Polymer 53 (2012) 1124–1130

Contents lists available at SciVerse ScienceDirect

Polymer

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

Impact of hydrogen bonding on inclusion layer of urea to cellulose: Study of molecular dynamics simulation

Lu Cai, Yuan Liu, Haojun Liang*

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ARTICLE INFO

Article history:
Received 22 March 2011
Received in revised form
18 November 2011
Accepted 7 January 2012
Available online 17 January 2012

Keywords:
Molecular dynamics simulation
Hydrogen bonding interaction
Inclusion layer

ABSTRACT

Molecular dynamics simulation was applied for investigating the inclusion layer of urea to a single cellulose chain in urea-water solvent mixture. The formation of urea layer surrounding the cellulose chain, which mediated by different patterns of hydrogen bonding, was confirmed by radial distributing function and angular number distribution. Furthermore, the temperature properties of hydrogen bonding revealed that urea molecules are more favorable to interacting with cellulose than water molecules at a certain temperature range. Cellulose-urea interaction energy and hydrogen bond number were also calculated as a function of temperature and the result of calculation further proved the hypothesis that there exists a dominative hydrogen bonding pattern between cellulose and urea, in which oxygen atoms of urea as proton-acceptors and hydroxyl hydrogen atoms of cellulose as proton-donors. The cellulose-urea interaction is dependent of temperature, in which hydrogen bonding between cellulose and urea decreased gradually with temperature increasing at temperature above 265 K and it reached a plateau phase with temperature above 283 K.

1. Introduction

The hydrogen bonding between solvent molecules and hydrogen bonded polymer plays a very significant role in the conformational stability of the polymer and is also a very important driving force contributing to the dissolution of polymers in the polymer-solvent system [1–5]. It was demonstrated that hydrogen bonding is a very important factor in protein stability, which results not only from the formation of a hydrogen bond network between the backbone groups of protein chains but also from the formation of many hydrogen bonds existing between the polar groups located on the protein chains surface and water molecules surrounding them [6]. In the other hand, urea can be used as a kind of stabilizer for proteins when the concentration of urea in protein solution is low enough [7,8]. However, more urea molecules in protein solution would cause protein denaturation [1,2,4], in which the most possible reason is that the preferential adsorption of urea molecules onto the protein hydrophilic residues mediated by hydrogen bonding decreases both intramolecular and intermolecular interactions of proteins, and then leads to a swelling of the protein [9–11]. Hydrogen bonding can further affect the solubility of the polymer [12]. It was reported that cellulose pretreated with water or ethanol can be dissolved in the imidazolium-based ionic liquids and the main reason to affect cellulose solubility is the formation of hydrogen bonding network between anion, small molecules and cellulose [3,13,14]. Now, hydrogen bonding between small molecules and hydrogen bonded polymer chains has attracted more and more interest because it could reveal the mechanism of conformational change or dissolution of hydrogen bonded polymers.

Cellulose is one of the typical hydrogen bonded polymers whose monomer structure is shown in Fig. 1a, but the application is limited due to its non-hydrosoluble property which is because of hydrogen bonding between the cellulose chains [15]. Many studies have been devoted to improve the solubility of cellulose. Now there are some environment-safe ionic liquids have been suggested as potential replacements of volatile organic compounds for cellulose dissolution [3,12]. And also, it has reported cellulose could be dissolved rapidly in pre-cooled NaOH/urea aqueous solution [16]. However, the mechanism of dissolution of cellulose in these solvents is still elusive. Zhang L. et al. suspect that hydrogen bonding between ions and cellulose and forming the NaOH hydrogen bonded cellulose-urea inclusion complexes may be one of the major factors in dissolution of cellulose in alkali-urea solvent mixture [17]. As a typical hydrogen bonding dominated organic

---

* Corresponding author. Tel.: +86 551 3600240; fax: +86 551 3601760.
E-mail address: hjliang@ustc.edu.cn (H. Liang).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2012.01.008

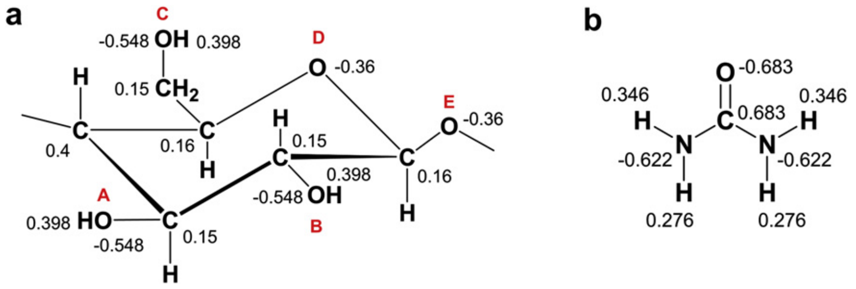

Fig. 1. Structures of (a) cellulose monomer and (b) urea molecule.

molecule, urea whose structure is shown in Fig. 1b with the hydrogen bond properties is also considered to be the 'host' molecules to constitutes inclusion complexes with various long-chain hydrocarbons [18–20], and becomes the denaturant or stabilizer for proteins in solvent mixtures [7,8]. Full understanding of hydrogen bonding between cellulose chain and the urea molecules is not only helpful to know about the mechanism of cellulose dissolution in urea-containing solvent mixture but also help us to bring on a consideration over the influence of the urea to the conformational and functional properties of polymers in many fields. Many experimental researches have been focused on cellulose-urea system [17,21–23]. In this study, molecular dynamics (MD) simulation was applied for investigating the hydrogen bonding between cellulose and urea.

MD simulation has been carried out into the investigation of cellulose conformation [24–27], cellulose dissolution [15,28], urea/water mixture system [11,29–31] and the typical inclusion complexes of urea molecules [19,32]. In this work, we apply MD simulation to study the interaction between the single cellulose chain and urea-water solvent mixture and associated temperature property. Our results could give significant insight of the hydrogen bonding behavior of polymer and small molecules, as well as its temperature property.

2. Model and simulation method

The GROMACS 3.3.1 software package [33] is used for the energy minimization and MD simulation and analysis of MD trajectories. It applies the FFGMX, which is based on the GROMOS-87 force field [34] for the single cellulose chain and urea molecules, and the SPC model [35] for water. The partial atomic charges of all the molecules were assigned with the standard module of this force field, as shown in Fig. 1. The potential energy of the system is described as follows:

$$V = \sum k_b(l-l_0)^2+\sum k_\theta(\theta-\theta_0)^2+\sum k_\phi[1+\cos(n\phi-\delta)] + \sum_{i<j} 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)+\sum_{i<j}\frac{q_iq_j}{4\pi\varepsilon_0 r_{ij}} \qquad (1)$$

where l is the bond length, θ is the bond angle, ϕ is the dihedral angle, l_0 is the equilibrium bond length, θ_0 is the equilibrium bond angle, k_b, k_θ and k_ϕ are the force constants, n is the multiplicity factor, and δ is the phase shift. In last two terms, r_{ij} is the distance between atoms i and j, and ε and σ are the energy and size parameters of the Lennard-Jones potential, respectively. An arithmetic average is used for the sigma's, whereas a geometric average is used for the epsilon's, as shown in the following equation:

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii}+\sigma_{jj}), \ \ \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}. \qquad (2)$$

In the last term, q_i is the charge of atom i and ε_0 is the dielectric constant of the vacuum. The last two terms are non-bonded potential functions.

All simulations were carried out with an initial box measuring 7.15 × 2.55 × 4.16 nm^3. The Lennard-Jones potential truncation cutoff was set to 1 nm, and all bond lengths were constrained using the LINCS algorithm [36]. At a distance shorter than 1.0 nm, electrostatic interactions were calculated explicitly, whereas particle-mesh Ewald summation (PME) [37] was adopted for lone-range interactions. All MD simulations were performed under the isothermal-isobaric, ensemble of the Berendsen method with a constant pressure of 1 atm [38]. Periodic boundary conditions were used in energy minimizations and MD simulations. The cellulose chain was energy-minimized in vacuum to obtain its unbent initial conformation and then was position-restrained in succeeding MD simulations to exclude the effect of polymer chain conformation change in the solute-solvent interaction.

Every MD simulation with a 2 fs time step was carried out for 38 and 12 ns to equilibrate the entire system and sample, respectively. Coordinates and velocities of atoms were collected every 1 ps. The radial distributing function (RDF) of the cellulose chain with urea molecules at all the temperatures chosen was examined to confirm that the system was in equilibrium. As shown in Fig. 2, the superposition of RDF curves of 12 ns sample period and 12 ns after it demonstrates system equilibration throughout the sample period. RDF curves at other temperatures (data not shown) are similar to those obtained at 261 K. At every temperature, three random

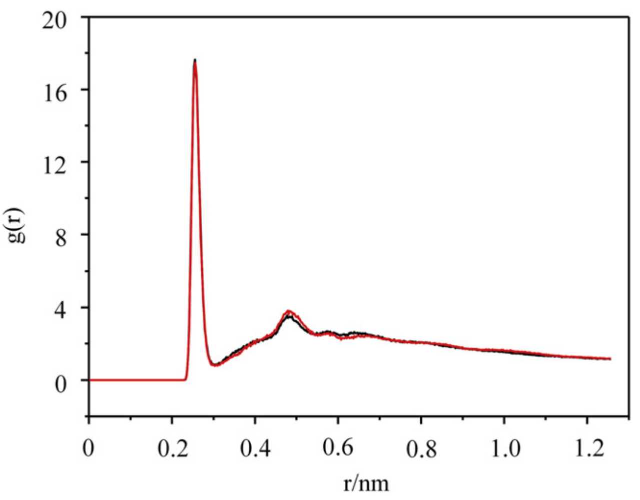

Fig. 2. RDF between O (A) of cellulose and oxygen atoms of urea for 12 ns sampling period (black curve), and for 12 ns after sampling period (red curve) at 261 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)