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Computational study to evaluate the birefringence of uniaxially oriented film of cellulose triacetate

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ABSTRACT

The intrinsic birefringence of a cellulose triacetate (CTA) film is evaluated using the polarizability of the monomer model of the CTA repeating unit, which is calculated using the density functional theory (DFT). Since the CTA monomer is known to have three rotational isomers, referred to as *gg*, *gt*, and *tg*, the intrinsic birefringence of these isomers is evaluated separately. The calculation indicates that the monomer CTA with *gg* and *gt* structures shows a negative intrinsic birefringence, whereas the monomer unit with a *tg* structure shows a positive intrinsic birefringence. By using these values, a model of the uniaxially elongated CTA film is constructed with a molecular dynamics simulation, and the orientation birefringence of the film model was evaluated. The result indicates that the film has negative orientation birefringence and that its value is in good agreement with experimental results.

1. Introduction

Cellulose is known as the most abundant hydrocarbon in the world. The chemical derivatives of cellulose are actively researched based on their renewable and biodegradable properties. Among them, cellulose triacetate (CTA), which is obtained by the acetylation of cellulose, is one of the most widely known cellulose derivatives. CTA has been used in a variety of commercial products, such as films and fibers, for many years. Recently, the widespread use of CTA has been further expanded to new high-technology application fields.[1] For instance, it is applied to the protective films of liquid crystal displays by taking advantage of its low birefringence. Further development of CTA has been aimed at controlling the birefringence of the film for displays with advanced functions. For this purpose, it is important to know the basic properties of the CTA film birefringence in relation to its molecular level of conformation and the orientation of CTA in the film.

The birefringence of the polymer film depends on the polarizability anisotropy of the repeating monomer unit and its orientation in the film.[2] For CTA polymer film, its repeating monomer unit can take several conformations according to the side-chain orientations in the film because of the flexibility of the acetyl groups. This flexibility can affect the birefringence of the entire film. Yamaguchi et al. indicated that the in-plane birefringence of the stretched CTA film has a negative value. They attributed the origin of this negative birefringence to the orientation of the carbonyl group, which is oriented perpendicularly to the stretching direction.[3] The orientation of the repeating unit in polymer films is an important factor for birefringence. In the industrial manufacturing process of CTA film, the raw materials are first dissolved in solvent. After the dissolution process, the solution is casted and dried to form a film.[4] During these processes, the CTA molecules flow and orient themselves to the flow direction. The molecular orientation obtained in the casting process can induce a noticeable amount of birefringence in the CTA film; in other words, we have the possibility to control the birefringence by changing its orientation during the film-making process. Therefore, in order to control the birefringence it is important to know the possible conformations of the unit and the orientation of the molecule in the film.

Several extensive experimental studies have been reported on the birefringence of CTA. Nishio et al. investigated the variation of the birefringence of the polymer alloy of cellulose acetate and a copolymer with different composition rates.[5] They concluded that the strong intermolecular interaction induces a slow relaxation of the orientation of the polymers and, as a result, it produces high birefringence.

We have been investigating the behavior of the CTA chain in various solvents by using the molecular dynamics (MD) simulation.[6–8] MD simulation methods are useful for the interpretation of the birefringence of CTA films in the molecular level. However, to our knowledge, there are no computational studies on the birefringence of CTA film. In this work, we performed density functional theory (DFT) calculations and MD calculations for the CTA

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polymer film and investigated in detail the relation between the conformation and orientation of CTA molecules in the film and the birefringence of the film. DFT calculation is one of the most powerful methods to obtain an accurate evaluation of the birefringence of the molecules. Ando et al. investigated the birefringence of several polyimide molecules by using DFT calculations.[9,10] They calculated the polarizability tensor of the repeating unit of polyimide by using DFT and then converted the polarizability tensors to birefringence by using the Lorentz–Lorentz equation. However, DFT calculations are very time-consuming and the calculation of an entire polymer with more than several residue lengths is generally considered unfeasible. To evaluate the birefringence of the CTA film, in this work we combined the DFT and MD calculations. Specifically, the DFT calculation was used to obtain the polarizability of the CTA repeating unit and the MD method was applied to evaluate the conformational information of the CTA chains in the film from the trajectory of the MD simulation.

2. Methods

2.1. DFT calculations

The refractive indices of molecules can be calculated from the polarizability using the Clausius–Mossotti equation:

$$\frac{n_r^2-1}{n_r^2+2}=\frac{\rho N_A \alpha}{3M\varepsilon_0} \quad (1)$$

where n_r is the refractive index, and α, ρ, N_A, M, and ε_0 are the polarizability, density, Avogadro's number, molar molecular weight, and vacuum dielectric constant, respectively.[11] To obtain the birefringence of the CTA polymer, the polarizability of a repeating unit of CTA was first calculated by using the DFT method. The monomer model of the CTA repeating unit (CTA monomer) used in this work is shown in Figure 1. It is acetylated at the 2, 3, and 6 positions of glucose and its C1 reduced and C4 non-reduced ends are capped with methoxy groups. Ando et al. proposed that the polarizability tensors of the polymers can be quantitatively reproduced by using B3LYP/6-311++G(d,p)-level calculations.[9,10] The same method and basis set described in their report were used in the present work. The initial geometry of the CTA monomer was constructed based on the crystal structure of CTA.[12] The CTA monomer was optimized using the B3LYP/6-311++G(d,p) basis set, and the vibrational frequencies were also calculated at the same level of basis set. The molecular axes of the CTA monomer were defined as shown in Figure 1. Specifically, the origin of the axes was set at the C4 atom, and the *x*-axis was defined as the direction of the CTA main chain from the C4 to the O1 atom. The *z*-axis was set perpendicular to the gluco pyranose ring plain, defined by the three atoms of C4, O1, and C2. The *y*-axis was positioned perpendicular to both *x* and z axes. The polarizability tensors were calculated along these molecular axes. The wavelength was set at 500 nm. All DFT calculations were carried out using Gaussian09.[13]

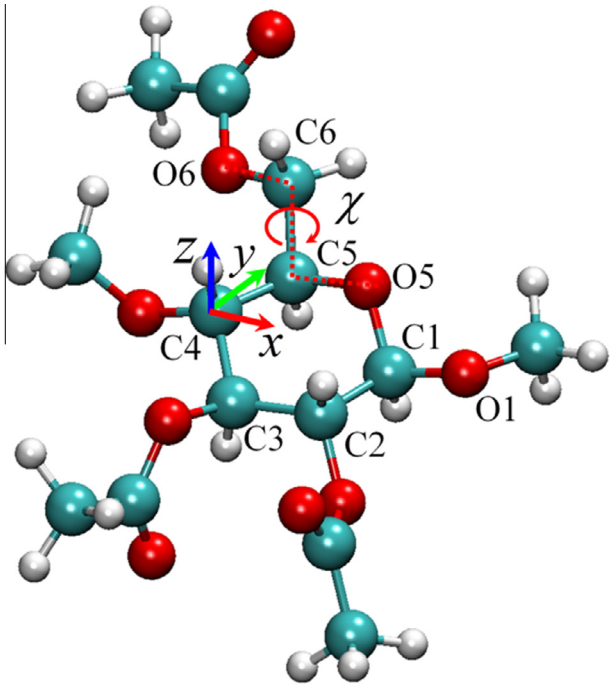

Figure 1. Nomenclature of the CTA repeating monomer unit.

2.2. MD simulation

A model of the CTA film was constructed using MD simulations in order to evaluate the refractive index of the polymer film. The model of a CTA polymer chain consisting of 40 CTA monomer repeating units was used. A total of 64 CTA polymer chains were produced and set in a simulation box with random orientation. After the construction of the initial structure, total 14 ns simulated annealing procedures with heating up at 2000 K and cooling down to room temperature simulations were repeated to relax the system. Isothermal–isobaric ensemble (NPT) was adopted in the annealing procedure. The final size of the simulation box was $X = Y = Z = 10.219$ nm and average density of the system was 1148 kg/m^3, which gives around 10% difference from the experimental value of 1290 kg/m^3. This discrepancy may come from the reason that the experimental sample usually would be a mix of the amorphous and crystal regions. Following the equilibrium stage, simulation cell box was deformed to mimic the elongation process of the CTA film. The simulation cell was changed by 0.001 nm along to *X* direction at every 1000 steps intervals until the 25% final elongation ratio of the film reached (Fig. 2). Therefore, the total simulation time becomes 2.555 ns, and the elongation rate of the simulation is 10^8 s^{-1}. This strain rate is still at the higher extreme of the experimental condition, but a best compromise with the expense of the computer resources in recent environment. Similar strain rate was used by Lee and Rutledge who performed elongation MD simulation of polyethylene with deformation rate from 5×10^6 to 5×10^7 s^{-1} by using united atom model.[14] Rahman et al. performed MD simulation of the elongation of cellulose nanocomposites with deformation rate from 1×10^8 to 2×10^8 s^{-1} by using all atom model.[15] During the elongation process, the volume of the simulation box was kept constant to maintain the polymer density of the system. The trajectories of the non equilibrium simulation are analyzed and the birefringence of the CTA film was evaluated using these results. All MD simulations were performed using the GROMACS program.[16–20] The Parrinello–Rahman method and Nose–Hoover thermostat were used to maintain a constant pressure and temperature.[21–24] The cut-off length of the non-bonding interactions was set at 1.35 nm, and the switching function was turned on at 1.2 nm and turned off at 1.35 nm. The electrostatic interaction was calculated using the Particle Mesh Ewald method.[25] The Charmm force field was used for the glucose unit and the acetyl residue.[26,27]

3. Result and discussion

3.1. Evaluation of the intrinsic birefringence of the CTA monomer unit using DFT

The monomer unit of CTA has three major stable conformations according to the rotation of the torsion angle, χ, at the C6 position