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First-Principle Simulations on the Elongation of Polymerized Cellulose Building Blocks

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This work presents first-principle simulations on the elongation effect of cellulose building blocks with different lengths. The models of finite oligomers and infinite polymers are both considered. The hydrogen bonding, total energies and electronic properties of the polymerized cellulose structures are investigated. The simulations confirm the hydrogen bonding in these cellulose building blocks. Due to the size-dependent effects at nanometer scale, the longer cellulose chains exhibit lower energies than the short. A quantitative relation of energy respect to number of glucose is obtained. It is found that the lengths of chains, the configuration and solvent effects are important factors for the electronic properties of the cellulose polymers. The energy band structures and Young's modulus of the cellulose polymers are also investigated based on first-principle calculations.

Keywords: Cellulose building blocks, Elongation effect, Density functional theory, Polymers.

INTRODUCTION

In recent years the shortage of petroleum resources has been become a problem with great concern for nearly ervey country in the word. At the same time, burning the fossil fuels brings environmental pollution at global scale due to the really vast carbon emissions. Thus more and more attentions have been paid to the development and utilization of new energy technology. Among various clean energy resources, the use of cellulose and other biomass has aroused considerable interests due to their many advantages over the fossil fuels. For instance, biomass has no such carbon dioxide side effects because of the completely nature products from seaweed, trees or dung. It is abundant and can be found almost everywhere of the earth. Also it often could take waste that is harmful to the environment and turn it into something useful.

Cellulose is the major structural material of plants and can be hydrolyzed to its constituent glucose units under different conditions[1,2]. As a result, the β-D-glucose can be seen as building blocks of cellulose. The polymerized glucose yet is treated as the model compound of cellulose in experimental and theoretical studies[3-5]. Thus, in order to achieve a further understanding of structure-property relationship of the cellulose and the derived materials, it is desirable to study the polymerized glucose. On the other hand, the computations and simulations have been adopted to the studies of biomass in recent years[1,6,7]. However, the elongation effect from viewpoint of first-principle study for the polymerized cellulose building blocks is still exiguous. There are some attempts by using the force field methods[8-10], but it is well-known that the results are relies heavily on the parameters adopted[11]. Conversely, first-principle calculations without any parameter could exhibit more enhanced accuracy and thus has been widely and successfully used in molecules, crystals and biomaterials[12-14].

In this paper, we perform a theoretical study on polymerized structures built from glucose by means of first-principle computations. The elongation effects on the structures, energies and electronic properties are investigated for cellulose blocks.

EXPERIMENTAL

In order to study the elongation effects of cellulose building blocks, the glucose is selected to construct the polymerized structures. Usually the glucose is favorable to exist in the pyranose from[2]. Thus the β-D-glucose (now as G1) is treated as the simple model, as shown in Fig. 1. Our first-principle calculations show that this structure has the lowest energy by 1.54 kJ/mol than α-D-glucose, which agrees well with previous studies[2]. Here the finite chains with the lengths of 2-4 glucoses unit cells (cellobiose, cellotriose and cellotetraose, denoted as G2, G3 and G4, respectvely) and the one-dimensional (1D) infinite structures are adopted to study the elongation effects. Also the *cis*- and *trans*-isomers with two different linking patterns are considered for these polymerized

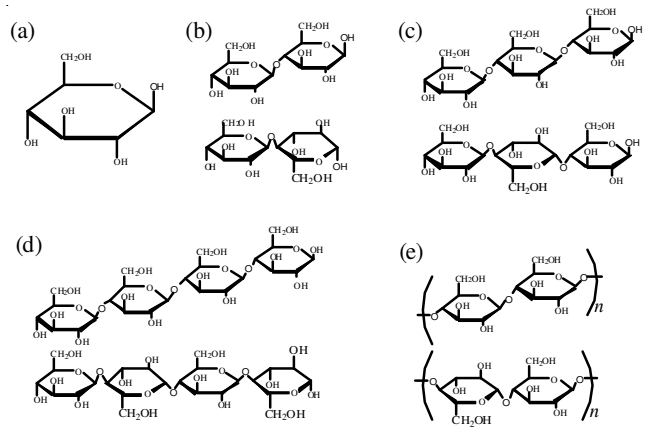

Fig. 1. Models of cellulose building blocks with different lengths. (a): G1; (b) G2; (c): G3; (d): G4 and (e) 1D polymers. The top is for *cis*-isomer and the bottom is for *trans*-isomer

cellulose building blocks. Since the parameter of the cellulose unit cell is close to 5 Å, thus the glucose chains studied have the lengths of about 5-20 Å in this work. As to the 1D polymers, it is investigated under the periodical boundary condition to simulate the behaviours of infinite cellulose chains. The similar strategy is also used in elongation studies of carbon-based materials[15,16].

The hydrogen bonding usually plays important roles in the cellulose-based materials. Thus a newly developed hybrid meta functional method[17] M06-2X within the scope of Kohn-Sham density functional theory (DFT) is adopted to calculate the cellulose building blocks in this work. This method has been successfully applied to the hydrogen bonding and non-covalent interactions such as cellulose-based and organic materials according to the previous calculations[17-19]. The geometrical optimizations, energies and electronic properties are all computed with Gaussioan09 package[20] under the framework of linear combination of atomic orbital (LCAO) theory. For the molecules, the DFT self-consistent field molecular orbital (SCF-MO) method at the 6-31++G** basis set theory level are used. Since many chemical reactions are performed in the water phase, thus the solvent effect is also considered for finite structures by the self-consistent reaction field (SCRF) method, with the geometrical structure obtained in the gas phase. For the infinite chains, the DFT self-consistent field crystal orbital (SCF-CO) method at 6-31G** level are adopted. In the SCF-CO calculation, k-points sampling in the first Brillouin zone is set to 500.

RESULTS AND DISCUSSION

Geometrical structure and energy: The obtained structures of G2-*cis* and G2-*trans* are shown in Fig. 2. It can be observed that the hydrogen bonding is present for the both isomers. The O···H distances are 1.995 and 2.155 Å, respectively for *cis*- and *trans*-G2, which are in the scope of common distances for the hydrogen bonding. The hydrogen bonding are also found in G3 and G4 series, with the distances in the range of 1.910-2.028 Å. These values are close to 1.8-2.4 Å obtained by previous studies for cellulose and cellobiose[2,21].

Fig. 3 showed the plot of the total energies of the finite models of cellulose. It is clear that the longer chains always

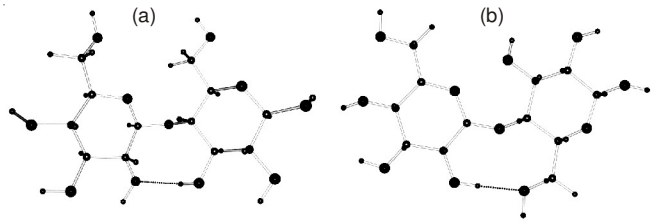

Fig. 2. Obtained *cis*- (left) and *trans*-isomers (right) of G2 by first-principle structural optimizations

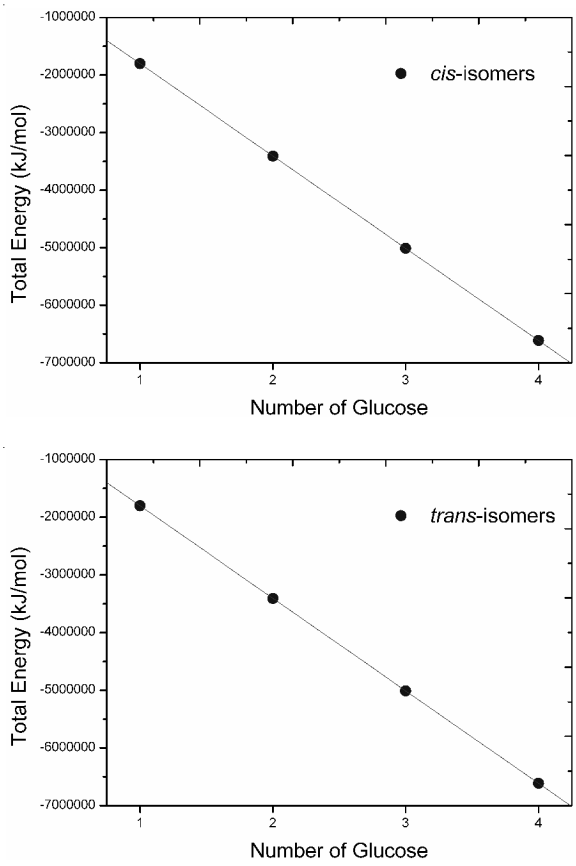

Fig. 3. Total energies of the cellulose building blocks with different lengths

exhibit lower energies than the short. This can be ascribed to the size-dependent effects at nanometer scale. In order to get quantitative information about the size-dependent energies, the linear-scale relation of energy respect to number of glucose (N) is obtained based on the equation E_{total} = -1603035N-200549 for *cis*-isomer (or E_{total} = -1603022N-200564 for *trans*-isomer) with correlation coefficient R > 0.99. Here the value of slope gives -1603035 and -1603022 for *cis*- and *trans*-isomers according to the equation, which agrees with the obtained 1602939 and 1602932 kJ/mol for half of the energies for 1D structures.

It is also noteworthy that the *cis*- and *trans*-isomers of the cellulose building blocks have very similar total energy. Actually, the differences of total energy for these isomers are within 35 kJ/mol. Moreover, the *cis*-structure always presents lower energy than the *trans*-one for not only oligomers but also 1D polymers. This means that the *cis*-structure is the favorable conformation from viewpoint of energy. The O···H interaction distance is 1.995 Å in the G2-*cis* and shorter than 2.115 Å in the G2-*trans*. The same trend is also valid for G3,

G4 and 1D cellulose chains. Thus stronger hydrogen bonding with shorter O···H interaction distances maybe one of the factors leading to higher stabilities for *cis*- than *trans*-isomers. These results are also supported by the calculations considering water-solvent effect as shown in Table-1, though the obtained energies with SCRF method exhibit somewhat lower values than in gas phase.

Electronic property: Since the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play an important role in chemical reactions for the reactant, the energy levels of the frontier orbital for the series of polymerized cellulose building blocks are computed as listed in Table-1. Though Koopmans' theorem is not fully valid for DFT calculations, the relative positions of the computed HOMO and LUMO reflect their abilities to lose and gain electrons and this will be internally consistent within the series of cellulose oligomers with various lengths.

Firstly, we pay attention to the finite structures in the gas phase. As shown in Table-1, HOMO and LUMO of G1 are computed to be -9.147 and -0.438 eV, respectively. As the chains made of β-D-glucose become longer, HOMO shift to a higher energy level, whereas LUMO decreased to a lower level for both *cis*- and *trans*-isomers. Thus the abilities to lose and gain electrons are both enhanced as the cellulose chains elongate. This is different from the elongation effect for the 1D carbon-based materials, such as carbon nanotubes (CNTs)[16]. As a result, the longer the cellulose chain is, the smaller HOMO-LUMO energy gap (E_g) will present, as shown in Table-1. These facts suggest that the electronic properties of the cellulose building blocks would be modulated by the polymer length. It is also found that the *cis*-structure exhibits higher HOMO and lower LUMO than its *trans*-isomer. Thus the conformation, besides the lengths of the chain, is one of the significant factors for the electronic properties of the cellulose polymers.

Now we turn to the results in the water solvent. As can be seen from Table-1, the trends of the HOMO, LUMO and E_g are largely preserved as the cellulose polymers get longer. Compared with those in the gas phase, the energy levels however become lower for HOMO and higher for LUMO, respectively, as the water solvent is considered. Thus the solvent effect is also important for the electronic properties of the cellulose polymers.

Then we pay our attentions to the infinite polymers. Since the 1D cellulose structures are calculated under the periodical boundary condition, what we obtained is not the isolated molecule orbital for finite models, but the energy band structure, as shown in Fig. 4. It is observed that a large energy band gap between top of the highest occupied band (HOB) and bottom of the lowest unoccupied band (LUB) is presented for both *cis*- and *trans*-isomers. Thus the 1D cellulose models exhibit insulating state due to the existed band gaps. This is consistent with the result by experiments that the cellulose fibre is free of electric conductivity[22,23]. Since the obtained band gaps of the 1D cellulose polymers are very larger (> 10 eV), we may expect that it would be useful as the candidate of insulating materials[22-24].

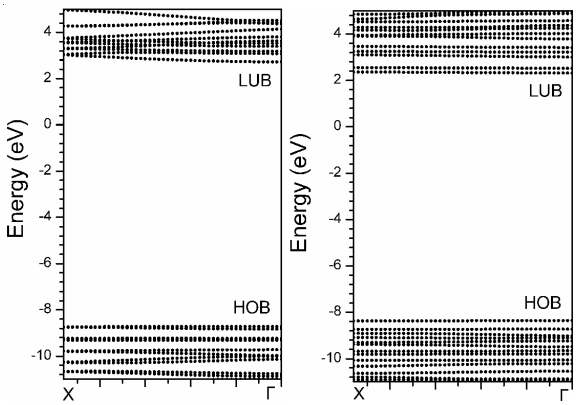

Fig. 4. Calculated energy band structures of the 1D cellulose polymers. The left for the *cis*- and the right for the *trans*-isomers

Young's modulus of the 1D cellulose polymers: To get more about the mechanical behaviour of the cellulose polymers, the Young's modulus of the 1D structure is studied. The calculation is based on the elastic stiffness of the 1D system using the second derivative of the strain energy of a unit cell with respect to the axial strain by equation:

$$Y = \frac{1}{V_0}\frac{d^2E}{d\varepsilon^2}\bigg|_{\varepsilon=0}$$

where V_0 is the volume of a unite cell and ε is a small deformation of the lattice constant. The volume is determined by electronic density in Gaussian program output files and tight option is taken for better accuracy in the computations. To obtain the values of Young's moduli, a numerical method is used[25]. We calculate the energies of unit cell with the deformations of the lattice constant 0, ± 0.5 and ± 1.0 %. The curve of the strain energy as a function of lattice constant deformations is drawn, as shown in Fig. 5. Then $d^2E/d\varepsilon^2$ is obtained from the second derivative with correlation coefficient > 0.99.

TABLE-1
ENERGIES AND ELECTRONIC PROPERTIES OF POLYMERIZED CELLULOSE BUILDING BLOCKS

Structure	Total energy (kJ/mol)		HOMO (eV)		LUMO (eV)		E_g (eV)	
	Gas	Solvent	Gas	Solvent	Gas	Solvent	Gas	Solvent
G1	-1803580.6	-1803640.9	-9.147	-9.251	-0.438	-0.030	8.709	9.220
cis-G2	-3406621.6	-3406706.9	-8.747	-9.083	-0.690	-0.117	8.058	8.966
trans-G2	-3406616.3	-3406706.0	-9.056	-9.147	-0.601	-0.093	8.455	9.055
cis-G3	-5009655.3	-5009770.7	-8.605	-9.062	-0.809	-0.197	7.796	8.864
trans-G3	-5009624.9	-5009745.6	-8.838	-8.862	-0.527	-0.123	8.311	8.739
cis-G4	-6612684.4	-6612828.7	-8.565	-9.135	-0.873	-0.235	7.692	8.901
trans-G4	-6612649.5	-6612794.9	-8.795	-8.834	-0.474	-0.145	8.321	8.689
cis-1D	-3205878.9	–	-8.720	–	2.721	–	11.441	–
trans-1D	-3205864.4	–	-8.357	–	2.319	–	10.676	–

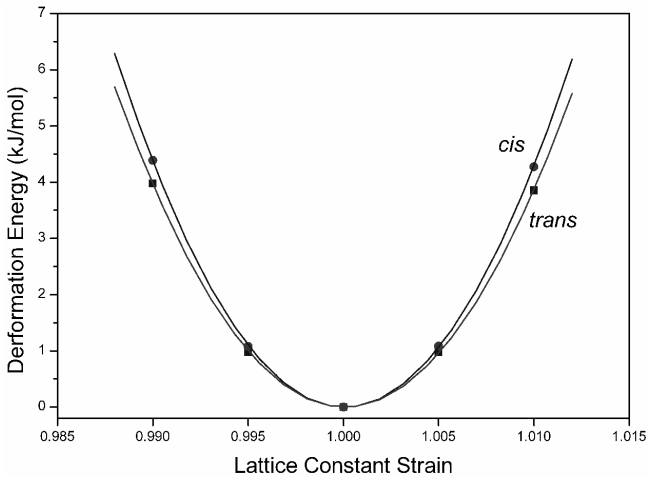

Fig. 5. Deformation energy as a function of lattice constant strain

The obtained Young's moduli are 60.8 and 55.8 GPa for *cis*- and *trans*-structures, respectively. The measured Young's module of the cellulose is very flexible and in the range of 25-120 GPa[26-28]. This is due to the various sources used in the measurements. Thus our results based on the first-principle calculations are accord with the experimental values. The Young's module of 1D carbon nanotubes usually is about 1000 GPa[25], thus the 1D cellulose polymers maybe not as stiff as carbon nanotubes. Nevertheless it still close to and even larger than those of carbon fiber reinforced plastic (30-50 GPa)[29] and Mg metal (about 45 GPa)[30], which are commonly used in aeronautic materials.

Conclusion

In summery, first-principle simulations have been performed to study the elongation effect of the cellulose building blocks with different lengths. The hydrogen bonding, total energies and electronic properties of the polymerized cellulose structures are calculated and compared. The hydrogen bonding is observed for all the models here with O···H distances of 1.910-2.155 Å. The longer cellulose chains exhibit lower energies than the short and this can be ascribed to the size-dependent effects at nanometer scale. The *cis*-configuration presents lower energy than the *trans*-isomer for both oligomers and 1D polymers. This fact indicates that the *cis*-structure is more stable from viewpoint of energy due to the shorter O···H interaction distances. HOMOs increase whereas LUMOs decrease for both *cis*- and *trans*-isomers as the elongation of cellulose chains. It is also found that the *cis*-structure exhibits higher HOMO and lower LUMO than its *trans*-isomer. Thus the lengths and conformations are significant factors for the electronic properties of the cellulose polymers. The solvent effect is considered and it has somewhat impact on the electronic properties. The energy band structures and Young's modulus of the 1D cellulose polymers with infinite structures are investigated. It is observed that the 1D cellulose models exhibit insulating state with large band gaps, which explains that cellulose are good candidate of insulating materials. The obtained Young's moduli of 1D cellulose polymers are 60.8 and 55.8 GPa for *cis*- and *trans*-structures, respectively. Thus the elastic stiffness of 1D cellulose chain is close to that of carbon fiber reinforced plastic and magnesium metals.

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