



# Molecular dynamics simulations of theoretical cellulose nanotube models

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## ABSTRACT

Nanotubes are remarkable nanoscale architectures for a wide range of potential applications. In the present paper, we report a molecular dynamics (MD) study of the theoretical cellulose nanotube (CelNT) models to evaluate their dynamic behavior in solution (either chloroform or benzene). Based on the one-quarter chain staggering relationship, we constructed six CelNT models by combining the two chain polarities (parallel (*P*) and antiparallel (*AP*)) and three symmetry operations (helical right (*H<sub>R</sub>*), helical left (*H<sub>L</sub>*), and rotation (*R*)) to generate a circular arrangement of molecular chains. Among the four models that retained the tubular form (*P-H<sub>R</sub>*, *P-H<sub>L</sub>*, *P-R*, and *AP-R*), the *P-R* and *AP-R* models have the lowest steric energies in benzene and chloroform, respectively. The structural features of the CelNT models were characterized in terms of the hydroxymethyl group conformation and intermolecular hydrogen bonds. Solvent structuring more clearly occurred with benzene than chloroform, suggesting that the CelNT models may disperse in benzene.

## 1. Introduction

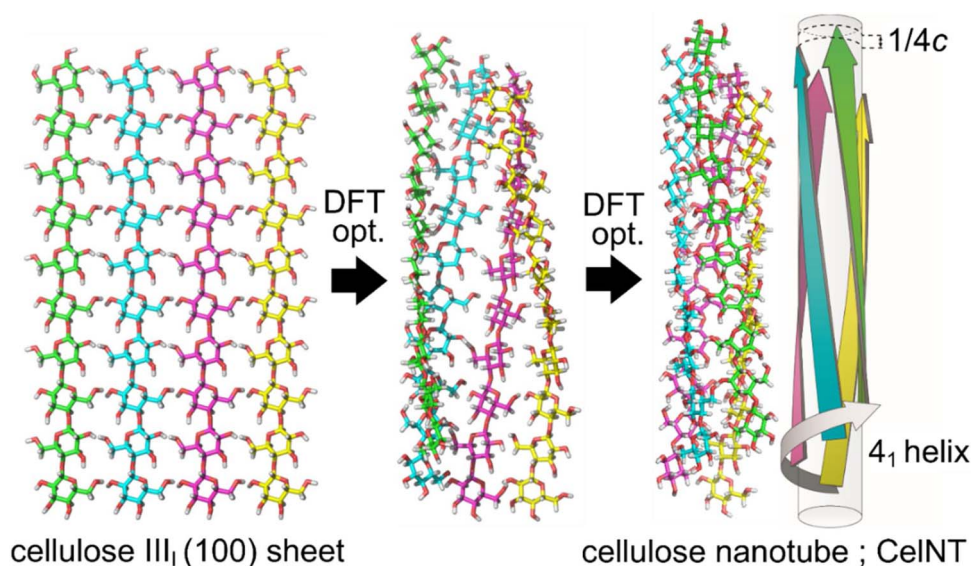
Nanomaterials, which have one external dimension or internal structures less than 100 nm, can be in the form of particles, tubes, rods, or fibers. Among these forms, high functionalities and diverse applications are most expected for nanotubes, such as carbon nanotubes (CNTs) (Iijima, 1991; Iijima & Ichihashi, 1993). Inorganic nanotubes, which are similar to CNTs, are formed by covalent, ionic, and metallic bonds. However, in some organic nanotubes, small molecules assemble by secondary interactions, such as hydrogen bonds and van der Waals forces, to form a tubular structure. The building blocks for polymer nanotubes are generally amphiphilic molecules, which possess both hydrophilic and hydrophobic moieties, and the units are often arranged with helical symmetry (Shimizu, Masuda, & Minamikawa, 2005). Biomolecules, such as DNA, proteins, and lipids (Frusawa et al., 2003; Raviv et al., 2005; Shimizu et al., 2005; Wilner et al., 2011), and carbohydrates can also form a nanotube structure in a similar fashion to polymer nanotubes. Curdlan and schizophyllan, which both have a  $\beta$ -(1  $\rightarrow$  3)-glucan backbone, form a triple-stranded helix structure (Chuah, Sarko, Deslandes, & Marchessault, 1983; Deslandes, Marchessault, & Sarko, 1980). The inner channel of the helical structure is relatively hydrophobic, whereas the outer surface, which is exposed to the solvent, is hydrophilic (Ikeda et al., 2007), giving a one-dimensional amphiphilic nanotube architecture. Cyclodextrin molecules can also form a nanotube because they can thread on another polymer chain along the molecular axis, forming a polyrotaxane (Harada, Li, &

Kamachi, 1992).

Cellulose, a linear poly (1  $\rightarrow$  4)- $\beta$ -D-glucan polysaccharide, is naturally produced as a highly crystalline fiber. In the crystalline form, the cellulose molecular chain forms a flat ribbon-like conformation with two-fold helical symmetry. The structure results in the isolated cellulose chain having an amphiphilic nature, where the polar functional groups mostly align along the side of a flat ribbon and the ribbon face consists of pyranose ring faces with a hydrophobic nature (Alqus, Eichhorn, & Bryce, 2015; Lindman, Karkström, & Stigsson, 2010). The two native cellulose crystals ( $I\alpha$  and  $I\beta$ ) are produced as almost single crystals (Atalla and VanderHart, 1984; Sugiyama, Vuong, & Chanzy, 1991; VanderHart and Atalla, 1984). Cellulose III<sub>i</sub> can be obtained by treatment of cellulose I $\beta$  with liquid ammonia or amines, and it readily converts back to cellulose I $\beta$  by hot-water treatment (Legrand, 1951; Wada, 2001). In the crystal structures of  $I\alpha$  (Nishiyama, Sugiyama, Chanzy, & Langan, 2003),  $I\beta$  (Nishiyama, Langan, & Chanzy, 2002) and III<sub>i</sub> (Wada, Chanzy, Nishiyama, & Langan, 2004) allomorphs, all of the molecular chains are aligned with the same polarity, which is known as parallel chain packing. In contrast, the crystal structure of cellulose II has chains oriented in opposite directions (Kolpak & Blackwell 1976; Langan, Nishiyama, & Chanzy, 1999; Nishimura & Sarko, 1987; Stipanovic & Sarko, 1976). The native crystal phases are irreversibly converted to cellulose II by either mercerization or regeneration processes accompanied by a complete change in the cellulose chain polarities from parallel to antiparallel. The cellulose chains of the amphiphilic flat ribbon assemble into crystal structures such that the

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**Fig. 1.** The cellulose III<sub>I</sub> (100) sheet model used as the starting structure and CelNT predicted by DFT optimization. A schematic representation of the corresponding nanotube with a four-fold right-handed parallel arrangement of the oligomers represented by arrows is also shown.

hydrophilic sides are connected by intermolecular hydrogen bonds to form a chain sheet and the hydrophobic ribbon faces are stacked by van der Waals forces (Glasser et al., 2012). When looking at the *ab* projection structures of the cellulose allomorphs, the two native structures (Nishiyama et al., 2002, 2003) are described by stacked layers of linear chain sheets, while the *ab* projection structures of cellulose II (Langan et al., 1999) and III<sub>I</sub> (Wada et al., 2004) allomorphs show zigzag shaped chain sheets, which allow cellulose chains to form intersecting chain sheets (but note that they are not like the sheets of chains in cellulose I). Therefore, despite their amphipathic nature, it seems to be very unlikely that the cellulose chains having a linear, flat ribbon shape can congregate to a tubular architecture similar to the helix-forming  $\beta$ -1,3- and  $\alpha$ -1,4-linked glucans.

Recently, we reported spontaneous formation of a tubular arrangement of cellulose chains in the course of density functional theory (DFT) structure optimizations of cellulose oligomer sheet models, each of which was derived from the chain sheets constituting the cellulose allomorph crystal structures (Uto, Hosoya, Hayashi, & Yui, 2013; Uto, Mawatari, & Yui, 2014a). Fig. 1 shows the sheet rolling process of the cellulose III<sub>I</sub> (100) chain sheet model and the architecture of the final tube structure (Uto, Miyata, & Yui, 2014b). The cello-oligomers oriented with parallel polarity arrange in a right-handed four-fold helix with one-quarter chain staggering. During the sheet rolling process, each oligomer deviated from the initial two-fold helical structure to develop a slightly left-handed twist, resulting in incomplete closure at the sheet edges. One-quarter chain staggering was first proposed in the tube structure since all of the parallel chain sheets composing the cellulose III<sub>I</sub> and native allomorphs have been reported to be of non-staggering (Nishiyama et al., 2002, 2003; Wada et al., 2004). The present DFT calculations indicated that the non-staggering chain assembly of the cellulose III<sub>I</sub> (100) chain sheet may have been only allowed under the crystal packing environment, which appears to represent the metastable feature of the cellulose III<sub>I</sub> allomorph. On the other hand, the isolated chain sheets of the native cellulose forms exhibited the right-handed sheet twist as a result of the DFT optimizations (Uto et al., 2013, 2014a). We thus suggested that the cellulose nanotube (CelNT) is a possible novel superstructure of cellulose and proposed six types of CelNT architectures based on the one-quarter chain staggering relationship (see Fig. 2). It is also expected that CelNTs may have a hydrophobic nature at both the outer surface and in the inner channel, which may allow it to disperse in a nonpolar medium. MD calculations of CelNT in aqueous solution resulted in rapid collapse of the tube form

with face-to-face stacking of the pyranose rings (Uto et al., 2014b). The relative stabilities of the three-dimensional structures of the six CelNT models were then investigated by performing MD calculations in chloroform for 10 ns (Uto et al., 2014b).

In the present study, six CelNT models were further investigated for extended MD simulation times of up to 100 ns. The structural details of the equilibrated CelNT models were investigated in terms of the interchain energy, hydrogen bonding, rotation of hydroxymethyl groups, and solvent distribution around the CelNT surface. In addition to chloroform, which we used as the solvent in our previous study, we also used benzene as the solvent because the tube structures are expected to be more effectively stabilized through pyranose ring to aromatic ring stacking, which is commonly observed in carbohydrate-related enzymes containing aromatic amino acids for substrate recognition (Beckham et al., 2010; Hudson et al., 2015; Morgan, Strumillo, & Zimmer, 2012; Ramirez-Gualito et al., 2009; Shiiba, Hayashi, & Yui, 2013). Thus, benzene, which has a wide range of derivatives, could be a suitable solvent to prepare CelNTs or a good starting point to search for a better solvent.

## 2. Computational methods

Although the six CelNT models were re-constructed, the structure of the component cellulose chains and the procedure used to construct the tube structures were essentially the same as those in our previous MD study (Uto et al., 2014b). In brief, 16 cellulose chains with degree of polymerization of 80 and the hydroxymethyl groups at the *gt* position (see Fig. 3) were systematically arranged to construct a tube structure based on either of the six symmetry operations and the one-quarter chain staggering relationship between adjacent chains. Fig. 2 shows the symmetry operations, where *P* and *AP* indicate parallel and antiparallel chain polarity, respectively, *H<sub>R</sub>* and *H<sub>L</sub>* represent right- and left-handed helical symmetry, respectively, and *R* represents rotational symmetry.

The CelNT models were placed in a rectangular periodic cell filled with about 35,000 chloroform (CHCl<sub>3</sub>) or 23,000 benzene (C<sub>6</sub>H<sub>6</sub>) molecules. The solution systems were optimized and then equilibrated by NTV (constant number of particles, temperature, and volume) MD simulations with a gradual increase in temperature from 20 to 300 K at a rate of 1 K/ps, followed by NTP (constant number of particles, temperature, and pressure) MD simulations at 300 K and 1 bar for 100 ns. Throughout the equilibrium process, the motion of the CelNT models were fixed by imposing positional constraints with a constrained force

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