Current Applied Physics xxx (2017) 1–11

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

A comprehensive molecular dynamics study of a single polystyrene chain in a good solvent

Sajad Rasouli, Mohammad Reza Moghbeli*, Sousa Javan Nikkhah

Smart Polymers and Nanocomposites Research Group, School of Chemical Engineering, Iran University of Science and Technology, Tehran, 16846–13114, Iran

ARTICLE INFO

Article history:
Received 27 July 2017
Received in revised form
1 October 2017
Accepted 10 October 2017
Available online xxx

Keywords:
Polystyrene
Molecular characteristics
Toluene
Dilute solutions
Molecular dynamics simulation

ABSTRACT

In this study, molecular characteristics of polystyrene (PS) was calculated measuring its dilute-solution properties in toluene at 288.15 K via molecular dynamics (MD) simulations. The solution models consisted of PS chains with different number of repeating units all of which were in a dilute regime. In order to investigate the compatibility between the polymer and the solvent molecules, interaction energy and Flory-Huggins (FH) interaction parameter were estimated. The simulation results indicate that increasing the chain repeating units enhanced the interaction between the solute and the solvent. Additionally, the chain dimensions were evaluated calculating the radius of gyration (R_g) and end-to-end distance, r0. To determine the dynamic behavior of the chains in the solutions, mean square displacement (MSD) and diffusivity coefficient were calculated. The simulation results indicated that the chain rigidity at low molecular weight and chain flexibility with increasing the molecular weight influenced chains dynamic behavior and diffusivity. Moreover, radial distribution function (RDF) illustrated the effect of steric hindrance of the chains in dilute solution on capturing the solvent molecules. In addition, solution viscosity was calculated by performing non-equilibrium molecular dynamics simulation (NEMD). The obtained results of chain characteristics and viscosity showed a good agreement with experimental results published previously. This agreement confirms the accuracy of the applied simulation method to characterize the dilute solutions and the chains characteristics.

1. Introduction

Polymer solutions are widely used in various industrial fields, such as coatings [1], fibers production [2], solution polymerization [3,4], paints [5] and recycling [6]. In most polymer solution applications, the desired solution properties, viscosity, polymer solubility, easily solvent separation and solution phase separation behavior, may be required. Understanding polymer solution properties at different process conditions can help to select a proper solution for intended applications. Polymer solution properties are mainly affected by interactions between polymer chain and solvent molecules. Accordingly, polymer and solvent type, temperature and pressure are some of the most important parameters, which influence the interactions and have a vital role on the solution properties [7–9]. Study of dilute polymer solution is one of the most important approaches to determine the polymer-solvent interactions and their effects on the chain conformation and characteristics [10,11]. In dilute polymer solution regime, the solute concentration is lower than a threshold value on which the polymer-polymer inter-molecular interactions and polymer coil overlapping are in minimum levels. In addition, polymer intra-molecular interactions, polymer-solvent and solvent-solvent interactions are significant parameters to control the polymer solution properties [12,13].

The dilute polymer solution behavior has been investigated by some researchers [1,14–18]. Han et al. [1] predicted the alkyd and epoxy resin-solvent interactions in different dilute solutions. Their main goal was to calculate the solubility parameter of two alkyd and epoxy resins via intrinsic viscosity, which can be a good alternative for inapplicable group contribution method. Yan et al. [14] studied the behavior of different branched polymer architectures through measuring their dilute solution properties. They classified the branched polymers and determined the characteristics of these complex polymers via combining the static data, e.g. chain size and intrinsic viscosity, and dynamic data, e.g. relaxation of the polymers. Abe et al. [15] achieved the intrinsic viscosity of

* Corresponding author.
E-mail address: mr_moghbeli@iust.ac.ir (M.R. Moghbeli).

https://doi.org/10.1016/j.cap.2017.10.010
1567-1739/

polystyrene and polyisobutylene with different molecular weights in different solvents. Their results showed that the intrinsic viscosity of the polymers in a good solvent is higher than that in the theta solvent. This behavior can be attributed to the expansion level of the polymer chains in a solvent which depends to the interactions between the polymer and solvent molecules.

Important role of interactions in solution properties, makes this necessity to achieve a deep insight about the interactions and polymer behavior in molecular level [19,20]. In recent years with advances in computer technology, molecular modeling has highly attracted the interest of scientists and industry to investigate the characteristics and behavior of macromolecules [19–30]. Theoretical molecular modeling can be used to produce applicable insights into molecular interactions in materials when there is complexity in experimental measurements. Additionally, molecular modeling in some cases provides fundamental knowledge, which is difficult or impossible to acquire it experimentally [19,21]. Monte Carlo (MC) and molecular dynamics (MD) simulations are two molecular simulations methods that can be applied to achieve deep knowledge of polymers solvation phenomena in a molecular perspective [22–30]. Furthermore, these molecular simulations have ability to predict the polymer solution properties and select a suitable solvent for various polymers efficiently [23,24]. Lu et al. [23] calculated the intrinsic viscosity of polymers with different molecular weights via MC simulations of their dilute solutions. The results showed that the chain conformation change in the solution can be predicted with consideration of the molecular behavior of the polymers. Dunweg et al. [25] investigated a dilute polymer solution by large-scale MD simulations. Their results proposed a primary-principle microscopic test of Kirkwood-Zimm theory for molecule motions of the polymer. Drew et al. [26] calculated intrinsic viscosity of dendrimers at different generations via equilibrium MD simulations using Green-Kubo relation. They also observed a peak in intrinsic viscosity-generation curve at generation five which showed a good agreement with experimental results.

Evaluation of physical parameters of dilute polymer solutions, such as solution viscosity, solute-solvent interaction, chains conformation and dimension seems to be essential parameters to evaluate the properties of polymer solutions. In the present research work, the properties of dilute polymer solution of polystyrene (PS) with different molecular weights in toluene were studied using MD simulations. All simulations were performed at 288.15 K in which toluene acts as a good solvent for PS. Thereafter, the equilibrated dilute solution models were studied from interactive, dimensional, orientational and viscometric aspects. The interaction energy and Flory-Huggins parameter (χ) were calculated to study the polymer-solvent interactions. The chains dimensions in the solution were evaluated calculating the radius of gyration (R_g) and end-to-end distance (r0). In addition, a novel method based on NEMD was proposed to estimate the viscosity of the dilute solutions via MD simulation. Its novelty is arisen from the way that it selects a proper shear rate range to determine the solution viscosity. But it should be mentioned that the simulation results were also compared with some of published experimental results to assess the accuracy and validation of the simulation data.

2. Simulation details

2.1. Model construction

Polystyrene is a very important thermoplastic material because of its widespread applications such as foam production [31], food containers [31] and oil sorption [32]. Despite the fact that this polymer has different tacticities, i.e. isotactic, syndiotactic and atactic, many researchers studied experimentally and theoretically atactic polystyrene because of its more likely production in polymerization process [15–18,33,34].

In this present work, atactic PS (aPS) chain with various polymerization degrees (N), 14, 17, 21, 31, 50 and 94, were examined. The polymer chains were symbolized by aPSN, in which N is the degree of polymerization. At first, the created non-periodic structure models of the polymer chains with different molecular weights and toluene molecules were optimized. In optimization process, each molecule was exposed to an initial energy minimization utilizing the conjugate gradient algorithm. Fig. 1(a) indicates the initial optimized structure of aPS31 chain. Initial atactic polystyrene/toluene (aPS/Tol) models containing a single polymer chain were constructed in periodic boundary conditions for performing MD simulations. Each created periodic box was then filled with toluene molecules. The dimensions of all the initial simulation boxes are presented in Table 1.

2.2. Molecular dynamics strategy

The initial models of aPS/Tol were optimized by using conjugate gradient algorithm. The simulations were performed until the total energy of the system became stabilized. Thereafter, the simulation boxes were exposed to main simulation containing a NVT followed by a NPT simulation at temperature of 288.15 K. All the NPT simulations were performed at constant atmospheric pressure. Finally, a NPT simulation was carried out on each simulation box for data collection. The NVT, NPT and sampling simulation times of each system were reported in Table 1. MD simulations were performed using LAMMPS software package [35]. One of the vital issues in MD simulation is the selection of an appropriate force field to describe all the interactions in considered systems. Until now, different force fields such as AMBER [36], GROMOS [37], CFF91 [38] and COMPASS [39] have been used to characterize the interactions in the systems containing PS chains. Herein, the intra- and intermolecular interactions within the systems containing an aPS chain and toluene molecules were evaluated via an *ab initio* polymer consistence force

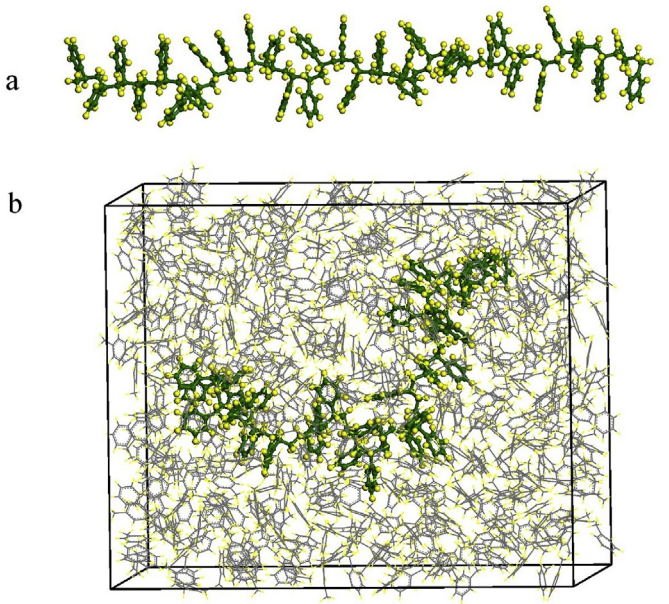

Fig. 1. (a) Initial optimized model of aPS31 (the green and yellow balls represent carbon and hydrogen atoms, respectively) and (b) the equilibrated simulation box of aPS31/Tol (toluene molecules are illustrated in line style). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: S. Rasouli, et al., A comprehensive molecular dynamics study of a single polystyrene chain in a good solvent, Current Applied Physics (2017), https://doi.org/10.1016/j.cap.2017.10.010