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Preparation of Uniform-sized Polymer Nanofibers by Extrusive Spinning Using Ordered Anodic Porous Alumina

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Uniform-sized polymer nanofibers were fabricated by the extrusive spinning of a photocurable monomer under UV irradiation using ordered anodic porous alumina as a nozzle for the spinning. The size of the resulting polymer nanofibers could be controlled by adjusting the pore size of the anodic porous alumina membrane.

There has been growing interest in the preparation of uniform-sized nanofibers owing to their potential applications in various fields, such as filtration and the preparation of culture media, catalysts, and optical materials.[1–5] Among various preparation techniques, electrospinning has been widely used for the formation of nanofibers of organic or inorganic materials. In this process, the electric force between a needle and a collector generates fine polymer fibers of nanometer to micrometer scale.[6–8] This is a simple and versatile process for the preparation of various types of nanofibers. However, it is not easy to achieve a high throughput, yield against time, in this process due to the difficulty in fabricating a multineedle nozzle. As a high-throughput process for the preparation of uniform-sized polymer fibers, extrusive spinning using a nozzle with multiple openings has been widely used. However, the smallest polymer fiber obtained by this process is on the order of microns to tens of microns owing to the difficulties in the preparation of nozzles with nanometer-scale openings. In the present report, we describe a novel high-throughput process for the preparation of polymer nanofibers by extrusive spinning using highly ordered anodic porous alumina as a nozzle. In this process, uniform-sized polymer fibers are formed by extruding a photocurable monomer through the pores of an anodic porous alumina membrane under UV light illumination. Anodic porous alumina, which is formed by the anodization of Al in an acidic electrolyte, is a typical self-ordered material with uniform-sized straight fine pores perpendicular to the surface.[9] The advantage of using this material as a nozzle for the extrusive spinning of polymer fibers is its controllability of the size of the resulting fibers of nanometer scale. On the basis of this new process, a high-throughput process for fabricating uniform-sized fibers of nanometer scale can be accomplished. In the present study we report the first example of the formation of fine fibers of nanometer scale based on extrusive spinning.

Figure 1 shows a schematic of the preparation of nanofibers using anodic porous alumina as a nozzle for extrusive spinning. The highly ordered anodic porous alumina was prepared by a similar process to that previously reported.[10] The pore arrangement was controlled through pretexturing by imprinting using a mold with ordered convexes. The anodization of pretextured Al generates the anodic porous alumina with an ideally ordered pore arrangement. The highly ordered hole arrangement contributes to the uniformity of the pore size, which is essential for the preparation of the uniform-sized nanofibers. After the pretexturing, the anodization of Al was carried out at a constant voltage of 200 V in 0.1 M phosphoric acid at 0 °C for 90 min. A through-hole membrane was obtained by the selective dissolution of Al in saturated methanolic I_2 solution and the subsequent etching of the bottom layer of porous alumina using an Ar ion milling apparatus.[11] The pore size of the membrane was adjusted by the postetching of porous alumina in 10 wt % phosphoric acid at 30 °C. The thickness of the porous alumina membrane was usually 15 μm. The formation of nanofibers was carried out by extruding 20 vol % toluene solution of the photocurable monomer (PAK-01 Toyo Gosei) into water-containing SDS as a detergent with the illumination of UV light from a high-pressure Hg lamp. PAK-01 is a kind of monomer for acrylic resin. For the extrusion, constant pressurization using N_2 gas (10–20 kPa) was adopted. The obtained samples were observed by scanning electron microscopy (SEM; JEOL JSM-6700F).

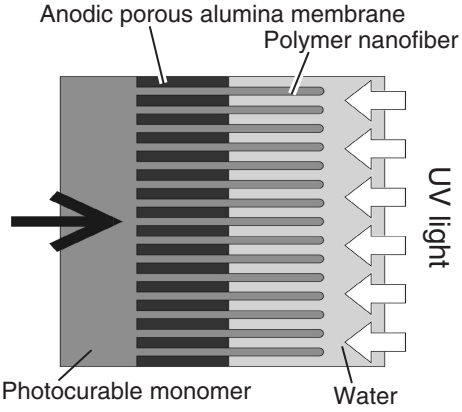

Figure 1. Schematic for the preparation of polymer nanofibers using anodic porous alumina.

Figure 2 shows a SEM image of typical nanofibers obtained by the present process. Anodic porous alumina with pore size of 220 nm was used. From the low-magnification SEM image in Figure 2a, it was observed that fine fibers were formed on the porous alumina membrane with used for the extrusive spinning. The high-magnification SEM image in Figure 2b reveals that uniform-sized fibers were obtained by the present process. The length of the fibers was approximately 30 μm, which was greater than the depth of the pores of the anodic porous alumina membrane, indicating the continuous formation of the fibers by this process. The nanofibers are thought to be prepared in isolated form in the liquid phase and attach each other during drying on the membrane. We will be able to obtain separate nanofibers by handling them in the liquid phase.

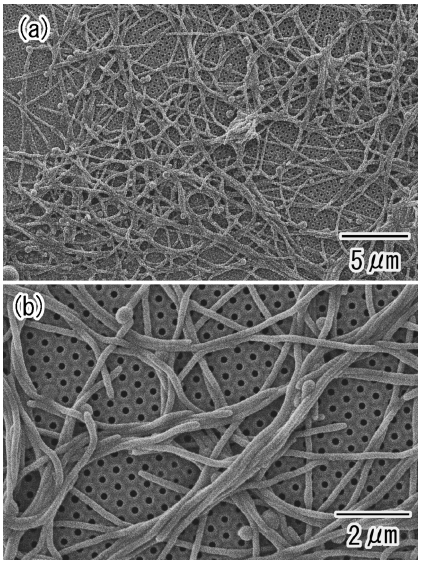

Figure 2. (a) Low-magnification and (b) high-magnification SEM images of polymer nanofibers.

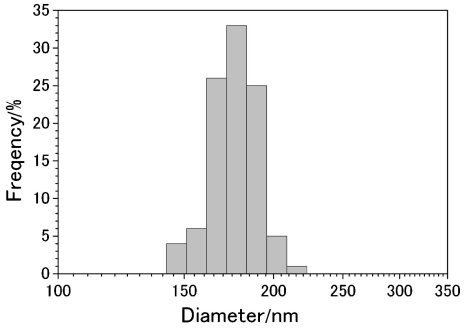

Figure 3. Size distribution of polymer fibers.

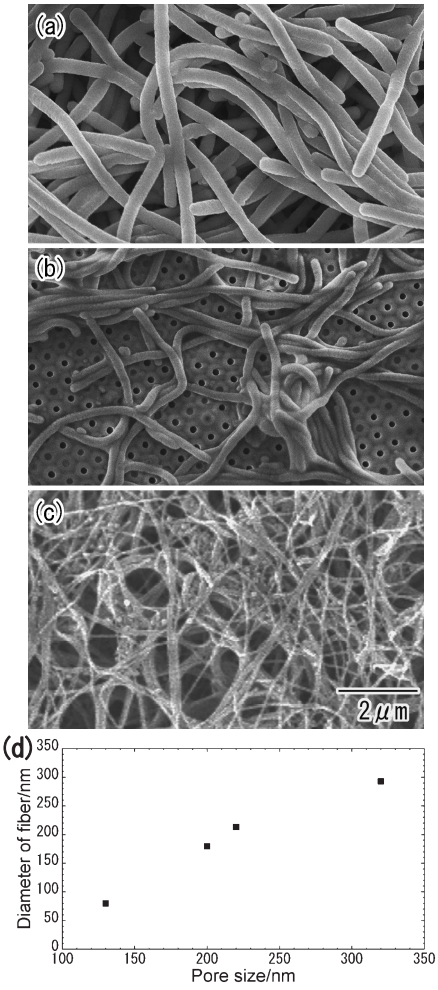

Figure 4. (a)–(c) SEM images of polymer fibers prepared using anodic porous alumina membrane with different pore sizes. (d) Relationship between diameter of fibers and the pore size of anodic porous alumina membrane.

Figure 3 shows the size distribution of the obtained fibers. The mean diameter and standard deviation were 180 nm and 7.1%, respectively. From this result, it is confirmed that uniform-sized fibers can be obtained by this process. The diameter of the fibers was smaller than the pore size of the porous alumina membrane. This is because of the decrease in the volume of fibers with the evaporation of toluene.

Figure 4 shows SEM images and the mean diameter of the fibers formed by extrusive spinning using porous alumina membranes with different pore sizes. The pore size of each alumina membrane was varied from 130 to 320 nm. From the SEM image in Figure 4a, it is confirmed that uniform-sized fibers were formed in all cases. The diameter of the obtained fibers showed a good linear relationship with the pore size of the porous alumina membrane (Figure 4d). This result indicates that uniform-sized fibers with desired diameters can be obtained by changing the pore sizes of the anodic porous alumina membrane used for extrusive spinning.

Uniform-sized nanofibers were obtained by the extrusive spinning of a photocurable monomer under UV irradiation using anodic porous alumina as a spinning nozzle. The size of the obtained fibers could be controlled by changing the pore size of the porous alumina membranes. The rate of fiber formation was dependent on the intensity of UV light, and the photocurable monomer could be polymerized rapidly, when the UV source with enough intensity could be available. By improving the extrusive system, the continuous formation of long fibers is expected to be achieved. The present process, which enables the high-throughput formation of uniform-sized nanofibers, is versatile and will be used for the preparation of starting materials for a wide variety of functional devices.

References

1 J. Doshi, D. H. Reneker, *J. Electrostat.* **1995**, *35*, 151.
2 N. J. Pinto, A. T. Johnson, A. G. MacDiarmid, C. H. Mueller, N. Theofylaktos, D. C. Robinson, F. A. Miranda, *Appl. Phys. Lett.* **2003**, *83*, 4244.
3 R. Zhang, Y. Lifshitz, S. Lee, *Adv. Mater.* **2003**, *15*, 635.
4 S. Virji, J. Huang, R. B. Kaner, B. H. Weiller, *Nano Lett.* **2004**, *4*, 491.
5 T. Takahashi, M. Taniguchi, T. Kawai, *Jpn. J. Appl. Phys.* **2005**, *44*, L860.
6 D. H. Reneker, I. Chun, *Nanotechnology* **1996**, *7*, 216.
7 E. Zussman, A. Theron, A. L. Yarin, *Appl. Phys. Lett.* **2003**, *82*, 973.
8 P. Zhu, Y. Hong, B. Liu, G. Zou, *Chem. Lett.* **2009**, *38*, 784.
9 H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.
10 H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, *Appl. Phys. Lett.* **1997**, *71*, 2770.
11 H. Masuda, M. Satoh, *Jpn. J. Appl. Phys.* **1996**, *35*, L126.

