method for non-bonded modes. Third, the CG potentials are implemented in CGMD simulations of the same system, from which the bonded PDFs and non-bonded PCFs can be obtained and directly compared with those from the atomistic simulation for the purposes of validation. Finally, we performed CGMD simulations of longer-chain xsPCHD systems to test transferability of the proposed model.

2. Simulation method

2.1. Atomistic simulation of xsPCHD

We combined the OPLS-AA [14,37] and the OPLS-UA [13] (for hydrocarbon groups CH_2 and CH) force fields to describe the intra-molecular and inter-molecular potential of PCHD molecules. In the combined potential model, OPLS-AA potential forms are used with most of the force field parameters taken from either the OPLS-UA or OPLS-AA force fields for hydrocarbons. When necessary, some of the parameters for bond bending, bond torsion and non-bonded potentials are taken from the simulation work of Nafion [38–40], poly(ethylene oxide) sulfonic acid anion [41], polyvinyl chloride (PVC) [42] and $C_3H_7SO_3H$ [43], while the potential forms are transformed to that of the OPLS-AA. The complete details of the force field parameters can be found in the supplementary information document. The spherically truncated charge-neutralized method developed by Wolf et al. [44] is used to evaluate the electrostatic energy. We simulated in the isobaric-isothermal (NpT) ensemble and implemented the Hamiltonian-based thermostat [45,46] and barostat [47] with controller frequencies set to 10^{-4} fs^{-1}. The XI-RESPA NPT algorithm developed by Tuckerman et al. [48] was used to integrate the equations of motion. The large time step was 2 fs and the small time step was 0.2 fs. The parallel code was built in-house and was written in FORTRAN-90, using MPI for inter-processor communication. It has been tested rigorously across a variety of applications. The cut-off distance used was 15 Å for the atomistic simulation. For all the simulations in this work, we used 64 chains. The state point was set at 1 atm and 353 K, corresponding to future fuel cell application. Following the equilibration procedure described elsewhere [12,33], we estimated the initial density and placed the particles in the simulation volume, avoiding significant overlap. We started with a higher temperature then gradually decreased the temperature and equilibrated to the correct density. Data production followed and lasted for at least 10 ns.

The composition of the xsPCHD used in this simulation includes four types of units corresponding to (1) cyclohexadiene without any functionalization, (2) cyclohexadiene functionalized with a sulfonic acid group, (3) cyclohexadiene functionalized with both a sulfonic acid group and an alcohol group and (4) cyclohexadiene functionalized with a cross-linking agent that includes both a chlorine and sulfur atom. See Fig. 1. The architecture of this polymer as well as the composition are based on characterization of experimental samples produced in our laboratory [9]. The purpose of the sulfonation and cross-linking of PCHD is to allow it to serve as an economical high-temperature proton exchange membrane with enhanced mechanical and thermal stability.

In Fig. 1, we show a chain segment that has 10 non-functionalized cyclohexadiene groups (bead C), 7 sulfonated cyclohexadiene groups (bead A), 2 sulfonated cyclohexadiene groups with an addition alcohol (bead B) and is terminated on each end by a cross-linking cyclohexadiene group (bead D). In this paper, short chains include two such segments of 21 beads each, in which the cross-linking groups are bonded to each other at both ends of the chains, as shown in Fig. 1. Long chains include three segments linked cyclically.

2.2. CGMD simulations of xsPCHD

We propose that xsPCHD can be modeled at a coarse-grained level with assignments of CG beads shown in Fig. 1, which corresponds to three monomer units of PCHD chains (bead A, B and C) and two cross-linkers (D) at the two ends. In order to construct PCFs for the coarse-grained beads from the short chain atomistic