Spectroscopic Study on Thermally Induced Changes of Molecular Alignment in Hydrogen-Bonded Fibrous Molecular Assemblage

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An amphoteric azopyridine carboxylic acid forms a fibrous molecular assemblage of 500 nm in average diameter from an aqueous solution based on intermolecular *head-to-tail* hydrogen bonding. In this study, we investigated molecular alignment in the molecular assemblage affected by heat treatment using polarization microscope FTIR and visible spectroscopies and simultaneous DSC-FTIR measurement. The visible spectroscopy study revealed that the order parameter of the azopyridine moiety in an as-formed fiber state was 0.25. When the fibrous molecular assemblage was heated, the order parameter increased up to 0.67 at 150 °C and the molecular anisotropy disappeared at 172 °C. It was suggested by the FTIR spectroscopy that the as-formed fibrous assemblage was composed of strong hydrogen bonds between pyridyl and carboxyl groups, which were transformed to weakened hydrogen bonds at 142 °C. These results clearly suggested that a phase transition took place in the fibrous molecular assemblage on the heat treatment.
Key words: self-assembly/ hydrogen bond/ DSC-FTIR/ phase transition/ order parameter

1. INTRODUCTION

Self-assembled architectures consisting of small organic molecules through noncovalent bonds have drawn attention, because a bottom-up technique in nanotechnology is promising for overcoming a top-down technique. In general, a main objective of the bottom-up technique is concentrated on fabrication of nano-structures integrating molecular functionalities by self-assembly and emerging an unprecedented function. For example, organic nanotubes organized from sugar derivatives [1] and organic rod-like micelles from amino acid derivatives [2] are fascinating supramolecular architectures. Since such supramolecular architectures made by self-assembly are composed of intermolecular interactions, we might be able to reveal formation mechanisms and to fabricate new nanostructures on demand by comprehending hierarchy of the complicated intermolecular interactions such as hydrogen bonding, dipole-dipole interaction, π–π stacking and van der Waals interaction.

We have ever studied the self-assembly of amphoteric azopyridine carboxylic acids in aqueous solutions [3-5]. The molecular structure of the amphoteric compounds is simple as shown in Fig. 1. Azopyridine carboxylate anions in an aqueous alkaline solution are neutralized by acidic substances such as air-containing CO_2, to give fibrous molecular assemblage of hydrogen-bonded supramolecular polymers formed through successive intermolecular *head-to-tail* hydrogen bonds between the pyridyl and carboxy groups [3]. The macroscopic organized morphology such as diameter and entire rod-like or helical-tape shape was tunable by varying slightly a side-chain group instead of the propyl group [4], self-assembling conditions and methods [5], and photoirradiation [3].
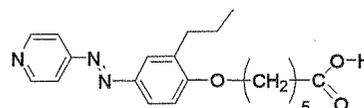

Fig. 1 Chemical structure of amphoteric APC (C5PR).

Taking a notice that the hydrogen-bonded fibrous molecular assemblage is readily disassembled to monomeric carboxylate species by immersion in an aqueous alkaline solution, we have recently proposed that the fibrous molecular assemblages are available as morphology-tunable and recyclable templates for preparing hollow Ni-P microfibers [4,6]. However, to prepare advanced templates with a precise diameter and a certain helical pitch, it is necessary to understand deeply the hierarchical intermolecular interactions forming the fibrous molecular assemblages and to reveal what factor determines the diameter and the entire morphology of the fibrous templates. We anticipated that intermolecular interactions composed of the fibrous molecular assemblage will be hierarchically cleaved step-by-step upon heating and the fibrous molecular assemblage will be transformed to other organized structures.

The objective of this study is to investigate thermally

induced structural changes in the fibrous molecular assemblage formed from 6-[2-propyl-4-(4-pyridylazo) phenoxy]hexanoic acid (C5PR) indicated in Fig. 1. The thermally induced structural changes of the fibrous molecular assemblage were followed by polarization microscope FTIR spectroscopy, polarization microscope visible spectroscopy, and simultaneous DSC-FTIR measurement [7].

2. EXPERIMENT

2-1. Sample preparation

The amphoteric compound of C5PR was dissolved in a 2.0 mmol dm^{-3} NaOH aqueous solution. The transparent yellow solution (100 ml) containing 1.0 mmol dm^{-3} C5PR was kept standing for 3 days under an air atmosphere, to give a yellow suspension containing fibrous molecular assemblage. After filtration and multiple rinses with distilled water, the fibrous assemblage was freeze-dried. To investigate thermally induced changes of molecular alignment in the hydrogen-bonded fibrous assemblage, we prepared three kinds of samples, which are molecular assemblages before and after annealing at 150 °C for 2 h and melting at 180 °C.

2-2. Physical measurement

The morphology of molecular assemblage was observed by an optical microscope (Olympus BX-60) equipped with a hot stage (Mettler FP-90) and a CCD camera (Olympus DP70).

2-2-1. Polarization spectroscopic measurement

Molecular anisotropy in molecular aggregates was investigated by a polarization microscope Fourier-transform infrared spectrophotometer (Jasco FTIR 660Plus, IRT-30; FTIR) and a polarization microscope visible spectrophotometer (Hitachi U-6500). In the IR measurement, a probe area, a scan range, a scan resolution and a polarization angle were 5 × 20 µm, 650 – 4000 cm^{-1}, 1 cm^{-1} and -90 – 90°, respectively. In the visible spectral measurement, a probe diameter of 1 or 3 µm, a scan range of 400 – 750 nm, a scan resolution of 1 nm and a polarization angle range of -180 – 180° were used.

2-2-2. DSC-FTIR measurement

Thermally induced changes of molecular alignment were investigated by a simultaneous DSC-FTIR measurement which was performed using a simultaneous DSC equipped with a FTIR spectrophotometer (Jasco FTIR 620) [7]. A heating rate of 2 °C min^{-1}, an IR sampling rate of 1 scan min^{-1}, a scan resolution of 2 cm^{-1} and a time interval of 50 sec were used. Fibrous assemblage made from C5PR was grind down with dried KBr powder and pressed to make a crystalline pellet. The pellet sample was heated from 50 to 200 °C.

3. RESULTS AND DISCUSSION

3-1. Thermally induced morphological change of fibrous molecular assemblage

Parts (a), (b) and (c) of Fig. 2 show the optical microscope images of hydrogen-bonded fibrous molecular assemblage formed from C5PR on a hot stage

at 25, 150 and 180 °C, respectively. The fibrous morphology of the molecular assemblage having a diameter of 500 nm was maintained below 150 °C. The long axis of the C5PR fiber began to shrink at 150 °C. The shrunk crystalline material as shown in Fig. 2(b) eventually became isotropic liquid at 172 °C as shown in Fig. 2(c) [8]. Uniform birefringence was observed for the molecular assemblage at 150 °C by a polarized optical microscope. The optical microscope observation indicated that the molecular assemblage in the range of 150 – 172 °C was in a more ordered state than the fibrous molecular assemblage below 150 °C. We anticipated that some structural transition took place around 150 °C due to alteration of intermolecular interactions in the fibrous molecular assemblage.
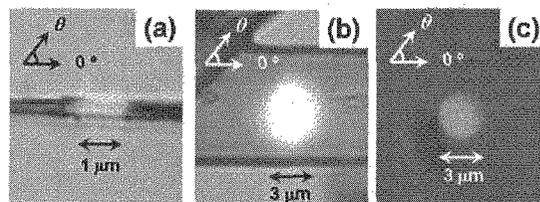
Fig. 2 Optical microscope images of a molecular assemblage at (a) 25 °C (fiber), (b) 150 °C (shrunk crystalline material) and (c) 180 °C (isotropic liquid). In the images, each brighten spot indicates the area probed by polarization microscopic visible spectroscopy. The polarization angle θ defined by two arrowheads was used in microscope visible and FTIR spectral measurements.

3-2. Anisotropy change of an n-π* absorption band upon heating

Azobenzene and azopyridine derivatives show two characteristic absorption bands attributable to a π-π* transition with a λ_{max} in a range of 310 – 360 nm and an n-π* transition with a λ_{max} in a range of 400 – 500 nm [9]. The transition bands are often used to evaluate molecular anisotropy of the aromatic azo compounds in a film state [10]. We assumed that molecular anisotropy in the fibrous material formed from C5PR might be evaluated because the amphoteric compound C5PR has an aromatic azopyridine moiety.

First, we measured polarization microscope visible spectra of one fibrous molecular aggregate at a polarization angle range of -180 – 180°. The polarization angle θ was defined by two arrowheads in Fig. 2. The angles of $\theta = 0$ and 90° correspond to parallel and perpendicular vectors against the longer axis of one fibrous molecular aggregate. As a result, it was found that the absorbance of the n-π* band showed an angular dependence. Therefore, we measured polarization microscope visible spectra of fibrous molecular assemblage at 25, 150, and 180 °C and plotted the absorbance at λ_{max} of n-π* band against the polarization angle.

Parts (a), (b) and (c) of Fig. 3 indicate the polar plots of n-π* absorbance at λ_{max} observed for C5PR molecular aggregate at 25, 150, and 180 °C. A maximum absorbance at 30° and a minimum absorbance at 120° in

the angle range of 0 - 180° were observed for the fibrous molecular assemblage at 25 °C. This result indicated that the azopyridine moieties in the aggregate were aligned in an anisotropic manner at a tilted angle of 30°.

As seen in Fig. 3(b), molecular anisotropy observed for the azopyridine moieties was significantly increased in the molecular aggregates at 150 °C. The molecular anisotropy disappeared at 180 °C over a melting point of C5PR (172 °C) as shown in Fig. 3(c).
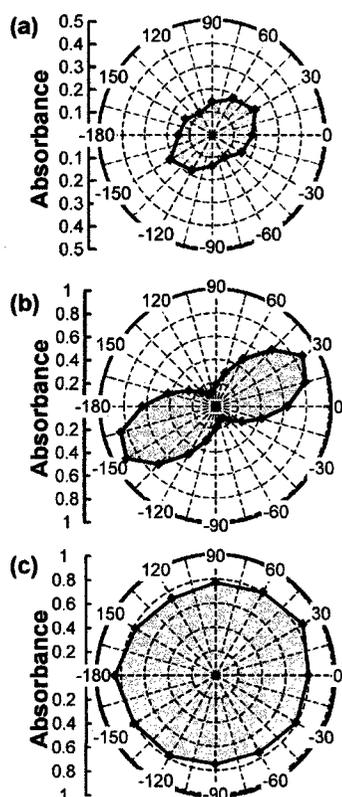
Fig. 3 Polar plots of the absorbance at λ_{max} of the molecular assemblage at (a) 25 °C, (b) 150 °C and (c) 180 °C by polarization microscopic visible spectroscopy. The polarization angle θ is defined by the arrowheads in each optical image of Fig. 2.

To evaluate thermally induced changes in the molecular anisotropy of the fibrous molecular assemblage upon heating, we used an order parameter. The order parameter, S, can be determined by the following equation [11]:

$$S = (A_{//} - A_{\perp}) / (A_{//} + 2A_{\perp}) \qquad (1)$$

where $A_{//}$ and $A_{\perp}$ mean the absorbance of the azo chromophore when the $\pi-\pi^*$ electronic transition vector of incident light is parallel and perpendicular to an orientation axis of the molecular long axis. The order parameter is usually adapted to $\pi-\pi^*$ transitions only.

To our knowledge, no one knows a relationship of the n-π^* electronic transition vector to the orientation axis of azo chromophore. Therefore, we herein calculated the order parameter using the minimum and maximum absorbance under an assumption that n-π^* electronic

transition vector of incident light is parallel to an orientation axis of the azopyridine long axis as similar to the $\pi-\pi^*$ transition vector.

The order parameter S of the fibrous assemblage at 25 and 150 °C was estimated to be 0.25 and 0.67, respectively. It was obvious from the increased order parameter at 150 °C that the azopyridine moieties in the hydrogen-bonded fibrous molecular assemblage at 150 °C were in an ordered manner more than those at 25 °C.

3-3. Anisotropy change in an O-H stretching vibration band upon heating

The amphoteric compound C5PR forms successive *head-to-tail* intermolecular hydrogen bonds between the pyridyl and carboxy groups, to give a supramolecular polymer composing fibrous molecular assemblage [3]. An O-H stretching vibration band of aliphatic carboxylic acid forming a hydrogen bond with a pyridyl group appears at 2500 cm^{-1} in FTIR spectra [12]. Since the hydrogen bond is formed at a certain direction, a vector of O-H bond is anticipated to be one tool to evaluate molecular anisotropy.
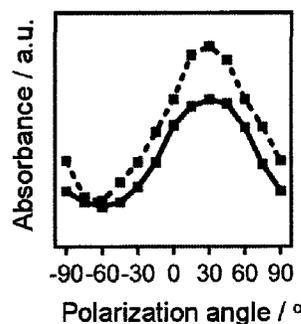
Fig. 4 Angular dependence of an O-H stretching vibration band at 2500 cm^{-1} observed for fibrous molecular assemblage at 25 °C (solid line) and 150 °C (dotted line). The polarization angle θ is defined by two arrowhead vectors indicated in Fig. 2.

We measured polarization microscope FTIR spectra of fibrous molecular assemblages at 25 and 150 °C. We chose a C-H symmetric stretching vibration band of methylene units at 2865 cm^{-1} as an internal standard peak. Based on the absorbance of the standard peak, the absorbance observed for an O-H stretching vibration band at 2500 cm^{-1} was plotted against a polarization angle of a probing linearly polarized IR light. The polarization angles of $\theta = 0°$ and $\theta = 90°$ correspond to parallel and perpendicular vectors against the long axis of one fibrous molecular aggregate. A minimum absorbance at 30° and a maximum absorbance at -60° were observed for both molecular assemblages at 25 °C and 150 °C. It was worthy of note that the ratio of the minimum absorbance to the maximum absorbance was increased at 150 °C. These spectroscopic features suggested two results as supported in polarization microscope visible spectroscopy. First, the O-H bonds of the carboxy groups were tilted at 30° to the long axis of the fibrous molecular assemblage. Secondly, the anisotropy was increased at 150 °C. To confirm molecular orientation in the fibrous molecular aggregate,

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it was necessary to reveal the directions of the n-π* transition vector and the O-H stretching vibration vector. Analyses of a single-crystal formed from C5PR by X-ray crystallography and polarization microscope spectroscopy will reveal the molecular orientation.

3-4. Structural transformation studied by DSC-FTIR

Simultaneous DSC-FTIR measurement [7] is a useful tool to investigate thermally induced structural transformation with regard to bond information. We applied the simultaneous measurement to the amphoteric molecular assemblage formed from C5PR.

To investigate a thermally induced change of hydrogen bonds formed in the fibrous molecular assemblage, we referred a previous work by Kolbe et al [13]. Kolbe et al. report that a C=O stretching vibration band subjected to a hydrogen bond formed between aromatic pyridyl and aliphatic carboxy groups appears at 1698 cm^{-1}, while a C=O stretching vibration band subjected to no hydrogen bond such as a carboxylic acid monomer appears at 1745 cm^{-1}. At 25 °C, the fibrous molecular assemblage exhibited a main absorption band at 1698 cm^{-1} with two small shoulder peaks at 1715 and 1745 cm^{-1}. This result indicates that the fibrous molecular assemblage is mainly composed of hydrogen bonds between the basic pyridyl and acidic carboxy groups [14].
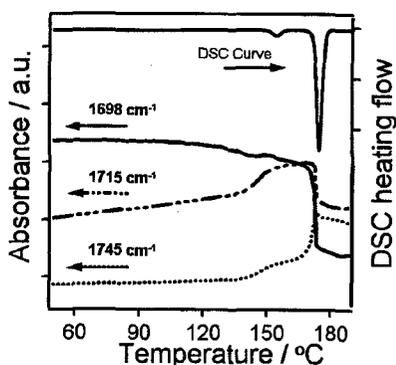

Fig. 5 Thermally induced changes in absorbance at 1698, 1715 and 1745 cm^{-1} attributable to different C=O stretching vibrations measured by DSC-FTIR.

Fig. 5 indicates that the DSC heating curve of the fibrous molecular assemblage from 50 °C to 200 °C and the thermal changes in absorbance at 1698, 1715, and 1745 cm^{-1} in the FTIR measurement. Upon heating up to 142 °C, the absorption intensity at 1698 cm^{-1} gradually decreased concomitantly with a gradual increase of the absorption intensity at 1715 cm^{-1}. The absorption intensity at 1715 cm^{-1} was steeply increased at 142 °C. The increased absorbance at 1715 cm^{-1} was decreased at 172 °C, until an increase of the absorption intensity at 1745 cm^{-1}. The DSC curve and the FTIR results clearly suggested that some structural transformation by heating occurred at 142 °C. At 172 °C, the hydrogen bonds were almost decomposed. As a result, an isotropic phase consisting of C5PR having a monomeric carboxy groups. What is the vibration band appearing at 1715 cm^{-1} attributable to? A likely

explanation is that the vibration band at 1715 cm^{-1} is due to C=O stretching of carboxylic acid dimer or another weakened hydrogen bond. Taking account of the fact that a O-H vibration band at 2500 cm^{-1} and its Fermi resonance at 1900 cm^{-1} were maintained below 172 °C, the vibration band at 1715 cm^{-1} is likely attributable to another weakened hydrogen bond formed between pyridyl and carboxy groups.

4. CONCLUSION

We described the thermally induced structural transformation of hydrogen-bonded fibrous assemblage formed from the amphoteric compound C5PR to understand the hierarchy of the intermolecular interactions. The less ordered fibrous molecular assemblage with regard to ordering of azo and carboxy groups was transformed to an ordered molecular assemblage with weakened hydrogen bonds between the pyridyl and carboxy groups at 142 °C. At 172 °C, the ordered molecular assemblage was transformed to an isotropic phase mainly consisting of the amphoteric compound in a state of carboxylic acid monomer. The result implies that strong hydrogen bonds with a C=O stretching vibration appearing at 1698 cm^{-1} was formed in advance before other molecular interactions such as π–π stacking and van der Waals interaction among hydrocarbons. It was found that it was necessary to make clear the thermally induced structural changes in detail by simultaneous DSC-XRD measurement.

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