Macromolecules **1998,** *31,* 9403−9405

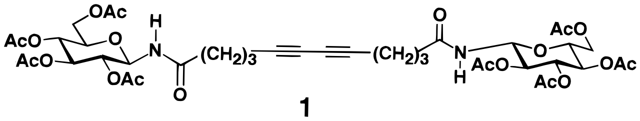
Polymerization of Bolaform Butadiyne 1-Glucosamide in Self-Assembled Nanoscale-Fiber Morphology

Mitsutoshi Masuda,* Takeshi Hanada, Kiyoshi Yase, and Toshimi Shimizu

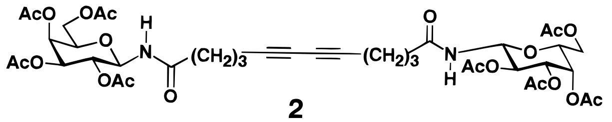
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received July 6, 1998

Polymerization of constituent molecules in supramolecular self-assemblies[1] will provide stable covalent assemblies. In contrast to a number of studies on bilayer-membrane(BLM)-templated polymerization of diacetylenes,[2] only few studies have been reported for the polymerization in monolayer lipid membranes (MLMs) such as liposomes[3] or multi sheets.[4] Furthermore, the characteristics of the polymerized entity have been uncertain, owing to the fairly poor solubility of the products. Bolaamphiphiles,[5] unlike one-headed amphiphiles, are characteristic of forming MLMs such as supramolecular tubes[6a] and rods.[6b−d] We have recently reported the supramolecular fiber formation from 1-glucosamide bolaamphiphiles.[7] Packing parameters of the alkylene chains in their crystals[8] are in good accord with those of reactive diacetylene monomers.[9] Thus, butadiynes were incorporated into the bolaamphiphile bridge to provide a potential candidate for the topochemical polymerization within the fiber MLMs, as represented by **1** and **2**. Here, we first describe nanoscale fiber (nanofiber) formation from the bolaform butadiyne 1-glucosamide **1** and its partial polymerization leading to oligodiacetylene-containing fibers.



1



2

The polymerizable bolaform (1-aldosamide)s **1** and **2** have been synthesized[10] by condensation of octa-acetylated 1-glucosamine and 1-galactosamine with 5,7-dodecadiynedioic acid, respectively, according to the method previously reported.[11] Upon slow cooling to room temperature, the solutions of **1** (7 g) in an ethyl acetate/*n*-hexane (300/700 mL) mixture solidified to a gel. Similar gelation also occurs for bolaform (1-aldosamide)s[11] and (urethane amide)s[12] with saturated oligomethylene chains. The gel from **1** is a little resistant to mechanical stress. No gels of **1** were produced from common organic solvents such as MeOH, $CHCl_3$, and DMF. Energy-filtering transmission electron microscopy (EF-TEM)[13] for the unstained specimens revealed that the gel from the ethyl acetate/*n*-hexane solution was composed of nanofibers with widths of 6−20 nm (Figure 1, parts a and b). In contrast to helical ribbons formed from the 1-glucosamide bolaamphiphiles,[7] the present fibers form ribbons without remarkable twisting or spirals. The nanofibers of **1** were robust during the EF-TEM observation, presumably because of the polymerization of the butadiynes by an electron beam of the EF-TEM. The formation of linear amide hydrogen bond chains can be confirmed by the appearance of the amide N−H and C=O stretching bands at 3343, 3060, and 1680 cm^{-1}, and the N−H deformation band at 1535 cm^{-1} in FT-IR spectra.[14] These findings are consistent with a layered structure of **1** within the fibers, stabilized by a one-dimensional hydrogen-bonded network (Figure 2a).[15] However, the 1-galactosamide homologue **2**, an epimer of **1**, formed no fibers but amorphous solids in the same solvent. It was due to steric hindrance between adjacent pyranose rings in a stacked conformation similar to that in Figure 2a.

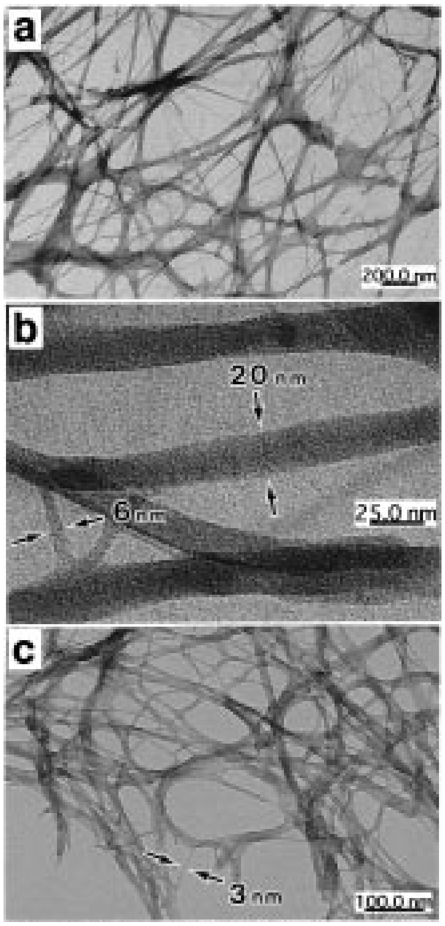


Figure 1. Nanoscale fibers (unstained) made of bolaform butadiyne 1-glucosamide **1** observed using EF-TEM. (a) and (b): unpolymerized fibers of **1**. (c): γ-ray-irradiated fibers of **1**.

Upon exposure to 254-nm light[16] or γ-ray[17] under an argon atmosphere, the fibrous gel of **1** (3.3 mg) in ethyl acetate/*n*-hexane (1/9 mL) changed the color from colorless to red (λ_{max} = 506 and 546 nm). The UV absorption maxima are blue-shifted as compared to those for solid-state-polymerized polydiacetylenes and consistent with that of poly{5,7-dodecadiyne-1,12-diol bis[((4-butoxycarbonyl)methyl)urethane]}, called poly-4BCMU (λ_{max} = 494 and 530 nm, at 56 °C in toluene).[18] Therefore, the occurrence of a coil-like conformation or moderate extension of π-conjugated polymer chains can be suggested. In contrast, the dried amorphous solids of **1** and **2** from the chloroform solution exhibit no such color

10.1021/ma981053s CCC: $15.00 © 1998 American Chemical Society
Published on Web 12/04/1998

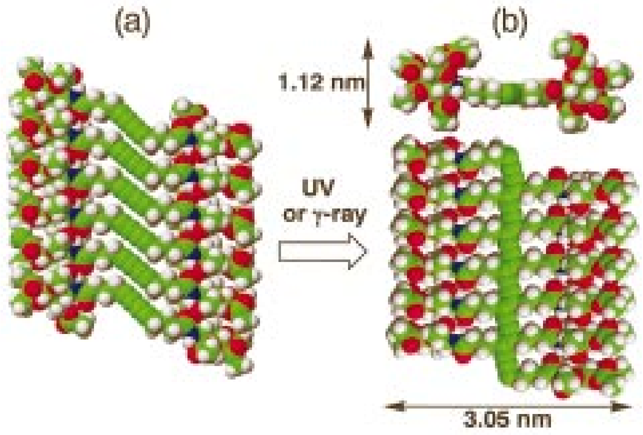


Figure 2. A possible model of the (a) self-assembled and (b) polymerized monomolecular fibers from **1** [(top): top view and (bottom): front view]. One-dimensional hydrogen-bond networks were formed between amide groups in (a) and (b).

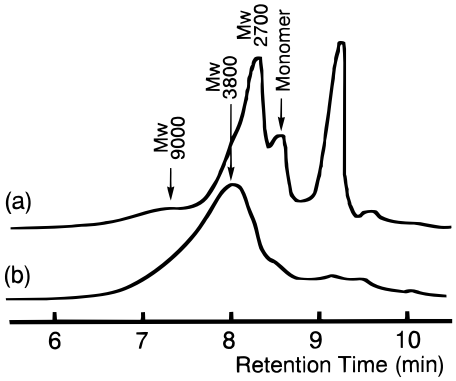


Figure 3. GPC profiles for the UV-irradiated fibers made from **1** [(a) 40-min and (b) 4-h irradiation].[16] Absorbance was monitored at 250 nm. Solvent: chloroform.

change by UV irradiation. It has been well-documented that diacetylenes incorporated into macromonomers can be polymerized readily in crystalline domains.[19] In addition, the polymerizability of diacetylene monomers in a crystal lattice strongly depends on their packing parameters.[9] Considering this strict positional requirement, the bolaform molecules **1** seem to align at a critical repeat distance near 5.0 Å and with an orientation angle of about 45° relative to the translation axis[9] within the nanofibers. The appearance of the FT-IR shoulder for the C═C double bonds (1625−1640 cm^{-1}) can also support the polymerization of the nanofibers from **1**.[20] The irradiated fibers proved to be insoluble in toluene which can dissolve the original ones, whereas both fibers were still soluble in chloroform. Thus, the solubility and UV−vis spectra of the irradiated fibers are similar to those of soluble polydiacetylenes such as poly-4BCMU.[18] The poly-4BCMU also forms gels in toluene.[21] However, this gelation behavior can be exhibited only by polydiacetylenic BCMUs, not by their monomers.

Gel permeation chromatography (GPC)[22] in chloroform provided definitive evidence of the polymerization (Figure 3). The GPC profile of the UV-irradiated (40 min) fibers showed that the mass-average molecular weight (M_w) ranged from 3.3×10^4 to 1.6×10^3 against the polystyrene standard (Figure 3a). These molecular weights correspond to 37mer−dimer. Further irradiation (4 h) induced a color change from red to orange. As a consequence, the monomer peak almost disappeared and the molecular-weight distribution shifted to a higher mass region (Figure 3b). The γ-ray-irradiated fibers also showed a similar molecular-weight distribution ($M_w = 2.8 \times 10^4 - 2.0 \times 10^3$). This oligomerization behavior indicates that the nanoscale fiber lacks the long-range molecular order needed for high-molecular-weight polydiacetylenes.

The EF-TEM observation of the γ-ray-irradiated fibers also gave nanofiber images similar to those before irradiation (Figure 1c). It is quite different from parallel linear features in the TEM image observed for poly-4BCMU thin films.[23] The minimum width of the fibers is found to be 3 nm (Figure 1c), which corresponds well to an extended molecular width (3.05 nm, Figure 2b). Taken together, the polymerization of the nanofibers from **1** produced oligodiacetylene chains within the fibers, utilizing a gel state as a template. We were able to estimate the molecular-weight distribution of the nanoscale-fiber-templated oligodiacetylenes. The possibility of solid-state polymerization of microcrystals[24] is ruled out in this case since optical microscopy and EF-TEM give no microcrystal images. X-ray diffraction analysis also shows no crystalline Bragg reflections for the nonirradiated fibers. In this report, we also provided an example of the direct TEM observation of bundles of oligodiacetylene-containing fibers. Further studies on the self-assembling and polymerization properties of deacetylated 1-aldosamide bolaamphiphiles in aqueous solutions are now in progress.

Acknowledgment. We thank our colleague Dr. Satoru Shimada for γ-ray irradiation and valuable discussions.

Supporting Information Available: Synthetic scheme and ^{1}H NMR of **1**, and FT-IR and UV−vis spectra of the nanofibers from **1** (4 pages). Ordering and accessing information is given on any current masthead page.

References and Notes

(1) Fuhrhop, J.-H.; Koening, J. *Membranes and Molecular Assemblies*: *The Synkinetic Approach*; The Royal Society of Chemistry: Cambridge, 1994.

(2) For review, see: (a) Fendler, J. H. *Acc. Chem. Res.* **1984**, *17*, 3−8. (b) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113−158. For diacetylenic LB films, see: (c) Tieke, B.; Wegner, G. *Topics in Surface Chemistry*; Kay, E., Bagus, P. S., Eds.; Plenum Press: New York, 1978 and references therein. For diacetylenic liposomes, see: (d) O'Brien, D. F.; Whitesides, T. H.; Klingbiel, R. T. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 95−101 and references therein. For diacetylenic fibers, see: (e) Frankel, D. A.; O'Brien, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 7436−7437. (f) Fuhrhop, J.-H.; Blumtritt, P.; Lehmann, C.; Luger, P. *J. Am. Chem. Soc.* **1991**, *113*, 7437−7439. (g) Frankel, D. A.; O'Brien, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10057−10069. For diacetylenic SAMs, see: (h) Kim, T.; Chan, K. C.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 189−193 and references therein.

(3) Bader, H.; Ringsdorf, H. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1623−1628.

(4) (a) Saremi, F.; Maassen, E.; Tieke, B.; Jordan, G.; Rammensee, W. *Langmuir* **1995**, *11*, 1068−1071. (b) Saremi, F.; Tieke, B. *Adv. Mater.* **1995**, *7*, 378−380.

(5) (a) Okahata, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1979**, *101*, 5231−5234. (b) Fuhrhop, J.-H.; Fritsch, D. *Acc. Chem. Res.* **1986**, *19*, 130−137. (c) Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1937−1940.

(6) (a) Fuhrhop, J.-H.; Spiroski, D.; Boettcher, C. *J. Am. Chem. Soc.* **1993**, *115*, 1600−1601. (b) Newkome, G. R.; Baker, G. R.; Saunders: M. J.; Russo, P. S.; Gupta, V. K.; Yao, Z. Q.; Miller, J. E.; Bouillion, K. *J. Am. Chem. Soc.* **1986**, *108*, 752−753. (c) Newkome, G. R.; Baker, G. R.; Arai, S.; Saunders: M. J.; Russo, P. S.; Theriot, K. J.; Moorefield, C.

N.; Rogers, L. E.; Miller, J. E.; Lieux, T. R.; Murray, M. E.; Philips, B.; Pascal, L. *J. Am. Chem. Soc.* **1990**, *112*, 8458−8465. (d) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Bechera, R. K.; Escamillia, G. H.; Saunders, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 917−919.

(7) Shimizu, T.; Masuda, M. *J. Am. Chem. Soc.* **1997**, *119*, 2812−2818.

(8) (a) Shimizu, T.; Masuda, M.; Shibakami, M. *Chem. Lett.* **1997**, 267−268. (b) Masuda, M.; Shimizu, T. *Chem. Commun.* **1996**, 1057−1058. (c) Masuda, M.; Shimizu, T. *Carbohydr. Res.* **1997**, *302*, 139−147.

(9) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91−136.

(10) Bolaform 1-glucosamide **1**; mp 116−127 °C, in 25% yield. Calcd for $C_{40}H_{52}N_2O_{20}$: C, 54.54; H, 5.95; N, 3.18. Found: C, 54.51; H, 5.97; N, 3.04. Bolaform 1-galactosamide **2**; amorphous, in 39% yield. Calcd for $C_{40}H_{52}N_2O_{20}$: C, 54.54; H, 5.95; N, 3.18. Found: C, 54.69; H, 5.98; N, 3.03.

(11) Masuda, M.; Shimizu, T. *J. Carbohydr. Chem.* **1998**, *17*, 405−416.

(12) (a) Bhattacharya, S.; Acharya, S. N. G.; Raju, A. R. *Chem. Commun.* **1996**, 2101−2102. (b) Hanabusa, K.; Tanaka, R.; Suzuki, M.; Kimura, M.; Shirai, H. *Adv. Mater.* **1997**, *9*, 1095−1097.

(13) The dried specimens were examined at 80 keV by using an analytical electron microscope (Carl Zeiss EM 902) with a Castain-Henry type electron energy filter at room temperature.

(14) FT-IR spectrum for the non-hydrogen-bonded bolaform **1** in chloroform solution shows the amide C═O streching band at 1696 cm^{-1}, the N−H stretching band at 3424 and 3367 cm^{-1}, and the N−H deformation band at 1515 cm^{-1}.

(15) (a) Chang, Y. L.; West, M.-A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991−6000. (b) Kane, J. J.; Liao, R.-F.; Lauher, J. W.; Fowler, F. W. *J. Am. Chem. Soc.* **1995**, *117*, 12003−12004.

(16) A 110-W low-pressure Hg lamp was used for UV irradiation.

(17) The fibers were irradiated with 9 kGy of ^{60}Co γ-rays at room temperature.

(18) (a) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 607−614. (b) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522−530.

(19) (a) Day, D.; Lando, J. B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 227−233. (b) Rubner, M. F. *Macromolecules.* **1986**, *19*, 2114−2128. (c) Pérez, J.; Burillo, G.; Roa, M.; Vázquez, C.; Ogawa, T. *Polym. Bull.* **1992**, *27*, 527−534.

(20) Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 3197−3198.

(21) Sinclair, M.; Lim, K. C.; Heeger, A. J. *Phys. Rev. Lett.* **1983**, *51*, 1768−1771.

(22) GPC anaysis was carried out with a JASCO Gulliver System with a Shodex K-804L column at 40 °C, using chloroform as an eluent.

(23) Howell, B.; Reneker, D. H. *J. Appl. Polym. Sci.* **1990**, *40*, 1663−1682.

(24) Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *35*, L221−L223 and references therein.

MA981053S