

Note

POROUS MEMBRANE TEMPLATED SYNTHESIS OF POLYMER PILLARED LAYER*

Zhong-wei Niu, Dan Li and Zhen-zhong Yang**

State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

Abstract The anodic porous alumina membranes with a definite pore diameter and aspect ratio were used as templates to synthesize polymer pillared layer structures. The pillared polymer was produced in the template membrane pores, and the layer on the template surfaces. Rigid cured epoxy resin, polystyrene and soft hydrogel were chosen to confirm the methodology. The pillars were in the form of either tubes or fibers, which were controlled by the alumina membrane pore surface wettability. The structural features were confirmed by scanning electron microscopy results.

Keywords Anodic porous alumina membranes, Template synthesis, Pillared layer, Polymers

INTRODUCTION

One-dimensional nanostructured materials including nanowires and nanotubes are of fundamental and technological significance. They have a variety of potential applications in chemistry, physics, electronics, optics, materials science, and biomedical science. These materials can be easily synthesized in porous media such as anodic porous alumina membranes and track-etched polymer nuclepores. Porous alumina membranes possess uniform and straight cylindrical pores with controlled diameter and aspect ratio, and they have been extensively used as templates to prepare uniformly sized metal nanowires, polymer nanorods and nanotubes^[1–3], oxide nanorods^[4], and composite nanostructure^[5]. Recently, binary hydrogel nanowires of invertible core/shell phases have been prepared in porous alumina membranes, in a process controlled by the pore surface wettability^[6]. However, most current reports focus on either individual one dimensional rods and tubes or their ordered arrays in the membranes.

In this paper, we are mainly concerned with polymer ordered arrays supported on thin layers, which have what is defined as pillared layer structure. The thin layers result from the remaining polymer film on the membrane surfaces. Some representative materials such as polycondensed epoxy resin, polystyrene and hydrogel by free radical polymerization are prepared in the form of either tubes or fibers.

EXPERIMENTAL

Sample Preparation

Typical modification procedure of anodisc 47

The alumina membranes Anodic 47 with a pore diameter 200 nm and length 60 μm were purchased from Whatman International Ltd. The pore surface was hydrophobically modified by a silanization process^[6]. The membranes were heated in air to 400°C at a heating rate of 10 K/min followed by a natural air-cooling to room

* This work was supported by the National Natural Science Foundation of China (No. 20023003 and 20128004).

** Corresponding author: Zhen-zhong Yang (杨振忠), E-mail: yangzz@infoc3.icas.ac.cn

Received September 4, 2002; Revised November 27, 2002; Accepted December 2, 2002

temperature. After the thermally treated membranes were soaked in boiling aqueous hydrogen peroxide (30%) for 30 min, they were boiled in a large amount of distilled water for 30 min to hydroxylate the pore surface. The dried membranes were re-immersed in a solution of 10% octachlorosilane in toluene, allowing a complete impregnation of octachlorosilane. Finally, the membranes were subjected to reflux at room temperature for 3 h under reduced pressure.

Preparation of epoxy resin by polycondensation

The alumina template membranes including the unmodified and modified ones were immersed in a mixture of epoxy resin (bisphenol A-618) and curing agent (H020) (10/3 wt/wt) at ambient temperature for 5 h for the infiltration of the mixture into the pores. The curing process occurred at 80 °C for 2 h.

Free radical polymerization of polystyrene and hydrogel

After the alumina membranes were immersed in styrene containing 0.1 wt% initiator AIBN for 5 h, the system was polymerized at 60 °C for 12 h. The alumina membranes were immersed in an aqueous solution of the monomer mixture consisting of acrylamide/ammonium acrylic (3:7 wt/wt) containing 5 wt% crosslinking agent *N,N'*-methylenebisacrylamide and 0.1 wt% initiator ammonium peroxydisulfate. The monomer content was 50 wt%. The polymerization was undertaken at 50 °C for 2 h to form hydrogels. The pillars were formed in the pores after removal of the alumina with 10 wt% NaOH aqueous solution follows by a wash with a large amount of water and ethanol. When the thin polymer layers on the membranes were preserved, thin layers resulted supporting the pillars.

Characterization

After the polymer materials were dried at room temperature, the pillared layer structures were vacuum sputtered with Au and observed under a JEOL 6700F field emission scanning electron microscope (SEM) at a voltage of 3 kV.

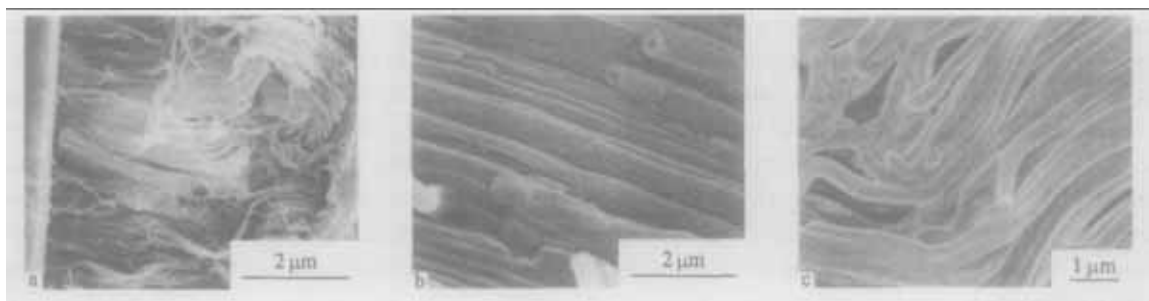


Fig. 1 Scanning electron micrographs of crosslinked epoxy resin samples

a) bi-layer supported pillar structure prepared using unmodified porous alumina membrane; b) magnified image of Fig. 1(a); c) fibers prepared in the hydrophobically modified porous alumina membrane

RESULTS AND DISCUSSION

After polycondensation of epoxy resin in the unmodified membrane, an epoxy resin/alumina composite was prepared. The bulk polymer was peeled off the alumina in a controlled fashion leaving two thin layers on both sides of the alumina membrane. After the removal of the alumina, pillared epoxy resin between two layers was obtained. A SEM image of the sample fracture is shown in Fig. 1(a). A magnified SEM image as shown in Fig. 1(b) revealed that the epoxy resin pillars were in the form of tubes. The tubes were easily deformed after the removal of the alumina membrane as shown in Fig. 1(a), which might be due to the elastic de-stabilization of the very long tubes. The regular pillar array might be useful as a chromatographic phase for the purification and separation of macromolecules^[7]. The formation of the tubes was explained by a rapid preferential wetting of the alumina pore surface by the monomer mixture^[5]. As shown in Fig. 1(c), when the porous alumina membrane was hydrophobically modified with octatrichlorosilane forming the hydrophobic group (Al—O—Si—C₈H₁₇) on the

pore surface, the obtained epoxy resin pillars were in the form of fiber.

Besides polycondensation, a free radical polymerization of styrene in the unmodified alumina membranes can also result in the pillared layer structure. When the polymer layer was removed from one side of the membrane, a mono-layer supported polymer pillar structure was obtained like a brush as shown in Fig. 2(a). The layer thickness was controlled by controlling the residual polymer amount on the membrane surface. As shown in Fig. 2(b), when another thinner polymer layer was left on the other side of the alumina membrane, an asymmetric pillared bilayer structure was formed as shown in Fig. 2(b). When two alumina membranes were separated with a pellet separator, multiple pillared layer structure was prepared as shown in Fig. 2(c). The middle layer thickness was controlled by the separator thickness. A magnified image (Fig. 2d) indicates that the pillars were in the form of fiber rather than tube.

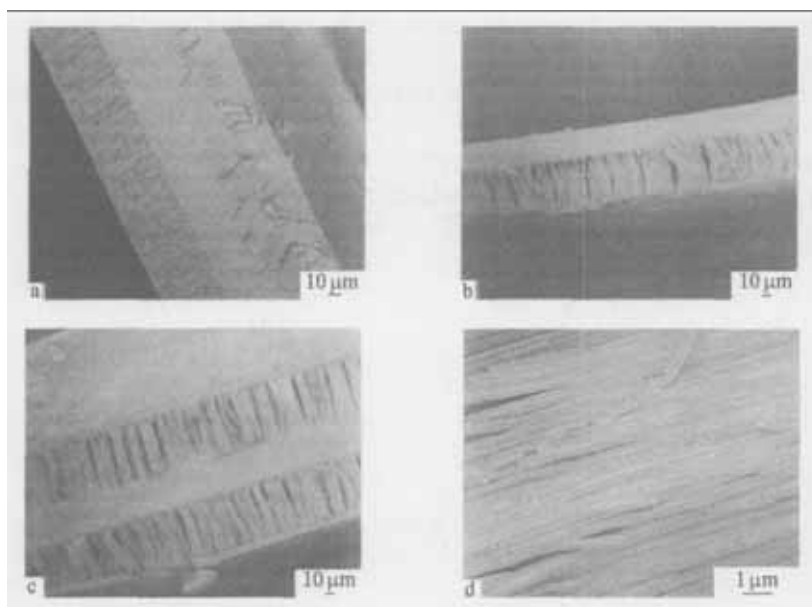


Fig. 2 Scanning electron micrographs of polystyrene samples prepared in the unmodified porous membrane

a) mono-layer supported pillar structure; b) bi-layer supported pillar asymmetric structure; c) tri-layer supported bi-pillar structure; d) magnified image of the fibers in Fig. 2(a)

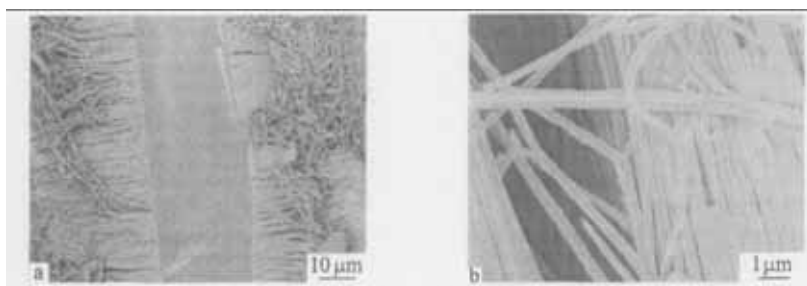


Fig. 3 Scanning electron micrographs of poly(acrylamide/ammonium acrylic) gel samples prepared in the unmodified porous membrane

a) mono-layer supported bi-pillar structure; b) magnified image of the fibers shown in Fig. 3(a)

Besides rigid polymers such as cured epoxy resin and polystyrene, poly(acrylamide/ammonium acrylic) hydrogel fibers were also prepared in the unmodified porous membrane. When the middle polymer layer was left

with the other layers removed from the surfaces, mono-layer supported two pillar structure was obtained as shown in Fig. 3(a). The fibers were easily twisted as shown in Fig. 3(a). In the magnified image Fig. 3(b), the pillars were uniform and in the form of fibers.

REFERENCES

- 1 Hulteen, J. C. and Martin, C. R., *J. Mater. Chem.*, 1997, 7: 1075
- 2 Huczko, *Appl. Phys. A*, 2000, 20: 365
- 3 Limmer, S. J., Seraji, S., Wu, Y., Chou, T. P., Nguyen, C. and Cao, G., *Adv. Funct. Mater.*, 2002, 12: 59
- 4 Cepak, V. M., Hulteen, J. C., Che, G., Jirage, K. B., Lakshmi, B. B., Fisher, E. R. and Martin, C. R., *J. Mater. Res.*, 1998, 13: 3070
- 5 Steinhart, M., Wendorff, J. H., Greiner, A., Wehrspohn, R. B., Nielsch, K., Schilling, J., Choi, J. and Gosele, U., *Science*, 2002, 296: 1997
- 6 Yang, Z.Z. and Niu, Z.W., *Chem. Comm.*, 2002, 17: 1972
- 7 Nykypanchuk, D., Strey, H. H. and Hoagland, D. A., *Science*, 2002, 297: 987