Molecular orientation in the Nematic Ordered Cellulose film using polarized FTIR accompanied with a vapor-phase deuteration method

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Abstract Previously, the authors reported "Nematic Ordered Cellulose (NOC)" that is a well-ordered state of β-1,4-glucan chains without exhibiting typical X-ray diffraction patterns of any cellulose polymorphs (Togawa and Kondo 1999; Kondo et al. 2001; Kondo 2007). The NOC was prepared by stretching water-swollen gel-like films at the draw ratio of 2.0 to provide highly oriented β-1,4-glucan molecular chains of cellulose, which was proved by the high resolution TEM observation. In this paper, a detailed study of the unique ordered state of the NOC was attempted to characterize orientation of the main chains as well as the OH groups of molecules using polarized FTIR accompanied with a vapor-phase deuteration method. The dichroic analysis suggested that the main chains were fairly oriented in the stretching direction whereas the OH groups remained unoriented. The disordered state of the OH groups regardless of the oriented state for the main chain may hinder the oriented crystallization during the preparation of NOC films.

Introduction

Crystallization in polymers is preferentially triggered by elongation parallel to the axis of the stretching direction of the molecular chains (Mandelkern 2002). However, our previous report (Togawa and Kondo 1999) revealed that the uniaxial drawing up to 2.0 times of water swollen gel-like cellulose films did not necessarily enhance crystallization. In this case, the increase of the drawing ratio yielded a diffuse wide-angle X-ray diffraction (WAXD) pattern in the equatorial direction, but it provided a typical reflection pattern in the meridional axis. Concerning the molecular orientation, the observation using a high-resolution TEM showed that the drawn film had a favorable orientation of β-1,4-glucan molecular chains towards the stretching direction. Nevertheless, crystallinity indices (Cr.I.) of the same film based on the density did not exhibit a high crystallinity (Togawa and Kondo 1999; Kondo et al. 2001; Kondo 2007); typically, the film contained more than 80% of the noncrystalline regions. This unique supramolecular structure, which has both the high molecular orientation and the relatively low Cr.I., has been

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termed as "Nematic Ordered Cellulose (NOC)" (Kondo et al. 2001; Kondo 2007).

A question still remains why the high orientation of β-1,4-glucan chains did not significantly encourage the crystallization, which totally differed from cases for synthetic polymers. It is assumed that this phenomenon could be due to the difference of the orientation behavior between the main chain and the side chain (hydroxyl (OH) groups) in the cellulose molecule. Therefore, our objective in this study is to characterize the orientation separately for the main chains and the OH groups in the uniaxially drawn NOC film. To perform this, we employed our proposed method (Hishikawa et al. 1999, 2005) with a vapor-phase deuteration and the simultaneous measurement using the polarized Fourier transform infrared (FTIR) spectroscopy.

Polarized IR spectroscopy is one of the most useful tools for analysis of oriented polymers because it can provide us both quantitative and qualitative information. Previous studies for drawn polymers using the method were mainly based on quantitative analyses concerning the relative orientation of the polymer chains. Most of such studies were carried out on synthetic polymers, for example, polyethylene (Stein and Norris 1956; Onogi and Asada 1967; Koenig et al. 1967; Read and Stein 1968; Karacan 2006), polypropylene (Samuels 1965; Shigematsu et al. 2001), poly(ethylene terephthalate) (Liang and Krimm 1957; Dulmage and Geddes 1958; Lofgren and Jabarin 1994; Radhakrishnan and Kaito 2001; Kandilioti et al. 2004), nylon 6 (Sibilia 1971), polyamide (Vasanthan 2005), poly(vinyl chloride) (Voyiatzis et al. 2000), poly(trimethylene terephthalate) (Lee et al. 2000), poly(methyloctadecylsilylene) (Kaito et al. 1999), poly(3-alkylthiophenes) (Gustafsson et al. 1991), poly(aryl ether ether ketone) (Voice et al. 1993) and isotactic polystyrene and poly(2,6-dimethylphenylene oxide) blends (Dikshit and Kaito 2003). As for cellulose, not so many quantitative investigations have been made except studies on orientation of drawn cellulose fibers (Smith et al.1963; Siesler et al. 1975), on hydrogen bonding in cellulose II (Šturcová et al. 2003) and on cellulose derivatives and synthetic polymers blends (Park et al. 2005), since many cellulose researchers were required to determine the chain conformation and the crystalline structure (Mann and Marrinan 1958; Tsuboi 1957; Liang and Marchessault 1959a, b;

Marchessault and Liang 1960; Liang and Marchessault 1960) and to assign the absorption bands (Tsuboi 1957; Liang and Marchessault 1959a, b; Marchessault and Liang 1960; Liang and Marchessault 1960; Maréchal and Chanzy 2000) on qualitative approaches.

Recently, we proposed the combination of a deuteration method and polarized FTIR to investigate the molecular packing domains based on the engagement states of the OH groups (Hishikawa et al. 1999, 2005; Kondo et al. 1998). The advantage of the method was that vapor-phase deuteration of cellulose films could isolate the absorption bands of OH groups due to the crystalline regions from those due to the noncrystalline regions in the IR spectrum. Simultaneously the absorption bands of OH groups due to the noncrystalline regions can also been estimated by subtraction of the obtained crystalline regions OH from OH bands of the entire regions. Therefore, the combined method could reveal the individual orientation behavior of OH groups in each region, which would explain that the high orientation of β-1,4-glucan chains in the NOC film did not extensively enhance crystallization.

Experimental

Materials and Methods

Materials

The starting material was bleached cotton linters with degree of polymerization of 1,300. The cellulose material was dried under vacuum at 40 °C before use. N,N-Dimethylacetamide (DMAc) was purchased from Katayama Chemicals Co. Ltd. (99+%) and dehydrated with molecular sieve 3A without further purification. Lithium chloride (LiCl) powder (Katayama Chemicals Co. Ltd.) was dried in the oven at least for 3 days at 105 °C.

Preparation of the NOC films

The NOC films uniaxially drawn up to 2.0 times from water-swollen gel-like cellulose films were prepared according to our previous reports (Togawa and Kondo 1999; Kondo et al. 2001). Namely, the dried cellulose of 1.3 g was submerged in 300 mL of water overnight

and filtered to remove water. Then the cellulose was immersed in 300 mL of methanol and filtered to eliminate excess methanol. This treatment was repeated at least five times. The swollen cellulose with methanol was drenched in 300 mL of DMAc and filtered to remove excess DMAc. The DMAc was exchanged more than eight times. The cellulose swollen by DMAc was then dissolved in 100 mL of DMAc/LiCl solution (the LiCl concentration of 5% (w/w)) with stirring at room temperature. After more than 3 weeks of stirring, the cellulose solution was centrifuged and filtered to remove cotton linters which remained insoluble. The actual concentration (wt%) of cellulose in the solution was determined by weighing a small portion of the dried cellulose film obtained by regenerating a certain amount of the solution using saturated water vapor as mentioned below.

The water swollen gel-like films were prepared using the cellulose solution with the concentration of 1.3 wt%. Then 3 g of the solution was poured into a flat-bottomed glass petri dish with 56 mm in diameter, and placed in a closed box together with a beaker containing water at room temperature. In this manner, saturated water vapor in the box slowly diffused into the solution and precipitated the cellulose. It was allowed to stand at room temperature for several days before the gel-like film was formed. The gel-like film was washed with running distilled water for several days to remove the solvent thoroughly. After washing, a water-swollen transparent gel-like film was obtained, and it was stored in water until needed.

The drawn films were prepared as follows: water-swollen gel-like films were cut into strips of approximately 30 mm long and 5 mm wide, respectively. The water-swollen strips were clamped in a manual stretching device and elongated uniaxially to the draw ratio of 2.0 at room temperature. The entire drawing process was carried out while the sample was still in a water-swollen state. To stabilize the drawn film, it was then air-dried at room temperature with the tension kept in the stretching device for overnight. After air-dried, the drawn sample in the stretching device was vacuum-dried at 40–50 °C for more than 24 h, providing with NOC films.

The NOC film sample employed for deuteration in vapor was 17 μm in thickness. The crystallinity index (Cr.I.) of the film determined by a density measurement was estimated as 16.3%, almost equivalent to that of the undrawn films as 13.8%.

Measurements

The film sample was mounted in a home-made modified IR absorption cell for vapor-phase deuteration (Hishikawa et al. 1999, 2005; Kondo et al. 1998). Polarized FTIR spectra before and after deuteration were measured using a Perkin-Elmer Spectrum 2000 FTIR spectrometer with the electric vector of the light parallel and perpendicular to the stretching direction, respectively. The polarized FTIR measurements were performed by 32 scans of a 2 cm^{-1} resolution using a DTGS detector and the wave number region investigated ranged from 4,000 to 400 cm^{-1}. Deuterium oxide used was purchased from Wako Pure Chemical Industries, Ltd. and the purity was more than 99.75%. The film sample was dried thoroughly in a vacuum oven at 50 °C for several days in order to remove all residual water prior to deuteration.

The estimation of the orientation behavior

The orientation behavior of both the main chains and OH groups were estimated from dichroic ratios, respectively. The ratios (R) were calculated in the same manner as Zbinden's (Zbinden 1964):

$$R = A_\perp / A_{//}, (0.0 < R < \infty)$$

where $A_\perp$ is the absorbance of the band due to the particular molecular moiety for radiation polarized perpendicular to the stretching direction, whereas $A_{//}$ is the absorbance of the same band measured with radiation polarized parallel to the stretching direction. Thus, a relative value giving $R < 1.0$ represents a preferentially parallel orientation of the molecular moiety, while a value showing $R > 1.0$ indicates a favorable orientation of the moiety perpendicular to the stretching direction. This implies that the closer the R value comes to 0.0, the more either the main chains or OH groups of the sample are oriented to the stretching direction. It should be also noted that $R = 1.0$ means complete disorientation.

In the following section, the orientation behavior of the main chains of the β-1,4-glucan chains and OH groups will be discussed using the R values. The R value for the main chains was obtained from the antisymmetrical bridge oxygen stretching band in spectra of Fig. 1 before deuteration. Moreover, the
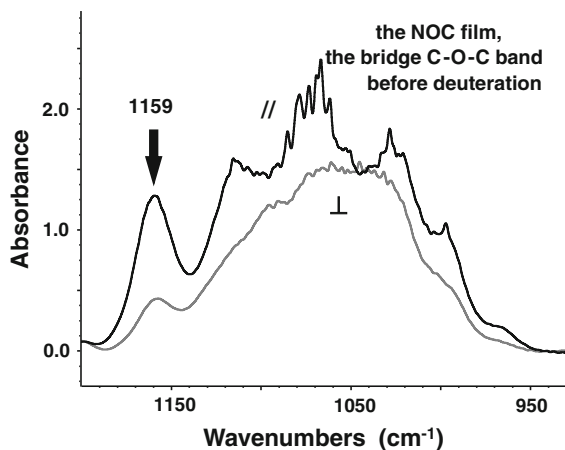
Fig. 1 The bridge C–O–C stretching band (1,159 cm^{-1}) in the polarized infrared spectra for the NOC film before deuteration; the *upper line* (//) electric vector parallel to the stretching direction; the *bottom line* (⊥) electric vector perpendicular to the stretching direction
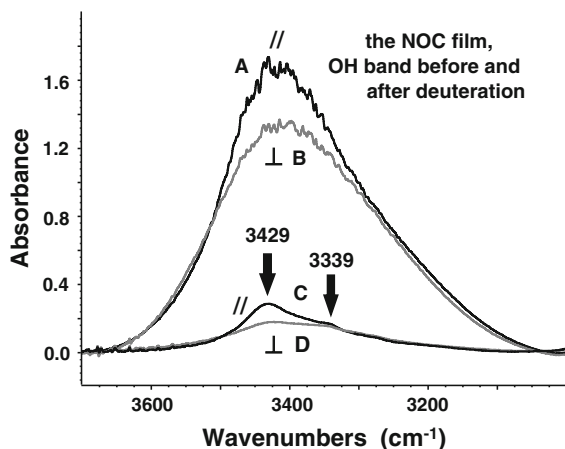

Fig. 2 The OH band in the polarized infrared spectra for the NOC film before (**A**, **B**) and after (**C**, **D**) deuteration; **A**, **C** (//) electric vector parallel to the stretching direction; **B**, **D** (⊥) electric vector perpendicular to the stretching direction

vapor-phase deuteration of the NOC film revealed that the amount of unexchangeable OH groups, 10.6%, of the total OH groups corresponded to the highly engaged intermolecular hydrogen bonded domains or crystalline domains (later, we will use crystalline domains as the term). The R value of the OH groups in the domains was calculated from the remaining OH stretching band in spectra of Fig. 2 after deuteration.
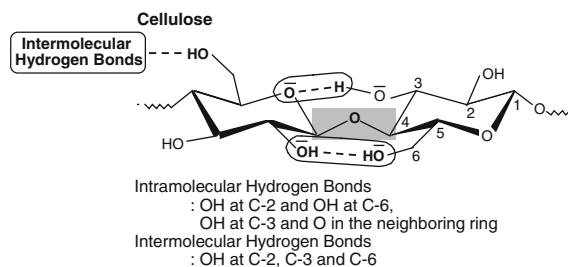

Fig. 3 Schematic image of the bridge C–O–C bond in the cellobiose unit (the *gray zone*) together with formation of intra- and intermolecular hydrogen bonds

Results and discussion

The orientation behavior of the β-1,4-glucans as the main chains of cellulose molecules in NOC

The R value of the main chains was estimated using the band that reflects the β-1,4-glucan chain axis without contribution of the transition moment of OH groups. The C–O–C band due to the antisymmetrical bridge oxygen stretching as shown in Fig. 3 was thought to be the most suitable for the above requirement because the transition moment of the stretching mode was regarded to correspond parallel to the molecular chains. Then, the band at 1,159 cm^{-1} in Fig. 1 was selected according to the assignment by Liang and Marchessault. They ascribed the band at 1,162 cm^{-1} for native celluloses (Liang and Marchessault 1959b) and the band at 1,155 cm^{-1} for regenerated celluloses (Marchessault and Liang 1960) to the antisymmetrical bridge oxygen stretching.

The value of R for the main chains (R_1) was calculated to be 0.32 before deuteration. This value indicated that the uniaxial drawing at the draw ratio 2.0 of water-swollen gel-like cellulose films enhanced orientation of the main chains in both the noncrystalline regions and the crystalline domains towards the stretching direction.

The orientation behavior of the OH groups in the minor crystalline domains of NOC

The bands C and D in Fig. 2 show the remaining OH stretching band after deuteration of the NOC film. For the present orientation study, the distinguished peak at 3,429 cm^{-1} and the shoulder at 3,339 cm^{-1} were

used, respectively. The former is considered due to the intramolecular hydrogen bonds; while the latter can be derived from the intermolecular hydrogen bonds (see Fig. 3; Hishikawa et al. 1999, 2005). Here, it was assumed that the transition moment of OH groups would be almost parallel along the chemical bond. Under the assumption, the OH bands due to the minor crystalline domains of NOC that appeared after deuteration were examined. The respective R value was $R_2 = 0.61$ for the peak and $R_3 = 0.91$ for the shoulder. Thus, in the spectra due to the crystalline states, the OH groups exhibited at least two kinds of the orientation behavior. The OH groups engaging in the intramolecular hydrogen bonds can be more sensitive enough to the uniaxial drawing and thereby to be oriented slightly to the stretching direction. On the contrary, the OH groups that could form the intermolecular hydrogen bonds were not significantly oriented.

The orientation behavior of the OH groups in the major noncrystalline regions of NOC

As for the R value of the OH groups in the noncrystalline regions as the major domain of NOC films, the OH stretching band in the difference spectra as shown in Fig. 4 was used by subtracting the spectrum after deuteration from the spectrum before deuteration as shown in Fig. 2. The shapes of the OH stretching bands due to the noncrystalline
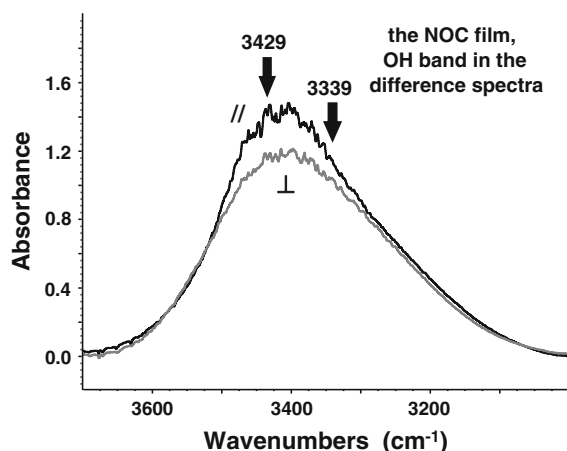

Fig. 4 The OH band in the difference spectra, which was supposed due to the OH groups in the noncrystalline regions; the *upper line* (//) electric vector parallel to the stretching direction; the *bottom line* (⊥) electric vector perpendicular to the stretching direction

states as shown in Fig. 4 were totally different from those (C and D of Fig. 2) due to the crystalline domains. The OH bands for the noncrystalline regions were very broad and vague, which did not show any major shoulders after subtraction of contribution of crystalline states. Then, the respective R values at 3,429 cm^{-1} (assigned as the intramolecular hydrogen bonds) and 3,339 cm^{-1} (assigned as the intermolecular hydrogen bonds) were obtained on the assumption described in the previous section. When compared with the frequencies of 3,429 cm^{-1} due to the intramolecular hydrogen bonds after deuteration (C and D of Fig. 2), the contribution of orientation was not necessarily significant in the noncrystalline regions as follows:

The R values based on Fig. 4 were $R_4 = 0.81$ at 3,429 cm^{-1} and $R_5 = 0.91$ at 3,339 cm^{-1}, respectively. Both values were close to 1.0, indicating less orientation. It was interesting that the difference between R_4 and R_5 was significantly smaller than that between R_2 and R_3 in the crystalline domains appeared after deuteration. Namely, the respective values of R_4 and R_5 were considered almost similar with each other. Therefore, not only the broad and ambiguous shape of the OH bands but the dichroism thus interpreted in the IR spectra indicated that all OH groups in the noncrystalline regions were likely to be kept unoriented toward the stretching direction. This was contrary to the orientation behavior of the OH groups particularly forming the intramolecular hydrogen bonds in the crystalline domains appeared after deuteration. In other words, once the intramolecular hydrogen bonds were engaged, crystallization might be initialized during the stretching process. This means that NOC films had less chances to allow the intramolecular hydrogen bonds to be engaged, because they comprises mostly noncrystalline domains, where the crystallinity index was estimated as 16.3% that is almost equivalent to 13.8% of the undrawn films.

Conclusion

According to our recent reports (Kondo et al. 2001, 2002; Kondo 2007), Nematic ordered cellulose (=NOC) exhibited quite unique surface properties that are due to the molecular orientation with the low crystallinity. NOC is prepared by the uniaxial

Table 1 R values for the main chains of β-glucan chains of cellulose molecules and the OH groups in the noncrystalline regions

	R value
Main chains	$R_1 = 0.32$
OH groups	
Intramolecular H. B.	$R_4 = 0.81$
Intermolecular H. B.	$R_5 = 0.91$

H. B. hydrogen bonds

drawing of water swollen gel-like cellulose films, which does not necessarily enhance crystallization. Namely, the drawn film had a favorable orientation of β-1,4-glucan molecular chains towards the stretching direction. Instead, the crystallinity indices did not exhibit a high crystallinity; typically, the film contained more than 80% of the noncrystalline regions. Therefore, it is of importance to clarify the molecular orientation in the noncrystalline regions in order to understand the structure–property relationship in NOC.

In the present study, polarized FTIR combined with the vapor-phase deuteration was enabled to reveal orientation of the cellulose main chains to the stretching direction in both the crystalline domains as the minority and major noncrystalline regions of NOC films. Concerning the hydroxyl groups, the orientation behavior was totally different from that of the main chains. In the minor crystalline domains of NOC, hydroxyl groups engaged in the intramolecular hydrogen bonds were slightly oriented to the stretching direction while those connecting the intermolecular hydrogen bonds were not significantly oriented. On the other hand, in the noncrystalline regions as the major part of the NOC films, both inter- and intrabridged OH groups were indicated unoriented.

Accordingly, in the noncrystalline regions as the NOC major part, the R value for the β-glucan main chains of cellulose molecules did not necessarily agree with that for the side chains of OH groups as listed in Table 1. Considering the R values in this study, the uniaxial drawing process to prepare the NOC film provided the oriented main chains to the stretching direction. On the other hand, the high R values (R_4 and R_5) indicate that the unoriented OH groups in the noncrystalline regions which occupy more than 80% of our drawn film sample would be the key for discouragement of the crystallization

induced by stretching. As the result, the NOC film was considered to have both the oriented main chains and the unoriented OH groups as the side chain. This flexible state of the OH groups might further hinder the oriented crystallization in the NOC preparation process and yet induce the unique properties particularly in the surface of the NOC film (Kondo et al. 2002).

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