Template Synthesis and Self-Assembly of Nanoscopic Polymer "Pencils"

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Anodized aluminum (aluminum oxide) membranes have nearly circular pores (impinging polygons) that are perpendicular to the macroscopic membrane surface. These materials have been used as templates for the preparation of nanoscopic rods with high aspect ratios.[1−3] These reports concern the preparation of rods in membrane pores consisting of metals or conducting polymers using electrochemical deposition. In these cases, the rod length can be controlled easily by controlling the current applied. We are interested in preparing rods consisting of organic polymers that cannot be electrochemically deposited and also interested in controlling the rod length, diameter, and surface chemistry of both rod ends and sides. These membranes have not been reported as templates for polymeric rods that cannot be electrochemically deposited, although a recent publication reported the use of these membranes to prepare nanotube arrays composed of polymers.[4]

We report here a simple method using commercial membranes for the preparation, functionalization, and self-assembly of rods that we term "pencils" to differentiate ends. Figure 1 summarizes the method. A glass-supported polystyrene[5] film was heated to 200 °C on a hot plate, and a commercial alumina membrane[6] (200 nm pore size) was placed on top of the liquid polymer and maintained at 200 °C for various lengths of time. Polystyrene enters the pores of the membrane due to capillary forces. After the desired length of time, the hot plate was allowed to slowly cool to room temperature, and then the polystyrene film/alumina membrane composite was removed from the glass slide by soaking the assembly in water. The alumina membrane was dissolved in sodium hydroxide solution.[7] Figure 2 shows SEM micrographs[8] of the pencils attached to the bulk polystyrene film for samples heated at 200 °C for 5, 10, 15, and 20 min. This crude temperature/time control allowed considerable control of pencil length with lengths of 0.6, 0.9, 1.2, and 1.6 μm for 5, 10, 15, and 20 min of heating, respectively. Also apparent in Figure 2 is that the pencils are uniform in length, not uniform in diameter (ranging from ∼0.15 to 0.3 μm; the specified diameter of the membrane pores is 0.2 μm), and contain defects. The commercial membrane was prepared for separation purposes and was not designed to control pore uniformity. This type of control is possible using controlled anodization and pretexturization techniques.[9,10] We have made similar structures using polyethylene, polypropylene, bisphenol A polycarbonate, nylon-6,6, and a block copolymer of styrene and methyl methacrylate, so this simple process appears general for thermoplastics. We report only results with polystyrene here.

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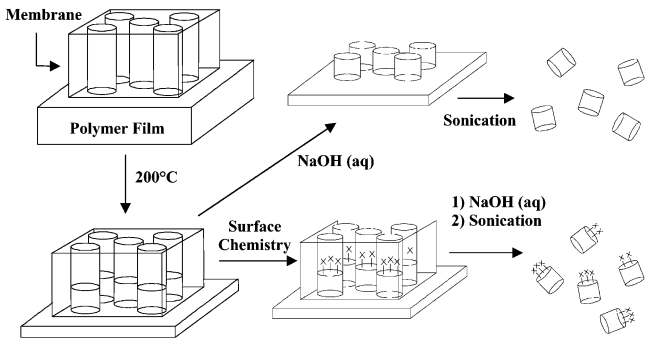

Figure 1. Scheme for preparing polymer pencils both with and without end-functionalization.

We have tried several techniques to remove the pencils from the bulk supporting film. Dissolving the bulk polystyrene by placing the polymer/membrane composite (the membrane is not dissolved at this point) at a water−organic solvent interface is promising, but removing the membrane at the point in time that the bulk film has dissolved and the pencils have not has been irreproducible. This is a technique that we are following up on because we want to prepare pencils with functionality at both ends. Ultrasonication in ethanol for 2−5 min has proven to be reproducible, but it allows us chemical access to only one end of the pencils. Figure 3 shows SEM micrographs of polystyrene pencils that were removed by ultrasonication and isolated by filtration on a polycarbonate nucleopore membrane. The pencils were prepared by heating for 5 and 20 min. The uniformity in length and the consistency in length with the micrographs in Figure 2 suggest that the pencils are cleaved by ultrasound near their base. An SEM of a polystyrene film sample taken after ultrasonication (a 20 min heated sample; not shown) confirms this: patches of intact pencils are still present, but the majority of the area consists of small "tree stumps", close to level with the film surface.

As stated above, we are interested in chemical functionalization of these pencils to permit specific interactions between pencils (of same or different type) that promote self-assembly. Such self-assembly, particularly using capillary forces between hydrophobic surfaces in hydrophilic media, has been investigated;[11,12] however, the size of individual assembly elements is usually in the multimicron range because it is difficult to make smaller structures with a surface available for such a treatment.[12] The exposed ends of the polystyrene pencils were modified at the polystyrene/membrane composite stage through the pores of the membrane (Figure 1) using two literature methods for polystyrene modification that are reported to prepare hydrophilic surfaces. Pencil ends were sulfonated[13] using concentrated sulfuric acid and were oxidized[14] using acidic potassium permanganate. X-ray photoelectron spectroscopy[15] revealed the presence of sulfur, oxygen, and sodium for the sulfonated pencils and oxygen for the oxidized pencils. After the modification reactions, the membranes were dissolved and the pencils were isolated using the same techniques used for unmodified pencils.

We have used various strategies to study the self-assembly of these hydrophilic-tipped hydrophobic pen-

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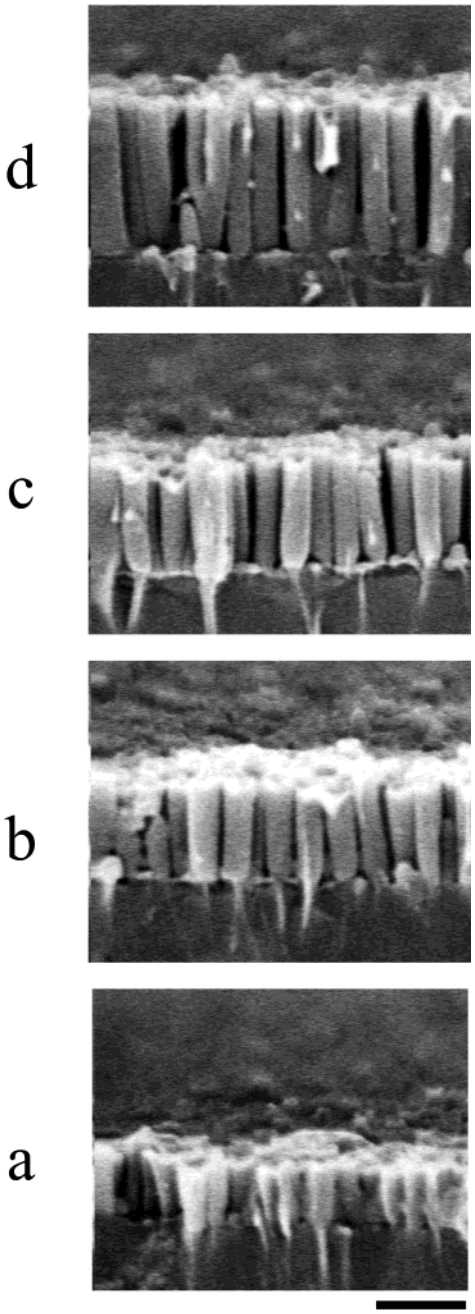

Figure 2. SEM micrographs of polystyrene pencils attached to a polystyrene film after the alumina membrane was dissolved. Time of heating at 200 °C: (a) 5, (b) 10, (c) 15, and (d) 20 min. The bar in the figure corresponds to 1 μm.

cils at interfaces, and two are described here. A small amount of a water-insoluble photocurable adhesive[16] was added to an ethanol dispersion of either sulfonated or oxidized pencils that was prepared from a single 13 mm diameter membrane. The dispersion was then concentrated from 10 to 1 mL. 10 mL of water was added, and a 1.5 × 1.5 mm silicon wafer was placed in the bottom of the vial. The pencils self-assembled at the air−water or air-adhesive interface as the ethanol/water mixture was allowed to evaporate. These experiments were performed using ~25 mm diameter vials so there were fewer than enough pencils to form a "close-packed monolayer" over the cross-sectional area of the vial. (The original membranes were 13 mm in diameter.) After complete evaporation, the silicon wafer was isolated and exposed to UV light.[17] An SEM micrograph of the

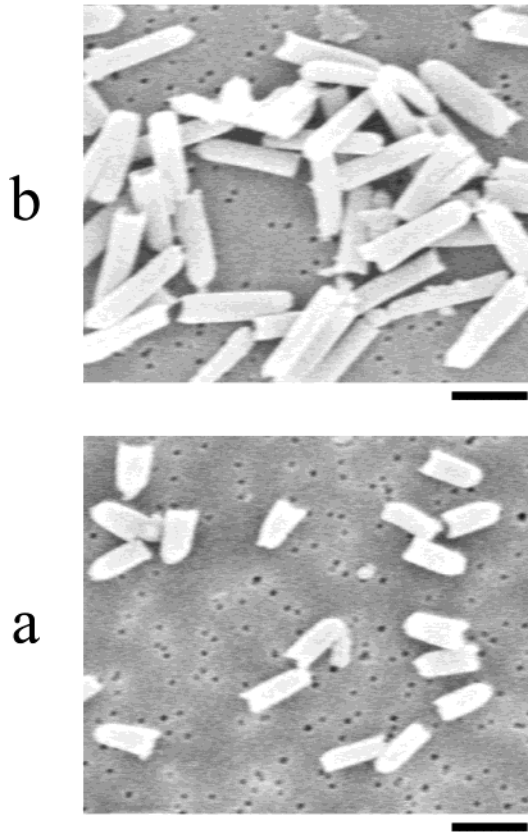

Figure 3. SEM micrographs of polystyrene pencils after removal by ultrasonification in ethanol and isolation on a polycarbonate nucleopore membrane. Time of heating at 200 °C: (a) 5 and (b) 20 min. The bars in the figure correspond to 1 μm.

silicon-supported self-assembled structure of sulfonated pencils is shown in Figure 4a. The micrograph indicates a larger polydispersity in pencil diameter than is suggested from Figures 2 and 3. We believe that this is an artifact of the commercial membrane structure ("pinched off" ends of pores) and that the midsections of the pencils are more uniform in diameter. We have no other proof than the relative area argument made above that these pencils are a monolayer, but we believe that these pencils act as particulate surfactants with their polar tips at the water/adhesive interface and their hydrophobic bodies in the adhesive or air. Oxidized polystyrene pencils behave identically.

A second approach to self-assembly involves evaporating small droplets of ethanol/water/adhesive dispersions of pencils on functionalized silicon wafers. Droplets were placed on trimethylsilyl-modified wafers[18] and allowed to evaporate. The droplets receded, depositing nothing until a critical water/ethanol ratio was reached. After this, pencils deposited at the three-phase receding contact line, and a "coffee ring" was formed. The adhesive was then cured with UV exposure. Figure 4b shows a SEM micrograph of the oxidized self-assembled pencils. The pencils lie parallel with the surface in a smectic morphology. We have not carried out experiments to determine the number of layers of pencils in these structures or the pencil concentration effect on structure but plan to do so. The smectic structures are telling of the uniform length of these pencils. Sulfonated polystyrene pencils behave identically. We do not know the role of the functionalized ends in forming these assemblies, but structured assemblies do not form using

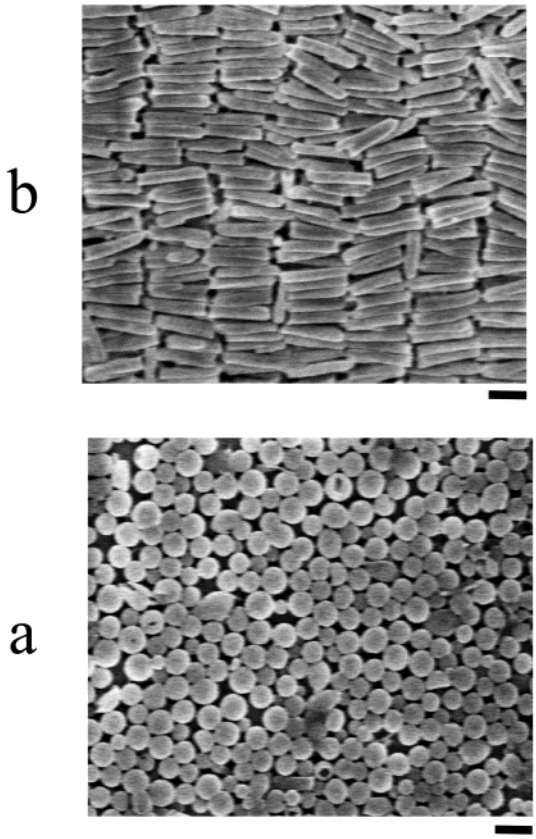

Figure 4. (a) SEM micrograph of silicon-supported sulfonated polystyrene pencils after self-assembly at the water−air/adhesive interface and UV exposure. (b) SEM micrograph of trimethylsilylated silicon-supported oxidized polystyrene pencils after self-assembly at the three-phase contact line of an evaporating (receding) droplet and UV exposure. The bars in the figure correspond to 1 μm.

unfunctionalized pencils or with functionalized pencils on hydrophilic surfaces.

We have future plans in addition to those described above. We want to prepare more uniform and hexagonally shaped pencils by preparing our own membranes to achieve long-range order. We want to probe the effect of membrane pore diameter on this process to learn what range of pencil diameters we can prepare. We want to study block copolymer morphology when samples are confined to pencil-shaped structures.

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Supporting Information Available: Details of the pencil fabrication technique. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(5) Polystyrene (Aldrich, M_w = 280 000) films were prepared on glass microscope slides by coating a toluene solution with an application blade. The dry film thickness was ~50 μm.
(6) The anodized aluminum membranes were Whatman Anodisc™ membrane filters with pore size of 0.2 μm and 13 mm diameter.
(7) Alumina membranes were dissolved using a 5 wt % sodium hydroxide solution in water/methanol (8:2) at room temperature for 12 h.
(8) Scanning electron micrographs are secondary electron images of gold-coated samples obtained using a JEOL JSM 6320F microscope.
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(15) X-ray photoelectron spectra were recorded with a Perkin-Elmer-Physical Electronics 5100 with Mg Kα excitation (400 W). Spectra were obtained at a 15° takeoff angle (between the plane of the surface and the entrance lens of the detector optics).
(16) The hydrophobic photocurable adhesive was a mixture of dodecyl methacrylate, 1,6-hexanediol diacrylate, and benzoin isobutyl ether (96:2:2 wt %). Approximately 0.02 μL was used.
(17) A UVP B100A UV lamp (365 nm) was used for 30 min.
(18) Silicon wafers were treated with trimethylsilyl chloride in the vapor phase at 70 °C for 24 h.

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