Poly (ethylene terephthalate) Nanofiber Made by Sea-island Type Conjugated Melt Spinning and Laser-heated Flow Drawing

Kazuhiro Nakata*, Kenji Fujii*, Yutaka Ohkoshi*, Yasuo Gotoh*, Masanobu Nagura*,

Miyuki Numata**, Mie Kamiyama**

*Faculty of Textile Science & Technology, Shinshu University 3-15-1 Tokida, Ueda-City, Nagano, 386-8567, Japan

**Teijin Fiber Limited.

Keywords: nanofiber, conjugate spinning, laser drawing, PET, nylon6

ABSTRACT

Nylon6/poly (ethylene terephthalate) ultra-multi-island sea/island conjugated melt-spun fibers were flow-drawn at a draw ratio of 174 with heating by CO_2 laser irradiation. Continuous PET nanofibers having a diameter of 39 nm could be obtained from the flow-drawn fiber with further drawing and removal of the sea component. In addition, the drawn fiber had a strength of 0.54 GPa. This result shows that a PET nanofiber having a strength almost equal to that of a conventional PET fiber can be obtained by the combination of conjugate-melt-spinning and laser-heated flow-drawing.

1. INTRODUCTION

A fiber having a diameter less than 10 μm is called an “ultra-fine fiber,” and a fiber having a diameter less than 100 nm is called a “nanofiber” [1]. By virtue of its large surface area, ultra-fine fiber has many applications, including high-performance filters. Nanofiber, which has not only greater surface area than ultra-fine fiber, but also a possibility of good biocompatibility and low fluid resistance, is expected to find advanced applications [2].

Production methods for ultra-fine fiber fall into three categories: self-ordering type, random type, and filament type [2]. One of the typical products made by the self-ordering production method is carbon nano-tube [3], [4], [5]. Poly (ethylene) nanofiber that has a 30-50 nm diameter was also produced by the method with the polymerization in extremely narrow space [6]. On the other hand, melt-blowing, flash spinning, and electro-spinning are known as the random type production method. In particular the electro-spinning, recently receives attention as a technique to make the new kinds of ultra-fine fiber hardly produced by the other methods [7]. The electro-spinning was invented in 1934 [8], and the production of ultra-fine fiber less than 1 μm diameter was reported in 1971 [9]. In recent years, some novel electro-spinning techniques are investigated. For example, Huajun et al. reported melting-type electro-spinning technique which does not need to use solvent [10], and Zussman et al. made a bundle of aligned ultra-fine fibers by taking-up on the edge of disc shape roller [11]. The latter study is interesting as the random-type production method for aligned ultra-fine fiber. However, the fiber obtained by the method has too thick diameter as the nanofiber.

Although there are some exceptional trials as mentioned above, aligned fibers are generally difficult to obtain by self-ordering-type and random-type production methods. But aligned continuous fiber bundles, which can be applied to various product forms, can be obtained by filament-type production methods. Two typical filament-type production methods are available: the direct spinning method and the conjugate spinning method. However, the smallest fiber diameter that can be obtained by the direct spinning method is known to be about 3 μm [12]. On the other hand, fiber of diameter less than one μm can be made by the conjugated spinning method, in which two polymer components are extruded together from a spinning die. The sea-island type conjugate spinning is the typical spinning method used for the purpose, in which many island fibers are arranged in sea component that is later removed by extraction. However, even by the conjugate spinning method, it is difficult to produce the nanofiber having a diameter less than 100 nm.

In view of the above, we attempted to produce poly (ethylene terephthalate) (PET) nanofiber by high-draw-ratio drawing of conjugate spun fiber. Two stable drawing states co-exist in the continuous drawing process of PET fiber; a neck drawing state, which leads to orientation-induced crystallization, and a flow drawing state, which leads to low molecular orientation. Obtaining a PET nanofiber by high-draw-ratio flow drawing may be possible, in view that the flow drawing state

involves no theoretical limit in draw ratio, whereas the draw ratio is limited to about 10 for the neck drawing process by orientation-induced crystallization. Unfortunately, the flow drawing state tends to be unstable, because the fiber is drawn with decreasing viscosity; i.e., drawing with increasing temperature, in particular because of the lower drawing tension and longer deformation region as compared with the neck drawing state. The stability of the flow drawing state can be discussed on the analogy of melt-spinning process. It was summarized qualitatively in the textbook written by Ziabicki [13], and was analyzed quantitatively by the computer simulation by Toriumi and Konda [14]. By the results, it was found that the viscosity profile along the spin-line is the governing parameter of the stability for high draw ratio spinning. The steeper cooling make the melt-spinning process stable. Therefore, the high-draw-ratio flow drawing tends to be unstable by the ordinary heat transfer heating of fiber.

The unstability can be avoided by rapid and uniform heating of laser irradiation [15][16]. This procedure is reported to produce an ultra fine fiber having a diameter of about 1 μm [17][18][19]. In this study, we attempted to produce PET nanofiber by laser-heated flow drawing of PET/nylon6 sea-island type conjugated melt-spun fiber [20].

2. EXPERIMENTAL

2.1 Conjugated-spun fiber

The fiber drawn in this study was PET/nylon6 sea-island type conjugated melt spun fiber provided by Teijin Fiber Limited. The fiber has a nylon6 sea, and PET islands, at a mass ratio of 50/50. In this study, two kind of conjugated-spun fibers were used for flow-drawing; “single fiber,” having a diameter of 88 μm, and “fiber bundle,” consisting of 12 single fibers each having a diameter of 44 μm. The diameters of island fibers were 1.7 μm for the single fiber and 0.7 μm for the fiber bundle.

2.2 Drawing

The fiber was drawn with laser irradiation heating. Figure 1 is a schematic diagram of the drawing system. The fiber run from a feed roller to a take-up roller was drawn at the speed ratio of the rollers. Between the rollers, the running fiber was heated by CO_2 laser generated by a PIN-30S CO_2 laser generator provided by Onizca Glass Co. Ltd. [15]. Fiber feed speed was 1 m/min, laser beam diameter was 5 mm, laser wavelength was 10.6 μm, and laser power was 1.1 W for the single fiber and 0.8 W for the fiber bundle. The laser beam was radiated perpendicular to the fiber running direction from 9 different directions to heat the fiber more uniformly with mirror reflection. The flow drawn fibers were batch drawn again at room temperature. In the batch drawing process, the sample length was 40 mm, and strain rate was 100 %/min. The draw ratios for each drawing process are listed in Table 1.

2.3 Electron Microscope Observation

The cross section of the flow drawn fiber was observed under a transmission electron microscope

(TEM). For the observation, the fiber was cut off after being surrounded by resin and the cross-section was dyed with OsO_4. Extracted PET nanofibers produced by two-step drawing and removal of nylon component were observed by a scanning electron microscope (SEM). The nylon sea component was removed by immersing the fiber in formic acid and applying ultrasonic waves for 24 hours.

2.4 Tensile Test

A tensile test was performed on the as-spun fiber and flow drawn fiber by Orientec Tensilon UTM-II-20 tensile tester with a gage length of 40 mm and an initial strain rate of 10 mm min^{-1}. The diameters measured by SEM were employed to calculate stress for the single fiber, and the values calculated from the diameter of as-spun fiber and draw ratios were employed for the fiber bundle.

3. RESULTS AND DISCUSSION

The single fiber was flow-drawn at draw ratios of 80 and 174, and the bundle fiber was flow drawn at a draw ratio of 174 times. For each drawing condition, the fiber could be drawn continuously for more than two minutes. Because a draw ratio of 174 times is the mechanical limit, finer fiber may be obtained by increasing the take-up speed. Figure 2 shows cross sectional TEM images of the single fiber after flow and batch drawing (Sample No. 5), and Figure 3 shows a TEM image of drawn fiber produced by the same condition as Sample No. 8 but the filament number is 6. Both Figures 2 and 3 shows that the PET island fibers were completely separated from the nylon6 sea. Furthermore, Figure 3 shows that the fiber bundle was welded into a monofilament. Figure 4 shows an SEM image of PET nanofiber produced by extraction of Sample No. 8. The individual PET island fibers were separated from each other.

Table 1 shows the diameters and mechanical properties of drawn fibers. The diameter values measured by SEM are listed for fiber obtained by drawing of “single fiber,” whereas the other listed diameters are estimated values, calculated from mass-flow rate, take-up speed, and draw ratios while ignoring density change. For drawing of single fiber, PET island fibers having a diameter of 86 nm were produced by flow drawing to a draw ratio of 174 and batch drawing to a draw ratio of 2.5 (Sample No. 5). The fiber bundle could be flow drawn to a draw ratio of 174 and then batch drawn to a draw ratio of 3 (Sample No. 8). The diameter of PET island in the obtained fiber is calculated as 39 nm, which is ascertained by the SEM image shown in Figure 4. These island fibers, having diameters of less than 100 nm, are sufficiently small to be called nanofiber. However, these fibers show the same mechanical properties as commodity PET fiber; that is, strength of 628 MPa and 23 % elongation (Sample No. 3) for example.

These result shows that the continuous PET nanofiber having sufficient mechanical properties for conventional use can be produced by sea-island type conjugated melt spinning of PET/nylon components, laser-heated flow drawing, other drawing processes and/or annealing, and extraction.

Acknowledgment

The authors would like to express their gratitude to Teijin Fiber Limited. for supplying samples. We also thank Ms. Nagata, Mr. Ishii, and Ms. Mifune for their effort to seek the best setting for stable flow drawing. This research was supported by a Grant-in-Aid for 21st Center of Excellence (COE) Research from the Japanese Ministry of Education, Culture, Sports, Science, and Technology.

References

1. Nakajima, T., Kajiwara, K., Mclntyre, J. E., Advanced fiber spinning technology; Woodhead Publishing Ltd.: 1994, p.187.
2. Shirai, H., Yamaura, K., "Fiber Kougaku", Maruzen Co. Ltd., 2005, p.33, 38.
3. Kroto, H. W.; Heath, J. R.; O'brien, S. C.; Curl, R. F.; Smalley, R.E., Nature, 318, 162, 1985.
4. Endo, M., Chemtech, 18(9), 568, 1988.
5. Iijima, S., Nature, 354, 56, 1991.
6. Kageyama, K.; Tamazawa, J.; Aida, T. Science, 285, 2113, 1999.
7. Fang. X.; Reneker, D. H., J. Macromolecular Sci. Phys., 36, 2, 169, 1997.
8. Formhals, A., US Patent, 1975504, 1934.
9. Baumgarten, P. K., J. of Colloid and Interface Science, 36, 71, 1971.
10. Huajun, Z.; Thomas, B. G.; Young, L. J., Polymer 47, 7497, 2006.
11. Zussman, E.; Burman, M.; Yarin, A. L.; Khalfin, R.; Cohen, Y., J. Polym. Sci. Part B: Polym. Phys., 44, 10, 1482, 2006.
12. Yoshimura, M., Koubunshi Gakkaishi, 47, 416, 1998.
13. Ziabicki, A., "Fundamentals of Fiber Formation", John Wiley & Sons, p.13, 1976.
14. Toriumi K., Konda A., Sen-i Gakkaishi, 40, T-193, 1984.
15. Ohkoshi, Y., Japanese Patent Publication 2002-115117.
16. Ohkoshi, Y.; Watanabe, J.; Okumura, W.; Gotoh, Y.; Nagura, M., Sen'I Gakkaishi, 58, 182, 2002.
17. Suzuki, A., Koubunshi Gakkaishi, 52, 833, 2003.
18. Suzuki, A.; Mochizuki, N., Japanese Patent Publication 2003-166115.
19. Suzuki, A.; Mochizuki, N., J. Appl. Polym. Sci., 88, 3279, 2003.
20. Kamiyama, M.; Iohara, K.; Ohkoshi, Y.; Nagata, R., Japanese Patent Publication 2005-325494.

Table 1 Tensile properties of as-spun and flow-drawn sea-island fiber

Sample No.	Diameter of as-spun fiber /μm	Filament Number	Draw Ratio	Diameter /μm	Diameter of PET Island /μm	Tensile Strength /GPa	Elongation x100
1			as-spun	88	1.8	0.12	410
2			80	9.8	0.20	0.18	260
3	88	1	80x3.5	5.6	0.11	0.63	23
4			174	6.3	0.13	0.31	150
5			174x2.5	4.4	0.086	0.56	27
6			As-spun	44	0.90	0.13	330
7	44	12	174	3.4	0.068	0.17	160
8			174x3	1.9	0.039	0.54	27

Figure Captions

Figure 1 Schematic diagram of laser drawing system.

Figure 2 Cross-sectional TEM image of conjugated -spun and flow-drawn fiber (No. 5); A: PET island fiber, B: Nylon 6 sea.

Figure 3 Cross-sectional TEM image of conjugated-spun and flow-drawn “bundle” fiber produced by the same condition as Sample No. 8 but the filament number is six. Fiber bundle composed of six conjugated-spun fibers are welded into a single fiber during the flow-drawing process.

Figure 4 SEM images of PET nanofibers obtained by removing sea component of conjugated-spun and flow-drawn bundle fiber (No. 8).

Fig.1

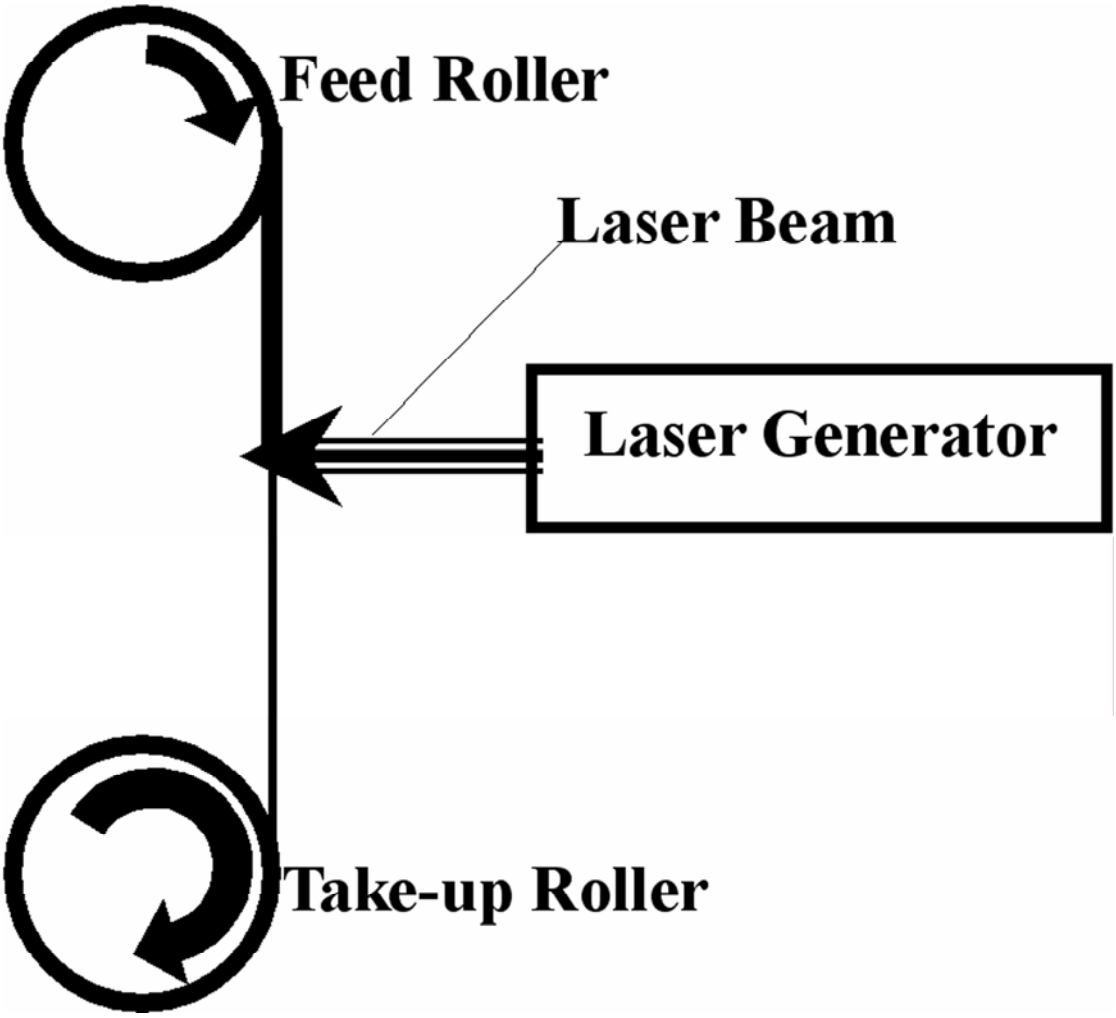

Fig.2

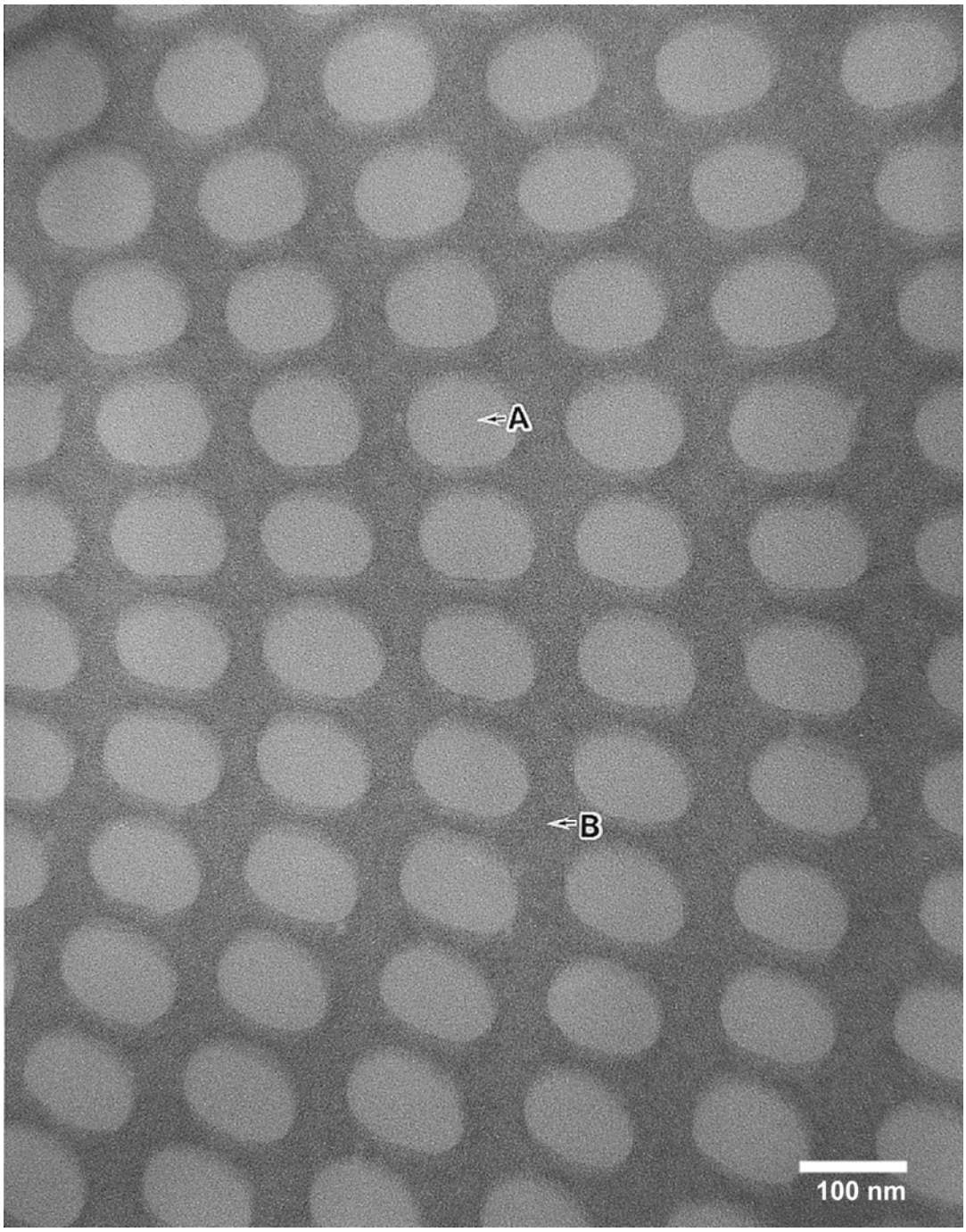

Fig. 3

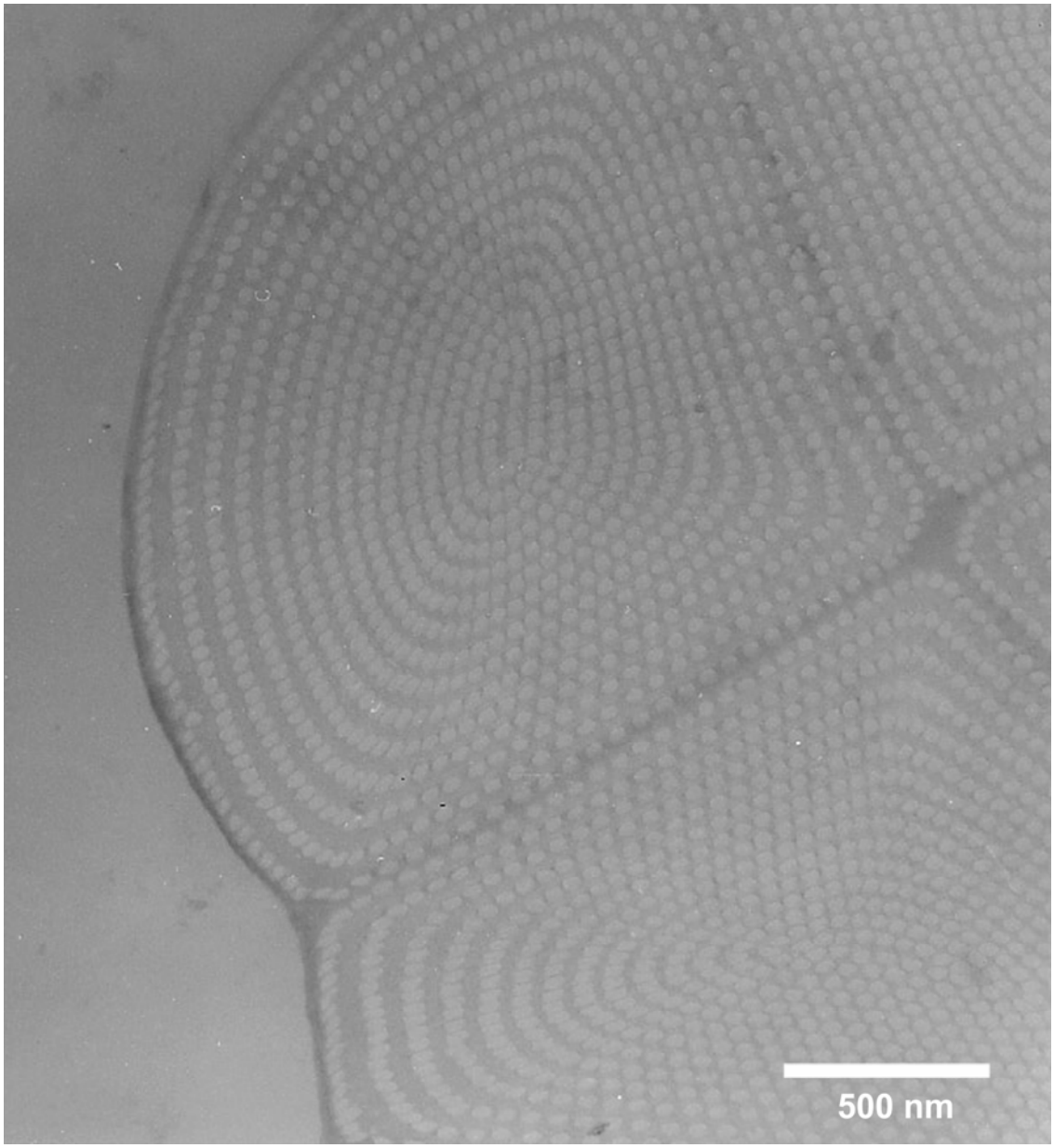

Fig.4