

## Morphology Control of Fibrous Molecular Self-Assemblages Formed from an Azopyridine Carboxylic Acid

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We describe how to control macroscopic morphologies of hydrogen-bonded fibrous molecular assemblages formed from one amphoteric azopyridine carboxylic acid of 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid **1**. The fibrous morphology and crystallinity of the molecular assemblages prepared through three methods of acidic substance addition, crystal growth, and surfactant addition were investigated by scanning electron microscopy and X-ray diffraction analysis. In the acidic substance addition method, the fibrous molecular assemblages possessing a small width of 300 ~ 500 nm and 100 ~ 300 nm were obtained under carbon dioxide and hydrogen chloride atmospheres, respectively. The fibrous molecular assemblages with a large width up to about 8  $\mu\text{m}$  were formed step-by-step in the crystal growth method. It was found that the width of fibrous molecular assemblages formed from **1** was controllable in the range of 100 nm ~ 8  $\mu\text{m}$ .

Key words: molecular assemblage, self-organization, submicron, organic fiber, hydrogen bond, control

### 1. INTRODUCTION

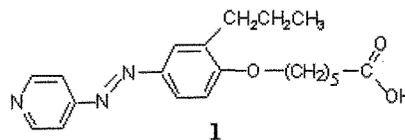
Since single- and multi-walled carbon nanotubes were found [1], various kinds of inorganic, organic, and metallic tubular materials have been attracting much attention due to their potential ability in wide applications [2]. The tubular materials are fabricated mainly by template-directed synthesis, because the methodology is simple, high-through-put, and cost-effective. Lipid-based cylindrical tubules [3], electrospinning degradable polymer fibers [4], porous anodic aluminum thin films [5], and others [6] have been used as reliable templates for preparation of metallic tubular materials. Most of the organic templates are removed by pyrolysis causing  $\text{CO}_2$  emission, so that the organic templates are not recyclable.

Previously, we reported that nickel-phosphorus (Ni-P) [7] and copper [8] tubular materials were successfully obtained through electroless plating by the template-directed synthesis using hydrogen-bonded molecular assemblages formed from an amphoteric azopyridine carboxylic acid [9] as fibrous templates. Moreover, we found that Ni-P tubes with a rod-like or helical-tape morphology and with a controlled sub-micrometer pore could be molded from hydrogen-bonded molecular assemblages self-organized by a series of amphoteric azopyridine carboxylic acids with a slight difference in their chemical structure [10]. It was revealed that the supramolecular templates were recyclable based on assembly and disassembly of the hydrogen bonds composing the fibrous molecular assemblages [10].

The objective of this study is how to control macroscopic morphology of fibrous molecular assemblages formed from one amphoteric azopyridine carboxylic acid. If the self-organized morphology such as width, length and entire shape could be adjusted, it is

anticipated that metallic tubular materials with morphology variety could be molded through electroless plating that we developed [10].

In this paper, we report on the width control of fibrous molecular assemblages self-organized from one amphoteric compound of 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid **1** (Figure 1). It was found that the organized morphologies formed from the amphoteric compound were controllable by three kinds of preparation methods including (1) acidic substance addition, (2) crystal growth, and (3) surfactant addition. The organized morphology and crystallinity of the molecular assemblages were discussed through scanning electron microscope observation and X-ray diffraction analysis.



**Figure 1.** Chemical structure of an azopyridine carboxylic acid used in this study.

### 2. EXPERIMENT

#### 2-1. Materials

An amphoteric azopyridine carboxylic acid, 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid **1** was used as a material forming hydrogen-bonded fibrous molecular assemblages [9]. Sodium dodecyl sulfate (SDS) was purchased from Kanto Chemicals, Ltd. Deionized water was prepared using a Milli-Q system and used throughout.

#### 2-2. Preparation of fibrous molecular assemblages with various morphologies

The amphoteric compound **1** in a powder state was dissolved in a  $2.0 \text{ mmol dm}^{-3}$  NaOH aqueous solution, to give an alkaline aqueous solution containing  $1.0 \text{ mmol dm}^{-3}$  **1**. The alkaline aqueous solution of **1** was neutralized to form hydrogen-bonded molecular assemblies by following methods including (1) an acidic substance addition method, (2) a crystal growth method, and (3) a surfactant addition method.

#### 2-2-1. Acidic substance addition method

The alkaline aqueous solution of **1** was neutralized by three kinds of acidic substances including air-containing substances [9], carbon dioxide gas, and hydrogen chloride vapor. In the first, the solution was placed in a vial, which was capped with an aluminum foil with small holes to contact air and kept standing under an air atmosphere at room temperature for one week. In the second, the solution was placed in a vial and kept standing under a carbon dioxide atmosphere for 3 h. In the third, the solution was placed in a vial and kept standing under a hydrogen chloride atmosphere at  $50^\circ\text{C}$  for 3 h. Molecular assemblies self-organized under these conditions were filtered and observed by scanning electron microscopy (SEM).

#### 2-2-2. Crystal growth method

300 ml of the alkaline aqueous solution containing **1** was placed in a glass beaker and kept stirred at 300 rpm for 2 days at room temperature under an air atmosphere, to give a dispersion containing fibrous molecular assemblies.  $150 \mu\text{l}$  of a  $1.0 \text{ mmol dm}^{-3}$  NaOH aqueous solution was added in the dispersion to dissolve a fraction of the fibrous molecular assemblies and kept intact for 2 days. This partial dissolution process was repeated three times. Step-by-step growth of molecular assemblies was observed by SEM.

#### 2-2-3. Surfactant addition method

An anionic surfactant, sodium dodecyl sulfate (SDS) was added in the alkaline aqueous solution of **1**, to prepare five kinds of aqueous solutions with a SDS concentration of 4.05, 8.10, 16.2, 40.5, and  $81.0 \text{ mmol dm}^{-3}$ . The SDS concentration of  $8.10 \text{ mmol dm}^{-3}$  corresponds to a critical micelle concentration (CMC) in water at  $25^\circ\text{C}$  [11]. These solutions were placed in each glass beaker and kept stirred at 300 rpm for one day at room temperature under an air atmosphere. Self-organized molecular assemblies were observed by SEM.

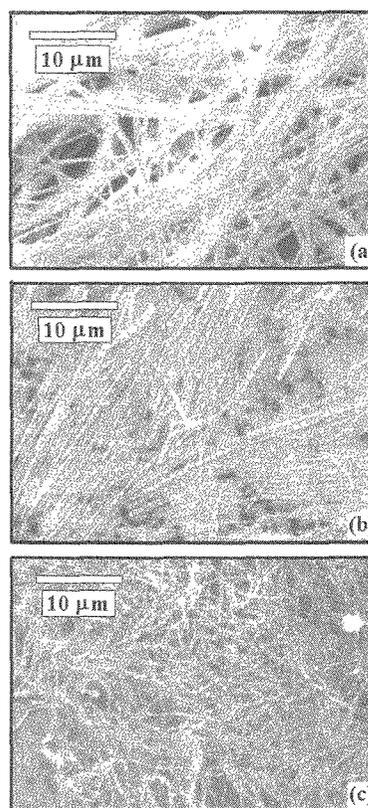
#### 2-3. Physical measurement

SEM images were taken on a Hitachi S-3000N scanning electron microscope. X-ray diffraction was measured with a MAC Science M21X-SRA X-ray diffractometer.

### 3. RESULTS AND DISCUSSION

#### 3-1. Self-organized morphology of fibrous molecular assemblies affected by the kind of acidic substances

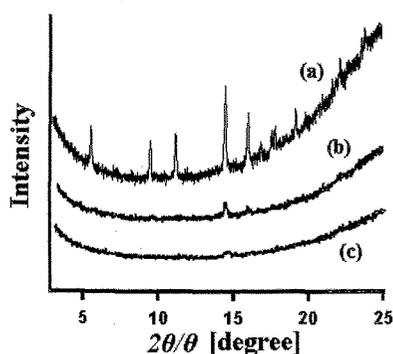
Amphoteric azopyridine carboxylic acids possessing both an acidic carboxy group and a basic pyridyl group are dissolved in an alkaline aqueous solution as a result of dissociation to a carboxylate group, causing disassembly of hydrogen-bonded molecular assemblies.



**Figure 2.** SEM images of fibrous molecular assemblies formed from **1** under (a) an air atmosphere, (b) a carbon dioxide atmosphere, and (c) a hydrogen chloride atmosphere.

In the neutralization, the dissociated carboxy group is gradually protonated by air-contained acidic substances such as carbon dioxide, and fibrous crystalline molecular assemblies formed from the amphoteric azopyridine carboxylic acids grow in the aqueous solution [9]. Therefore, it is anticipated that a rate of neutralization by acidic substances affects the crystallinity of the fibrous molecular assemblies. In addition, taking into consideration the fact that the side-chain propyl group substituted to the aromatic azopyridine skeleton suppresses intermolecular  $\pi$ - $\pi$  stacking formation to allow one-dimensional growth of the fibrous molecular assemblies [9], we also assume that self-organized morphology of the hydrogen-bonded molecular assemblies is affected by the kind of acidic substances.

To investigate the effect of the neutralization methods on the crystallinity and entire morphology of the fibrous molecular assemblies, we prepared hydrogen-bonded molecular assemblies from an alkaline solution containing **1** under three conditions. Figure 2 indicates the SEM images of molecular assemblies formed from **1** under three kinds of atmospheres, with result for an air atmosphere, a carbon dioxide atmosphere, and a hydrogen chloride atmosphere shown in parts a, b and c of Figure 2, respectively. In the case of an air atmosphere condition, it took one week for rod-like molecular assemblies to be formed. The fibrous molecular assemblies with a length of  $500 \sim 800 \text{ nm}$  and a width of  $500 \sim 700 \text{ nm}$  were obtained as shown in Figure 2a.



**Figure 3.** XRD patterns of fibrous molecular assemblages formed from **1** under (a) an air atmosphere, (b) a carbon dioxide atmosphere and (c) a hydrogen chloride atmosphere.

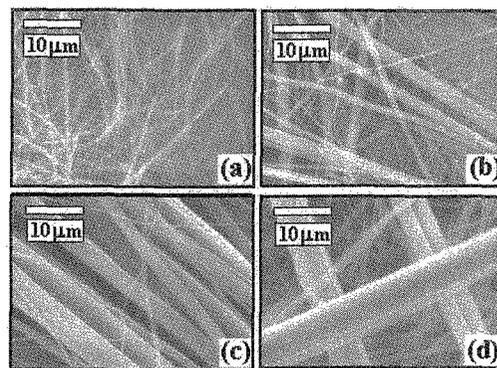
In contrast, fibrous molecular assemblages formed at a short time of 3 h under carbon dioxide and hydrogen chloride atmospheres seemed to more flexible than those under an air atmosphere, as shown in parts b and c of Figure 2. In the case of a carbon dioxide atmosphere, the fibrous molecular assemblages had a 30 ~ 50  $\mu\text{m}$  length and a 300 ~ 500 nm width. In the case of a hydrogen chloride atmosphere, the molecular assemblages possessed a 50 ~ 100  $\mu\text{m}$  length and a 100 ~ 300 nm width. It was found that the organized morphology of the fibrous molecular assemblages was obviously affected by the atmospheric conditions for neutralization.

X-ray diffraction (XRD) measurements were carried out to investigate the crystallinity of these fibrous molecular assemblages under three kinds of atmospheric conditions. Figure 3 indicates the XRD profiles of the molecular assemblages, with result under an air atmosphere, under a carbon dioxide atmosphere, and a hydrogen chloride atmosphere shown in lines a, b and c in Figure 3, respectively. As seen in Figure 3a, several sharp diffraction peaks were observed at  $2\theta = 5.5, 9.5, 11.3, 14.5, 16.0$  and  $19.1^\circ$  in the case of the molecular assemblages formed under an air atmosphere. On the other hand, small broad diffraction peaks were observed at  $2\theta = 14.5$  and  $16.0^\circ$  in the cases of the molecular assemblages formed under a carbon dioxide atmosphere (Figure 3b) and under a hydrogen chloride atmosphere (Figure 3c). It was revealed that the molecular assemblages formed at a short period of 3 h possessed less crystallinity than those formed gradually under an air atmosphere.

In this section, we could prepare the fibrous molecular assemblages with small widths and lengths under carbon dioxide and hydrogen chloride atmospheres in comparison with those under an air atmosphere that we reported previously [9]. The SEM and XRD results suggested that the entire morphology and crystallinity of the molecular assemblages formed from **1** were controllable by the neutralization rate and the kind of acidic substances.

### 3-2. Width growth of fibrous molecular assemblages by crystal growth method

It is well known that a large organic single-crystal suitable for X-ray crystallography is obtainable by the



**Figure 4.** SEM images of the fibrous molecular assemblages fabricated by crystal growth method; (a) original, (b) first time, (c) second time and (d) third time.

partial dissolution and subsequent crystal growth of small single crystals. We applied the crystal growth method to obtain fibrous molecular assemblages with a large width.

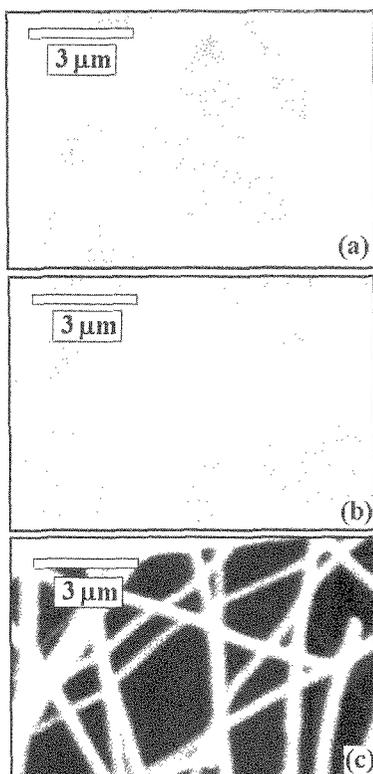
Figure 4 shows the SEM images of the fibrous molecular assemblages formed from **1** under an air atmosphere by the crystal growth method. When a small amount of an aqueous alkaline NaOH solution was added to an aqueous dispersion containing fibrous molecular assemblages possessing a width of 500 ~ 700 nm (Figure 4a) and the mixture kept intact for fiber growth, the width of molecular assemblages formed from **1** became large up to 1 ~ 3  $\mu\text{m}$  as shown in the SEM image of Figure 4b. Moreover, it was found that fibrous molecular assemblages with a larger width could be obtained as the crystal growth method was repeated more times. At the second and third times, the fibrous molecular assemblages possessed a width of 3 ~ 5  $\mu\text{m}$  and 6 ~ 8  $\mu\text{m}$ , as indicated in parts c and d of Figure 4, respectively.

It was confirmed from the XRD measurements that all the fibrous molecular assemblages prepared through the crystal growth method showed diffraction peaks identical to those prepared initially under an air atmosphere, although a diffraction peak intensity at  $2\theta = 14.5^\circ$  became relatively strong among the other peaks. The XRD results suggested that organized structures in these fibrous molecular assemblages formed from **1** were identical even when the macroscopic entire morphology of the fibrous molecular assemblages was changed by the fiber growth procedure. The fibrous molecular assemblages in the width range of 500 nm ~ 8  $\mu\text{m}$  could be prepared by the crystal growth method.

### 3-3. Shortened width of fibrous molecular assemblages by anionic surfactant addition

It has been attempted in template-directed syntheses that organized entire morphologies of nanometer-sized particles, tubes, fibers, and so forth are adjusted by surfactant addition upon their preparation. We also attempted this methodology using surfactants to control entire morphologies of the fibrous molecular assemblages formed from **1**.

In the case of a cationic surfactant of cetyltrimethylammonium chloride, hardly dispersed, aggregated fibrous molecular assemblages were formed



**Figure 5.** SEM images of fibrous molecular assemblies obtained from an alkaline aqueous solution containing  $1.0 \times 10^{-3} \text{ dm}^{-3}$  **1** and SDS of (a)  $4.05 \times 10^{-3} \text{ mol dm}^{-3}$ , (b)  $8.10 \times 10^{-3} \text{ mol dm}^{-3}$  and (c)  $16.2 \times 10^{-3} \text{ mol dm}^{-3}$ .

from an aqueous alkaline solution containing **1** and the cationic surfactant. In contrast, well-dispersed fibrous molecular assemblies were formed from an aqueous solution containing  $1.0 \text{ mmol dm}^{-3}$  **1** and  $4.05 \text{ mmol dm}^{-3}$  sodium dodecyl sulfate (SDS) as an anionic surfactant as shown in the SEM image of Figure 5a. A noticeable feature to describe here is that fibrous molecular assemblies possessing a small width of  $100 \sim 300 \text{ nm}$  were formed partially from the SDS-containing solution. As the concentration of SDS in the aqueous solution of **1** was increased, population of the small organic fibers was increased. When the SDS concentration was over a critical micelle concentration (CMC) of SDS in deionized water, the small fibrous molecular assemblies with a  $100 \sim 300 \text{ nm}$  width were formed more, as indicated in Figure 5c showing the SEM image of fibrous molecular assemblies formed from a solution containing  $16.2 \text{ mmol dm}^{-3}$  SDS. However, fibrous molecular assemblies were hardly formed in solutions containing  $40.5$  and  $81.0 \text{ mmol dm}^{-3}$  SDS. The XRD measurements revealed that the fibrous molecular assemblies formed under conditions containing more than  $8.10 \text{ mmol dm}^{-3}$  SDS showed a diffraction peak at  $2\theta = 14.5^\circ$ . Furthermore, the diffraction peak was broadened and became small by increasing the amount of SDS. The SEM and XRD studies suggested that the SDS addition in an aqueous alkaline solution of **1** caused the width of fibrous molecular assemblies to be small and less crystalline. It was difficult to obtain only the small fibrous

molecular assemblies with a  $100 \sim 300 \text{ nm}$  width by the surfactant addition method.

#### 4. CONCLUSION

We displayed that the macroscopic organized morphologies of the fibrous molecular assemblies formed from an amphoteric azopyridine carboxylic acid **1** were highly affected by the preparation conditions such as the kind of acidic substances for neutralization, the rate for neutralization, and the surfactant addition. Rapid neutralization under carbon dioxide and hydrogen chloride atmospheres caused the width and crystallinity of the fibrous molecular assemblies to become small. To obtain smaller fibrous molecular assemblies formed from **1**, the acidic substance addition method was available. On the other hand, to obtain larger fibrous molecular assemblies, the crystal growth method involving partial dissolution and subsequent growth seemed suitable. These fibrous molecular assemblies with a different width will be available to templates for metallic tubular materials prepared through electroless plating methods.

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#### REFERENCES

- [1] S. Iijima, *Nature*, **354**, 56 (1991).
- [2] (a) Y. Xia, P. Yang, *Adv. Mater.* **15**, 351 (2003). (b) K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem. Int. Ed.* **42**, 980 (2003).
- [3] (a) J. M. Schunur, *Adv. Mater.* **6**, 971 (1994). (b) W. Shenton, T. Douglas, M. Young, G. Stubbs, S. Mann, *Adv. Mater.* **11**, 253 (1999).
- [4] M. Bognitzki, H. Hou, M. Ishaque, T. Frese, M. Hellwig, C. Schwarte, A. Schaper, J. H. Wendorff, A. Greiner, *Adv. Mater.* **12**, 637 (2000).
- [5] C. J. Brumlik, V. P. Menon, C. R. Martin, *J. Mater. Res.* **9**, 1174 (1994).
- [6] (a) J. Y. Ying, C. P. Mehnert, and M. S. Wong, *Angew. Chem. Int. Ed.*, **38**, 56 (1999). (b) A. Stein, B. J. Melde, and R. C. Schroden, *Adv. Mater.*, **19**, 1403 (2000).
- [7] D. Ishii, K. Aoki, M. Nakagawa, and T. Seki, *Trans. Mat. Res. Soc. Jpn.*, **27**, 517 (2002).
- [8] D. Ishii, M. Nakagawa, T. Seki, and T. Iyoda, *Trans. Mat. Res. Soc. Jpn.*, **28**, 577 (2003).
- [9] (a) K. Aoki, M. Nakagawa and K. Ichimura, *Chem. Lett.*, 1205 (1999). (b) K. Aoki, M. Nakagawa, and K. Ichimura, *J. Am. Chem. Soc.*, **122**, 10997 (2000). (c) K. Aoki, M. Nakagawa, T. Seki, K. Ichimura, *Bull. Chem. Soc. Jpn.*, **75**, 2533 (2002).
- [10] M. Nakagawa, D. Ishii, K. Aoki, T. Seki and T. Iyoda, submitted.
- [11] P. H. Elworthy and K. J. Mysels, *J. Colloid Interfac. Sci.* **21**, 331 (1966).

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