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Effect of solvent exchange on the supramolecular structure, the molecular mobility and the dissolution behavior of cellulose in LiCl/DMAc

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Abstract—We investigated the effect of solvent exchange on the supramolecular structure and the molecular mobility of the cellulose molecule to clarify the mechanism of the dissolution of cellulose in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc). Among the celluloses that were solvent exchanged in different ways, the DMAc-treated celluloses dissolved most rapidly. Dissolution of the acetone-treated celluloses was much slower than the DMAc-treated ones, but considerably faster than the untreated one. Such differences in the dissolution behavior were well explained by the differences in the surface fractal dimension calculated from the small-angle X-ray scattering profiles and in the ^{1}H spin–lattice and spin–spin relaxation times estimated from the solid-state NMR spectroscopic measurements. Furthermore, it was suggested from the IR spectra and the ^{13}C spin–lattice relaxation times of cellulose that DMAc is adsorbed on the surface of cellulose even after vacuum-drying and affects the molecular mobility and hydrogen-bonding state of cellulose.

Keywords: Cellulose; LiCl/DMAc; Solvent exchange; Supramolecular structure; Solid-state NMR spectroscopy; SAXS

1. Introduction

Cellulose is one of the most abundant biological polymers available to humans. While cellulose is used in the form of fabrics and yarns, it is also used as a raw material for making films, fibers, and molded materials. Furthermore, various cellulose derivatives have been developed to improve the mechanical and thermal properties of cellulose. Dissolution of cellulose is indispensable throughout these processes, because cellulose itself is not a thermoplastic material. Therefore, many kinds of cellulose solvents have been developed and industrially used. However, most of the conventional cellulose solvents contain harmful and/or volatile substances that cause environmental pollution. Because of these shortcomings, processing of cellulose from the dissolved state has been limited. From the 1980s, various kinds of novel cellulose solvents have been developed to overcome the problems of conventional cellulose solvents. Lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) is one of those newly developed cellulose solvents.[1,2] This solvent can dissolve cellulose with a molecular weight of more than 10^6 under ambient conditions without severe degradation or other undesirable reactions.[3] Owing to these advantages, LiCl/DMAc has been utilized in an analytical use to investigate the molecular properties of cellulose, such as the chain dimension and flexibility

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in the dissolved state.[2,4–6] It has also been utilized as a medium for derivatizing cellulose under homogeneous conditions.[7] Control of the degree of substitution and chemical structure (regiospecificity) of cellulose derivatives has been realized by using this solvent system.

Several different methods have been developed for the dissolution of cellulose in LiCl/DMAc. Among them, a solvent exchange procedure is generally employed to dissolve cellulose in LiCl/DMAc.[1,2] This procedure consists of the immersion of cellulose in water and the subsequent exchange of water in the cellulose by acetone and further by DMAc. Some researchers have explained the effect of solvent exchange as 'activation'.[1] As a phenomenological approach, Pionteck et al. investigated the effect of solvent exchange by observing the morphological changes of the cellulose solid during the dissolution in LiCl/DMAc using microscopic methods.[8] However, the mechanism on how the 'activation' affects the supramolecular structure of cellulose is still unknown. To clarify the mechanism, we have employed small-angle X-ray scattering and solid-state NMR spectroscopy to investigate the changes in the nanometer-scale heterogeneity in the solid structure and molecular mobility.[9,10] As a result, we have shown that the solvent exchange affects the molecular mobility and the 100 nanometer-order heterogeneity of cellulose. Such length scale corresponds to the 'level-off degree of polymerization'[11] of cellulose, known as a kind of dynamic heterogeneity in cellulose solid. Nevertheless, several questions remain unresolved on the effect of solvent exchange on cellulose. One question is why the sequential immersion using water and some kinds of organic liquid is required. Another question is what kind of molecular motion of cellulose is affected by the solvent exchange. Following our previous investigation, small-angle X-ray scattering (SAXS) measurements were performed to investigate the nanometer-order structure of cellulose. In addition, the measurements of $T_{1\mathrm{H}}$ (laboratory-frame ^{1}H spin–lattice relaxation time) and $T_{2\mathrm{H}}$ (^{1}H spin–spin relaxation time) were also performed to investigate the dynamic heterogeneity of cellulose. As translation of the molecular chain is impossible in the solid state, it is supposed that the rotation and/or the vibration of the specific sites in the cellulose molecule are affected by the solvent exchange.

Solid-state NMR[12–15] and infrared (IR) spectroscopy[16–21] can give the information on the motional state of the specific sites in the cellulose molecule. However, the relation between the motional state of the molecule and the solubility of cellulose has not yet been clarified. Therefore, we performed the measurements of ^{13}C spin–lattice relaxation time ($T_{1\mathrm{C}}$) and the Fourier-transform (FT) IR spectra to investigate the effects of solvent exchange on the motional state of the cellulose molecule.

2. Experimental

2.1. Sample preparation

Cellulose material employed was softwood sulfite pulp of dissolving pulp grade (DP, Nippon Paper Industry Co., Ltd). After vacuum-drying at 60 °C for 24 h, the cellulose was treated in either of the following ways: immersion in water followed by exchange to acetone and the further exchange to DMAc (sample A); immersion in water followed by exchange to acetone (sample B); immersion in water followed by exchange to DMAc (sample C); immersion in acetone followed by exchange to DMAc (sample D); immersion in acetone (sample E); immersion in DMAc (sample F). Water was deionized from tap water to an electrical conductivity of less than 0.2 μS cm^{-1} and further distilled in the laboratory. Reagent-grade acetone, DMAc, and LiCl were purchased from Nacalai Tesque, Japan and were used without further purification. While the immersion in water was performed once for 2 days, the immersion in acetone or DMAc was performed for 1 day and repeated twice. About 10 g of cellulose samples were immersed in 100 mL of water, acetone, or DMAc at room temperature. After the above-mentioned treatments, these celluloses were vacuum-dried again at 60 °C for 40 h. In addition to the solvent-exchanged celluloses, decrystallized cellulose was prepared by cryogenic milling using a Japan Analytical Chemistry AFC-300 cryogenic sample crusher.[9] None of the solvent-exchange procedures applied to samples A to F were applied to the milled cellulose.

2.2. Dissolution of cellulose

The cellulose samples were mixed with 8 wt % LiCl/DMAc at a ratio of 3:97 (w/w), and the mixtures were allowed to stand at room temperature. When the visible turbidity or solid residues were lost from the mixture, we regarded that the dissolution of cellulose was completed.

2.3. Small-angle X-ray scattering (SAXS)

A 6-m point-focus SAXS camera at the High-Intensity X-ray Laboratory of Kyoto University was utilized.[22] The sample-to-detector distance was set to 1.6 m, covering the real-space length scales between 3 and 40 nm. A scattered intensity of Cu Kα irradiation ($\lambda = 0.1542$ nm, 40 kV, and 50 mA) was acquired using two-dimensional position-sensitive proportional counter for more than 5000 s. The two-dimensional scattering profiles so obtained were corrected for the transmittance in the samples, the incident beam intensity (calibrated using high-density polyethylene as secondary standard), and the background intensity from air scattering and electronic noise. By circularly averaging the corrected two-dimensional profiles, one-dimensional profiles were finally obtained.