Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Non-Covalent Synthesis of Twisted Organic Fibers by Self-Assembling of Sugar-Based Bolaamphiphiles in Water

Toshimi Shimizu [a] & Mitsutoshi Masuda [a]

[a] Department of Organic Materials, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305, JAPAN

Version of record first published: 04 Oct 2006

To cite this article: Toshimi Shimizu & Mitsutoshi Masuda (1997): Non-Covalent Synthesis of Twisted Organic Fibers by Self-Assembling of Sugar-Based Bolaamphiphiles in Water, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 197-200

To link to this article: http://dx.doi.org/10.1080/10587259708042829

Mol. Cryst. Liq. Cryst., 1997, Vol. 295, pp. 197–200
Reprints available directly from the publisher
Photocopying permitted by license only

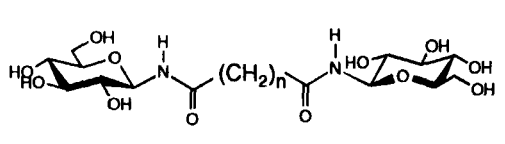
NON-COVALENT SYNTHESIS OF TWISTED ORGANIC FIBERS BY SELF- ASSEMBLING OF SUGAR-BASED BOLAAMPHIPHILES IN WATER

TOSHIMI SHIMIZU AND MITSUTOSHI MASUDA
Department of Organic Materials, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, JAPAN

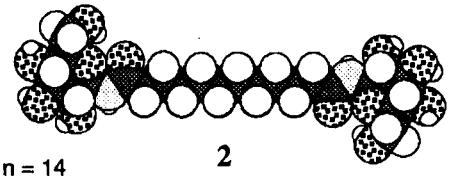
Abstract Chiral and air-stable fibers were obtained by the self-assembling of 1-D-glucosamide bolaamphiphiles in bulk water, and the even-odd effect of the spanned methylene chains on the chiral assemblies was discussed.

INTRODUCTION

Hydrogen-bond controls of molecular assemblies have been a key methodology to build up stable and structurally well-defined nanostructures. From this viewpoint, we have developed the non-covalent synthesis of stable supramolecular structures by the self-assembling of molecules.[1-3] We have recently synthesized novel 1-D-glucosamide bolaamphiphiles **1** - **5**, in which two D-glucosylamine rings are linked by a β-N-glycosidic bond to a hydrophobic α,ω-dicarboxylic acid.[4] They should self-assemble to form stable monolayers by multiple hydrogen bonds and hydrophobic interaction in water. We would like to report here the construction of a variety of chiral fibrous assemblies made up of the 1-D-glucosamide bolaamphiphiles with even-numbered methylene chains.



1 : n = 6, **2** : n = 10, **3** : n = 11, **4** : n = 12, and **5** : n = 14



2

EXPERIMENTAL

The novel 1-glucosamide bolaamphiphiles **1** - **5** were efficiently synthesized in 4 steps starting from α-D-acetobromoglucose. The new bola-form glycolipids gave correct

elemental analyses and satisfactory spectroscopic data. Self-assembling structures were investigated by using polarized or phase-contrast light microscopy, FT-IR spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction methods.

RESULTS AND DISCUSSION

The 1-glucosamide bolaamphiphiles **1** - **5** proved to be soluble at least in hot water and insoluble in nonpolar solvents like chloroform. When the saturated aqueous solutions of the bolaamphiphiles were allowed to cool slowly, they gave a variety of solid-like fibrous assemblies (Figure 1). To date, there have been no examples of bilayers and non-interdigitizing chains for cyclic carbohydrate amphiphiles.[5] Therefore, this result is novel and noteworthy in one important respect: It could not have been predicted that a cyclic sugar-head group allowed the formation of the amide hydrogen bond chains and thereby stable fibers. It is also of interest that the fiber-growth feature depends strongly on both the *n*-alkylene chain lengths and the even- and odd numbers of the methylene carbons.

The hexamethylene-group-spanned bolaamphiphile **1** is highly soluble in water at room temperature. It forms a common needle-like microcrystal with ill-defined twisting morphologies. On the other hand, flexible and long thin-fibers hundreds micrometers in length were formed in water from the decamethylene-group-spanned derivative **2**. This fiber formation competes with extended hydrogelation, depending critically on the concentration, the cooling rate, and preparation method of the sample.

Elongation of the spanning chain by two methylene groups allowed the formation of well-defined and right-handed helical ribbons from **4**. The helical pitches vary widely from 1 μm to 10 μm. Polarized light microscopy of the representative helical fibers exhibited birefringence, indicative of an extended crystalline structure. The octaacetylated derivative of **4** can not allow the crystallization in any nonpolar solvents. This means that the existence of free hydroxyl groups is crucial for the fiber formation in water. The fibers can be isolated and dried. The dehydrated fibers are somewhat

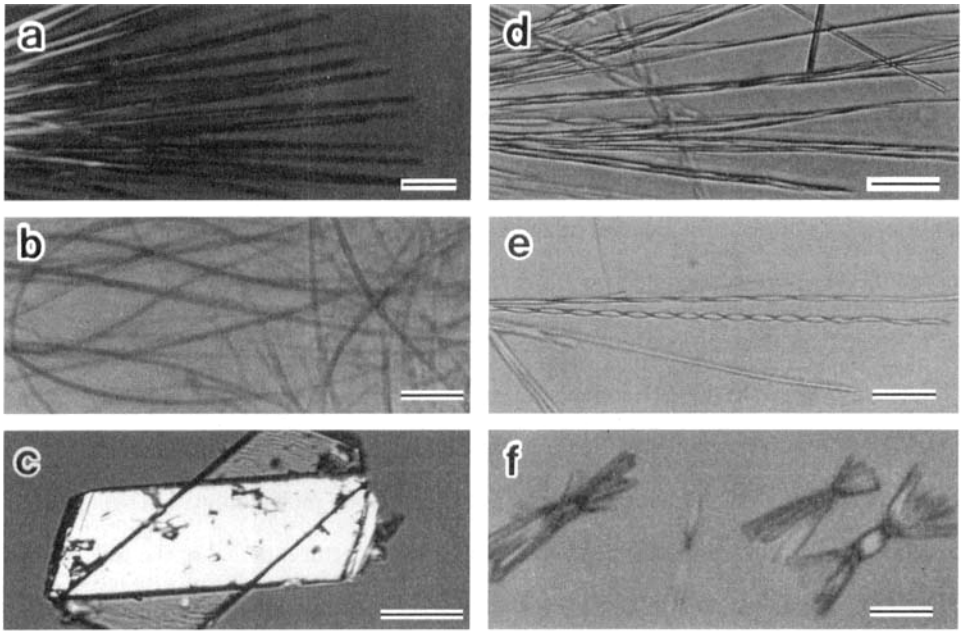


FIGURE 1 Light micrographs of fibrous assemblies in water. (a): **1**, (b): **2**, (c): **3**, (d) and (e): **4**, and (f): **5**, scale bar = 10 μm. (See Color Plate IX).

breakable, but extremely stable in a long term (> one year) at temperatures lower than 220°C in atmospheric pressure. This air-stability has not been appeared in the fibrous supramolecular structures obtained so far.[6,7]

Differential scanning calorimetry showed that the bolaamphiphile **4** has no phase transition in water from 20°C to 120°C; no melting occurs up to 220°C. To the best of our knowledge, the present fibers would be a unique example of air-stable and chiral solid-like fibers, which can be isolated. We also found that the bolaamphiphile **5** affords interesting "bow tie"-like microcrystals. However, the careful slow cooling of the saturated aqueous solution of **5** also proved to form helical thin-fibers.

In contrast with the fiber formation from the bolaamphiphiles **1**, **2**, **4**, and **5**, only platelets were generated from the bolaamphiphile **3** with an odd-numbered methylene chains (n = 11). Surprisingly, most of the crystals are twin. In the case of mono-headed amphiphiles, it is known that one enantiomer forms a chiral fiber, whereas racemate an achiral platelet.[7] Therefore, the above results show the first example of

stereochemical effect of the even-odd connecting links on the morphologies of chiral assemblies.

To presume molecular arrangements in the fiber from **4**, we conducted FT-IR spectroscopy, X-ray diffraction, and TEM. Amide hydrogen bond chains can be confirmed by the peak frequencies of amide I and II bands (1654 and 1534 cm^{-1}, respectively). The antisymmetric and symmetric CH_2 stretching bands support the occurrence of an all-*trans* conformation of the methylene chains in the fiber. Low- and wide-angle powder X-ray diffraction studies demonstrated the 2.45-nm long spacing and orthorhombic or monoclinic hydrocarbon packing for the fiber. TEM demonstrated that the fibers are 30~35 nm in width and retain a helical ribbon morphology. Taking all evidence into consideration, we can depict a possible structural model of the fiber from **4** (Figure 2). The bolaamphiphiles form a monolayer sheet, where the molecules are arranged with inclining the alkylene chains. The extended multiple sheets made of these monolayers will grow into the chiral fibers of light microscopic dimension.

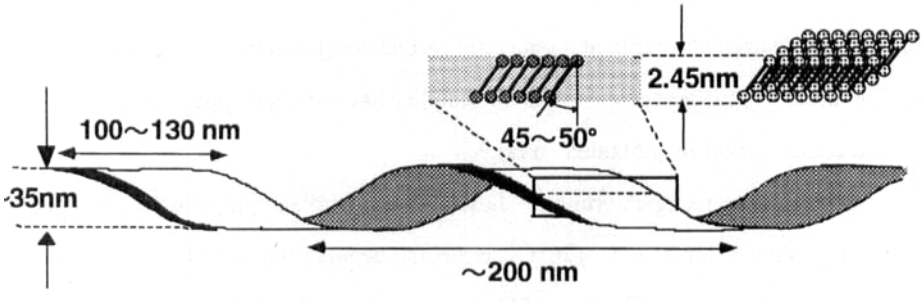


FIGURE 2 Self-assembling model of the bolaamphiphile **4** in the fiber

REFERENCES

1. T. Shimizu, M. Mori, H. Minamikawa, and M. Hato, J. Chem. Soc. Chem. Commun., 183 (1990).
2. T. Shimizu and M. Hato, Biochim. Biophys. Acta, 1147, 50 (1993).
3. T. Shimizu, M. Kogiso, and M. Masuda, Nature, 383, 487 (1996).
4. M. Masuda and T. Shimizu, Chem. Commun., 1057 (1996).
5. G.A. Jeffrey, L.M. Wingert, Liquid Crystals, 12, 179 (1992).
6. N. Nakashima, S. Asakuma, T. Kunitake, J. Am. Chem. Soc. , 107, 509 (1985).
7. J.-H. Fuhrhop, P. Schnieder, J. Rosenberg, and E. Boekema, J. Am. Chem. Soc., 109, 3387 (1987)