Raman microprobe analysis of single ramie fiber during mercerization

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ABSTRACT

The Raman microprobe technique was applied to structural analysis of single ramie fibers during mercerization. Polarized laser beam was irradiated on a ramie fiber in 0-30 % NaOD/D_2O with the electric vector at 0 or 90° to the fiber axis, and Raman spectra thus obtained were studied in relation to the concentration of NaOD in D_2O. Conversion of -OH to -OD in ramie cellulose with NaOD/D_2O proceeded with an increase in the concentration of NaOD, and almost all OH groups in ramie cellulose were converted to -OD by the treatment with NaOD/D_2O of more than 15 %; almost all intra- and inter-molecular hydrogen bonds originally present in native ramie cellulose are cleaved by NaOH during mercerization. Polarized Raman spectra of ramie fibers showed that clear orientation of cellulose chains along the fiber axis was present in both original and mercerized ramie states. On the other hand, Raman spectra of ramie fibers swollen in 17.5-30 % NaOD/D_2O showed isotropic patterns, indicating that the orientation disappeared in the swollen Na-cellulose states.

INTRODUCTION

The crystal structure of cellulose I in native cellulose can be converted to that of cellulose II by either mercerization or regeneration from cellulose solutions. The packing mode of cellulose chains and conformations of cellulose molecules in the unit cell were calculated from the X-ray diffraction intensities, and the results indicated that the anti-parallel cellulose chain packing was preferable for cellulose II, in contrast of cellulose I, which has probably the parallel chain packing (1,2). However, there are some questions about this anti-parallel structure of cellulose II; how the parallel cellulose chains in microfibrils of cellulose I are converted to the anti-parallel mode, keeping the fibrous forms during mercerization. Nishimura and Sarko (3-5) proposed the mechanism of the conversion on the basis of X-ray diffraction data of Na-celluloses. However, since the information about crystal structures of cellulose allomorphs as well as those of swollen Na-celluloses obtained by X-ray diffraction methods is insufficient for determining the absolute structures, recently solid-state ^{13}C-NMR, Raman and other spectroscopic methods have been applied to the structural analyses of cellulose allomorphs. Yokota et al. recorded solid-state ^{13}C NMR spectra of native and rayon celluloses in 0-30 % NaOH solutions, and found that almost all glucose residues of cellulose chains had homogeneous structures in about 20 % NaOH without having two phases such as crystalline and non-crystalline regions (6).

Raman spectroscopy can give us some information about, especially, secondary structures of solution-state, swollen-state and solid-state celluloses. Celluloses I_α and I_β, which have been found from solid-state ^{13}C-NMR spectra of native celluloses (7,8), have different hydrogen bonding patterns with similar conformations of heavy atoms (9). The Raman microprobe technique allows to give Raman spectra to be recorded from domains as small as 1 mm. This technique was applied to algal cellulose fibrils, ramie fibers and mercerized ramie fibers by using polarized laser beam, and information about the orientation of cellulose molecules in fibrils or fibers was obtained (10). Since Raman intensity due to the OH stretching vibration of water usually present in cellulosic materials is quite weak, the effect of OH groups of water is excludable form Raman spectra of cellulose. Furthermore, Raman scattered light can be collected even through a thin glass cover without any problems.

In this study, the Raman microprobe technique with polarized laser beam was applied to ramie single fibers soaked in 0-30 % NaOD/D_2O to study the following two issues; 1) whether or not all hydroxyl groups of ramie are converted to -OD during mercerization with NaOD/D_2O and 2) whether or not the orientation of cellulose molecules along fiber axis originally present in native ramie state is unchanged during mercerization.

METHODS AND MATERIALS

Ramie cellulose was purified, according to the conventional procedure (11). Several ramie fibers were soaked in about 5 ml NaOD/D_2O (0-30 %) for several hours. One single fiber with a small amount of the deuterated solution was put on a glass plate and was quickly covered with a cover glass, and the surrounding of the cover glass was sealed with grease. This single ramie fiber in 0-30 % NaOD/D_2O was set for the irradiation of polarized laser beam parallel (0°) or perpendicular (90°) to the fiber axis on a microscope (Fig. 1). Then, Raman-scattered light from the sample swollen in NaOD solutions was collected by using a multi-channel detector consisting of 1000 diodes. Data accumulation times were about 3 h for obtaining each Raman spectrum.

RESULTS AND DISCUSSION

Deuterium-exchange of OH groups in ramie during mercerization

Raman patterns of OH and CH stretching regions of ramie fibers soaked in 0-30 % NaOD/D_2O were recorded,

and the manner to decrease in Raman intensity due to the OH stretching vibration relative to that due to the CH stretching vibration with increasing the concentration of NaOD was examined. Hydroxyl groups of ramie accessible to the NaOD/D_2O solutions must be exchanged to -OD. If a part of hydroxyl groups in ramie are maintained as -OH without exchanging to -OD even in concentrated NaOD solutions, the conversion of parallel cellulose chains in the native state to anti-parallel ones in cellulose II is not plausible to occur during mercerization, *i.e.* the original parallel cellulose chains must be maintained by the non-cleaved hydrogen bonds in this case. Fig. 2 shows Raman patterns of the OH and CH stretching regions of single ramie fibers soaked in NaOD/D_2O. When a ramie fiber was soaked in D_2O (0 % NaOD/D_2O), hydroxyl groups accessible to D_2O were converted to -OD, thus resulting in a decrease in the Raman relative intensity, OH/CH. The OH/CH ratios of ramie decreased with increasing the concentration of NaOD, and no Raman bands due to the OH stretching vibration were observed for the samples soaked in 15 and 30 % NaOD/D_2O. After the ramie fiber swollen with 30 % NaOD/D_2O was washed with D_2O to remove NaOD, still no Raman bands due to OH groups were detected in D_2O.

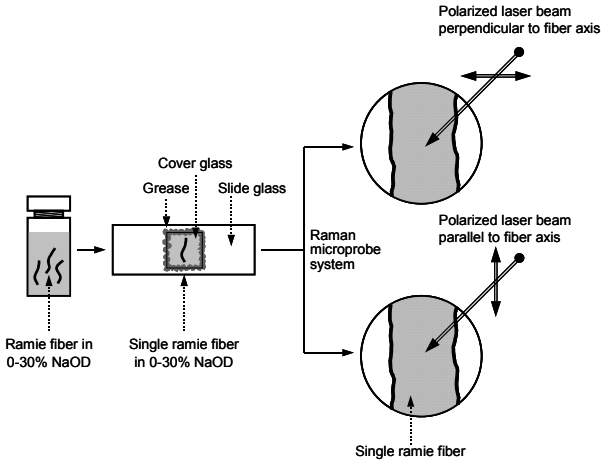

Fig. 1. Scheme for measuring Raman spectra of single ramie fiber in NaOD/D_2O by the polarized laser/ microprobe system.

The relationship between the NaOD concentration and the Raman relative intensity, OH/CH, was obtained from the Raman spectra in Fig. 2. In this study, the Raman intensity due to the OH or CH stretching vibration was obtained from the area of each Raman band separated from the base line, and the relative peak area, OH/CH, of ramie in the dry state was regarded as the value corresponding to 0 % OD or 100 % OH ramie. Since the orientation of cellulose molecules in ramie fibers mostly disappeared in 15-30 % NaOD/D_2O, Raman bands due to the OH stretching vibration of ramie were detected neither at 0° nor 90° of the electric vector of laser beam.

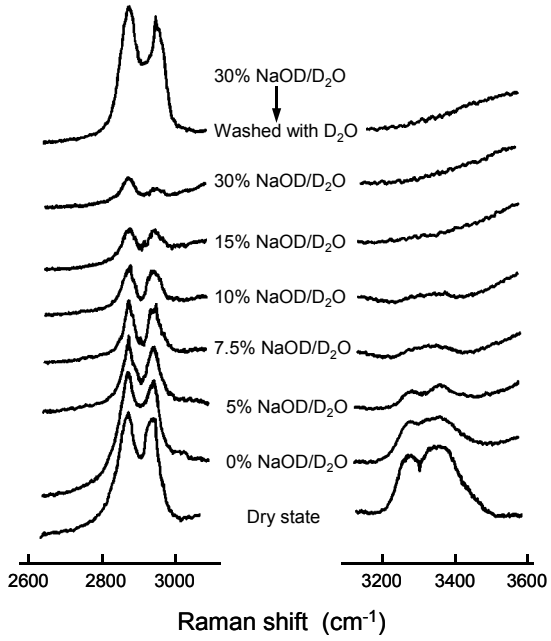

Fig. 2. Raman spectra (C-H and O-H stretching regions) of single ramie fiber subjected to various treatments. These spectra were measured by laser beam with electric vector parallel to the fiber axis.

As shown in Fig. 2, ramie had the deuterium-exchanging value of about 35 % at 0 % NaOD/D_2O, which was almost identical to those of accessibility of cotton and ramie celluloses measured by the conventional deuteration method (12). The deuterium-exchanged OH groups of ramie increased from 50 to 95 %, as the concentration of NaOD/D_2O increased from 5 to 10 %. Furthermore, almost all OH groups of ramie were converted to -OD in 15-30 % NaOD/D_2O. These results show that almost all intra- and inter-molecular hydrogen bonds originally present in native ramie state were cleaved at least once during mercerization, and that all hydroxyl groups in ramie had chances to contact with the alkali components in the swollen state. As described later, the cellulose I structure of ramie as well as the orientation of cellulose molecules along the fiber axis was maintained in 5-10 % NaOD/D_2O solutions, even though 50-95 % of hydroxyl groups were converted to -OD groups in 5-10 % NaOD/D_2O; the deuterium-exchange or the cleavage of hydrogen bonds proceeds not only in non-crystalline but also even crystalline regions without allomorphic changes. Thus, intra- and inter-molecular hydrogen bonds even in crystalline regions of cellulose I are unstable to alkaline solutions.

Orientation of cellulose chains in ramie during mercerization

The orientation of cellulose molecules along the fiber axis of ramie soaked in 0-30 % NaOD/D_2O was studied from polarized Raman spectra (7,9); the intensities of CH and OH vibration bands of oriented cellulose molecules depend on directions of the electric vectors of laser beam irradiated on the fibrous cellulosic samples. Since five methine C-H bonds (C1-H, C2-H, C3-H, C4-H and C5-H) in anhydroglucose residue of cellulose chains have the axial conformation, most of the methine C-H bonds are oriented perpendicularly to the fiber axis. In contrast, most of the O-H bonds in ramie are oriented in parallel to the fiber axis. The two Raman peaks due to the CH stretching vibration of ramie observed in polarized Raman spectra in Fig. 2 are assigned to the two methylene C-H bonds at C6, which have relatively large vectors in the parallel direction to the fiber axis.

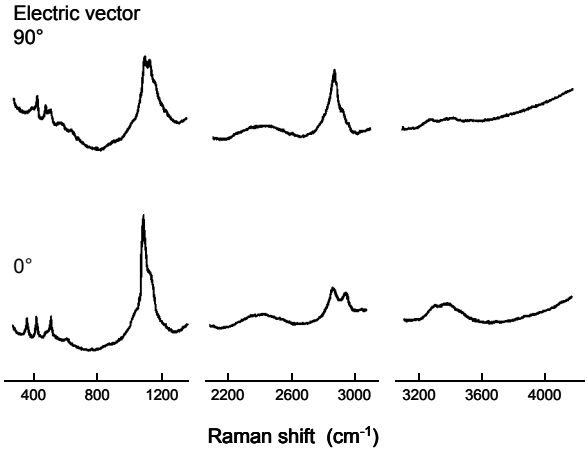

Fig. 3. Raman spectra of ramie fiber in D_2O, measured by laser beam with electric vector at 90 and 0° to the fiber axis.

As shown in Fig. 3, the Raman patterns of the ramie fiber in D_2O, recorded at the electric vector of 90 and 0°, were clearly different, resulting from the orientation of cellulose molecules in the ramie fiber. Since the split Raman bands due to the two C6-H groups were observed for 0-15 % NaOD/D_2O in the polarized Raman spectra in Fig. 2, the orientation of cellulose molecules along the fiber axis was mostly maintained in NaOD/D_2O solutions with concentrations of lower than 15 %.

On the other hand, as shown in Fig. 4, the Raman patterns of a ramie fiber swollen in 30 % NaOD/D_2O, recorded at the electric vector of 90 and 0°, were quite s imilar, irrespective of the angles of the electric vector; the orientation of cellulose molecules along the fiber axis mostly disappeared in 30 % NaOD/D_2O. Furthermore, the sharp Raman band at 1095 cm^{-1} due to C-C and C-O stretching vibrations originally present in native ramie state became broad in 30 % NaOD/D_2O. The Raman peak at about 2630 cm^{-1} was due to the OD stretching band of NaOD. No Raman bands due to the OH stretching vibration of ramie were detected in Fig. 4. These results indicate that cellulose molecules are mostly isotropic in the swollen Na-cellulose state, similarly to those in solution states.

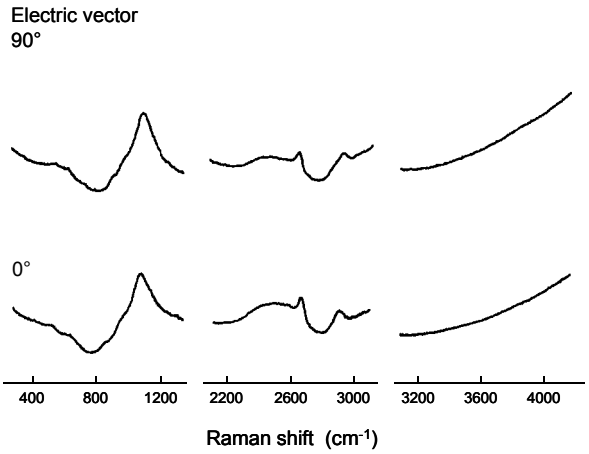

Fig. 4. Raman spectra of ramie fiber in 30 % NaOD/D_2O, measured by laser beam with electric vector at 90 and 0° to the fiber axis.

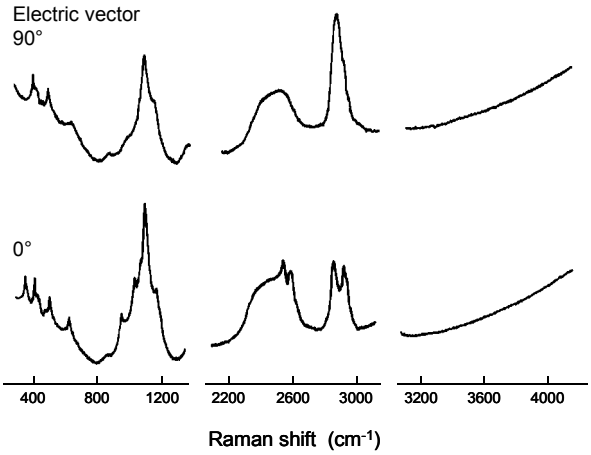

Fig. 5. Raman spectra of mercerized ramie fiber in D_2O, measured by laser beam with electric vector at 90 and 0° to the fiber axis. This ramie fiber was treated with 30 % NaOD/D_2O, and then washed with D_2O (never-dried).

Then the ramie fiber soaked in 30 % NaOD/D_2O was washed with D_2O to remove NaOD completely, and the never-dried mercerized ramie fiber in D_2O, thus obtained, was subjected to the Raman analysis. As shown in Fig. 5, the clear orientation of cellulose molecules along the fiber axis re-appeared in the mercerized cellulose state. Furthermore, the fine Raman patterns also re-appeared in

the range of 300-1300 cm^{-1}. Wiley and Atalla (9) reported that mercerized ramie has two sharp Raman bands at about 3470 and 3500 cm^{-1} due to the stretching vibrations of hydroxyl groups, which are characteristic for the secondary structure of cellulose II. Thus, the two sharp bands at about 2530 and 2560 cm^{-1} were assigned to the stretching vibrations due to the deuterated hydroxyl groups in the mercerized ramie, and the broad band in the range of 2250-2600 cm^{-1} was assigned to the stretching vibration due to other deuterated hydroxyl groups in mercerized ramie and those of deuterium oxide present in the system. No Raman bands due to hydroxyl groups were detected in Fig. 5. These results show that the orientation of cellulose molecules along the fiber axis is clearly recovered in the mercerized cellulose state by washing the Na-cellulose with D_2O. Furthermore, as shown in the Raman spectrum recorded at the electric vector of 0° in Fig. 5, the Raman pattern due to the C6-H stretching vibration was quite similar to that observed for the native ramie; the conformations of the methylene C6-H groups may be similar between celluloses I and II.

Secondary structures of celluloses I and II and Na-celluloses

Table 1. Secondary and tertiary structures of ramie cellulose in native, alkali-swollen and mercerized states.

	Native cellulose	Alkali-swollen cellulose	Mercerized cellulose
Secondary structure (Raman)	Ordered	Disordered	Ordered
Tertiary structure (X-ray diffraction)	Ordered	Ordered	Ordered

X-Ray diffraction studies showed that celluloses swollen with concentrated NaOH solutions have crystal structures, Na-cellulose I-VI; the swollen celluloses have some ordered tertiary structures (3-5,13,14). On the other hand, the Raman microprobe analysis showed that cellulose molecules have disordered structures in the swollen state with $NaOD/D_2O$, similar to those in the solution states. This result of Raman spectroscopy is consistent with that obtained by solid-state ^{13}C NMR analysis of alkali-swollen cellulose (6). These ordered and disordered structures of Na-cellulose in terms of the tertiary and secondary structures, respectively, indicate that cellulose swollen in concentrated NaOH solutions may have structures similar to liquid crystalline states (Table 1).

Since cellulose molecules swollen in NaOH solutions have structures similar to those in solution states, resulting from the cleavage of almost all intra- and inter-molecular hydrogen bonds at least once, the conversion of parallel cellulose chains to anti-parallel ones during mercerization is possible only from this aspect. It seems, however, that the reason why the fibrous form of ramie is maintained during mercerization has a key point for understanding the mercerization mechanism in aqueous NaOH solutions.

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