Controlling the Length of Conical Pores Etched in Ion-Tracked Poly(ethylene terephthalate) Membranes

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An etching procedure that allows for reproducible control of the length of conically shaped pores etched into poly(ethylene terephthalate) (PET) membranes is developed. At the lower etch temperature used (20 °C), the length of the pore is found to be linearly related to etch time. At the higher etch temperature (30 °C) the etch rate is five times faster and the pores quickly propagate through the entire thickness of the PET membrane. Hence, the lower etch temperature is best for controlling the pore length. Pores etched at this temperature are used to prepare arrays of gold cones where the length of the cones is controlled from 1 to 10 \( \mu \text{m} \). The track-etch rates and the radial-etch rates at both of the etch temperatures used are also reported.

1. Introduction

We have pioneered a general method for preparing nanomaterials called template synthesis.[1–7] This method entails using the pores in a porous membrane or other solid as templates to prepare the nanomaterials. In most cases the pores are cylindrical and correspondingly cylindrical nanowires and nanotubes are obtained. More recently, we have been interested in using the template method to prepare arrays of conically shaped micro- and nanostructures.[8–10] This is accomplished by using polymeric templates with correspondingly conically shaped pores.

A number of applications have been proposed for arrays of conically shaped micro- and nanostructures including use in field-emission devices,[11] dye-sensitized solar cells,[12] and electrochemical supercapacitors.[13] We are, however, investigating the possibility of using arrays of conical structures as microneedles for drug delivery and gene transfection. This follows earlier work on using arrays of cylindrical structures for such applications.[14–20] Arrays of conically shaped microneedles might be advantageous because cones would have a greater mechanical strength relative to a cylindrical structure and yet still retain a fine tip.

In order to exploit the full advantage of conically shaped structures for delivery applications, a method for controlling the length of the cones/needles in the array is needed. In all of the prior work on template-synthesized cones, the cone length was equivalent to the thickness of the polymeric template membrane used, typically on the order of 10 \( \mu \text{m} \). One way to make shorter cones would be to obtain thinner template membranes with conical pores, but such membranes are currently unavailable. Furthermore, membranes with thickness less than about 5 \( \mu \text{m} \) would become too fragile to handle, precluding their use in template synthesis. Another approach for making shorter cones would be to do electrochemical deposition within a conically shaped pore, but this would greatly limit the range of materials from which the cones could be prepared. This is because only a limited number of materials, primarily metals, can be electroplated.

An alternative approach for controlling cone length would be to control the distance the conically shaped pore propagates into the template membrane. This has been accomplished for cylindrical pores prepared by the well-known track-etch method[21] by controlling the etch time.[22] However, this has not been accomplished for conically shaped pores. We have recently discovered that by careful control of the pore-etching process, the distance that conically shaped pores propagate into polymeric templates can be controlled at will. This has allowed us to use these conical pores as templates to prepare arrays of gold cones with lengths ranging from 1 to 10 \( \mu \text{m} \). Here, we
describe this new pore-etching procedure and the gold cones prepared in the pores.

2. Results and Discussion

2.1. Effect of Etch Time and Temperature on Cone Length and Base Diameter

Scheme 1A shows a schematic of a single damage track in a poly(ethylene terephthalate) (PET) template membrane before etching. In this depiction, the face labeled “base side” (down in the scheme) is the face in contact with the etch solution. The face labeled “tip side” (up in the scheme) is the face in contact with the stopping solution. Also shown in Scheme 1A is the initial template membrane thickness, which is labeled as \( d_0 \). Scheme 1B represents a membrane etched for a short time to yield a conically shaped pore where the pore length, \( l_1 \), is much smaller than the membrane thickness. In addition, since the etch time is short, the base diameter, \( D_1 \), is also correspondingly small. This may be contrasted to Scheme 1C, which corresponds to a longer etch time. Now the length of the conical pore, \( l_2 \), approaches the thickness of the membrane, \( d_2 \). The base diameter of the pore, \( D_2 \), is also correspondingly bigger. Scheme 1D depicts the situation at the higher etch temperature (30 °C) and the longest etch times. Because the etch rate increases with temperature\(^\text{(23)}\), the etch solution has now penetrated all the way through the thickness of the membrane and broken through to the stopping solution on the other side. In this case, the length of the cone is equivalent to the thickness of the membrane. It is important to point out that etching also thins the membrane. This is shown in Scheme 1, where \( d_0 > d_1 > d_2 > d_3 \).

Representative field-emission scanning electron microscopy (FESEM) images of the gold cones prepared in this study are shown in Figure 1. In these images, etch time increases from A to E. In each case, the left images are from membranes etched at 20 °C, and the right images are from membranes etched for the corresponding times at 30 °C. The lengths of the cones obtained from such images are plotted against the etch time in Figure 2. For the 20 °C etch, the cone length increases linearly with etch time (correlation coefficient of 0.992) over the entire range of etch times used. The slope of this plot provides the rate of etching along the damage track, the track-etch rate.\(^\text{(24)}\) A value of \(21.2 \pm 0.4\) nm s\(^{-1}\) was obtained. As noted in the introduction, the primary objective of this research effort is to show that cone length can be controlled. These data show that this has been successfully achieved.

At 30 °C, the cone length initially increases with etch time but then decreases at longer etch times. This occurs because the etch rate is higher at the higher temperature\(^\text{(23)}\) and as a result, the pores quickly (<150 s) break through the entire thickness of the membrane. Once the pores have broken through the membrane, the gold cone length now becomes equivalent to the membrane thickness. The decrease in length at longer etch times reflects membrane thinning (Scheme 1D). The effect of thinning can also be seen by comparing the cone lengths at 500 s. The cones etched at 20 °C are larger because the membrane has...
not been thinned as much as the membrane etched for 500 s at the higher temperature.

The effect of the pore breakthrough can also be seen by comparing the sharpness of the cone tips. Before breakthrough, the pores have a truly conical shape with very sharp tips. All of the cones from pores etched at the lower temperature have such sharp tips because breakthrough was not achieved. When the higher etch temperature is used, such sharp-tipped cones are only observed at the two shortest etch times where, again, breakthrough has not yet been achieved. In contrast, at longer etch times at 30°C, where breakthrough has been achieved, the cone tip reflects the diameter of the pore’s tip opening. Since the tip opening increases with etch time, blunter-tipped cones are obtained at longer etch times (Figure 1E, inset).

The base diameters of the cones were also obtained from the FESEM images, and plots of base diameter versus etch time are shown in Figure 3. At the lower etch temperature, the base diameter increases linearly (correlation coefficient of 0.993) with etch time throughout the 500 s time window. The slope of this line provides a radial etch rate. A value of 4.7 ± 0.1 nm s⁻¹ was obtained. As per prior etching studies, the radial etch rate is significantly lower than the track-etch rate.

At the higher etch temperature, the base diameter initially increases linearly (correlation coefficient of 0.991) with etch time, and a radial etch rate of 15.6 ± 0.3 nm s⁻¹ was obtained from the slope. However, the diameter obtained for the longest etch time falls well below the extrapolation of the short time plots (Figure 3). This, again, is a reflection of the enhanced rate of membrane thinning observed at the higher etch temperature. Since thinning occurs from the base side, the consequence of membrane thinning is to etch away the widest part of the pore. As a result, the thinned membrane has a smaller base diameter than what would be observed if no thinning had occurred.

It is also of interest to compare the relative slope values in Figures 2 and 3. As has been discussed above, the slopes in Figure 3 reflect the radial etch rates, and we find that the radial etch rate at 30°C is three times faster than the rate at 20°C. In contrast, the plots of cone length versus etch time in Figure 2 reflect the track-etch rate. It is harder to compare slopes in Figure 2 because at the higher temperature the plot is nonlinear. However, if we estimate the slope from the short time data, we find that the track-etch rate at 30°C is five times faster than the rate at 20°C. This observation — that the track-etch rate shows a higher temperature dependence than the radial etch rate — is in agreement with data obtained by Oleinikov et al. for cylindrical pores using a different etch solution.

### 2.2. Effect of Etch Time and Temperature on Cone and Pore Surface Roughness

Close inspection of the cones in Figure 1 show that at both etch temperatures cone surface roughness increases with etch time. This roughening effect is, however, much more pronounced at the higher etch temperature (compare images in Figure 1E). To understand the cause of this cone-surface roughening, we obtained images of the base openings of pores in membranes etched at 30°C (Figure 4). In agreement with the FESEM images of the cones obtained in such pores, the pore...
walls clearly become rougher with increasing etch time. Hence, the cone surface is simply reflecting the pore-wall surface.

Atomic force microscope (AFM) measurements on the membrane surface were used to obtain a more quantitative measure of how surface roughness increases with etch time. Non-tracked PET membranes etched at 30 °C were used for these studies. Before etching, the root-mean-square (RMS) roughness of the surface was 9 ± 2 nm and there is little deviation in the height profile across the AFM image (Figure 5A). After 250 s of etching, the surface roughness increased to 24 ± 2 nm and evidence of pitting on the surface is clearly seen in the AFM image (Figure 5B). One such pit is outlined with a white circle in the AFM image. After 500 s of etching, the surface roughness increased to 40 ± 4 nm and more extensive pitting is seen (Figure 5C).

Komaki et al. have also discussed surface roughness in etched PET membranes.[26] They point out that PET is a partially crystalline polymer and suggest that surface roughness results because the crystalline and amorphous domains etch at different rates. Lüeck investigated this amorphous-versus-crystalline etch-rate phenomenon and concluded that the amorphous domains etch at a faster rate than the crystalline domains.[25] We suggest that roughness increases with etch time (Figure 5) because longer etch times allow for deeper etching into the amorphous regions, relative to the slower-etching crystalline regions. As a result, enhanced pitting is observed at long etch times.

2.3. The Effect of Biaxial Stretching on PET Etching

Figure 6A shows a lower magnification image of cones etched at 30 °C for the longest etch time. Highlighted in this image are cones with large circular and flat projections protruding from the sides of the cones. Figure 6B shows a higher magnification image of cones with such projections. Much smaller projections of this type are occasionally observed for membranes etched at shorter times (Figure 1A).

The PET membranes used here were biaxially stretched by the supplier to improve mechanical strength. It is well-known that such biaxial-oriented PET membranes are laminar.[27–29] We suggest that the planar projections observed at long etch times result because the etch solution is able to penetrate deeper into the polymer along the interfaces between the strata. Evidence for this preferential etching along the strata can also be obtained from base-side surface images of membranes etched for long times (Figure 7). These images show scalloping around the pore bases (highlighted in Figure 7), again a consequence of etch-solution penetration along the interfaces between strata.

3. Conclusions

We have developed an etching procedure that allows for reproducible control of the length of conically shaped pores etched into PET membranes. At the lower etch temperature
used (20 °C), the length of the pore was found to be linearly related to etch time (Figure 2). At the higher etch temperature (30 °C) the etch rate is five times faster and the pores quickly propagate through the entire thickness of PET membrane. Hence, the lower etch temperature is best for controlling pore length. We have used pores etched at this temperature to prepare arrays of gold cones where the length of the cones was controlled from 1 to 10 μm. We are currently using such cones as microneedle arrays for delivering genes to algae cells.

We report here the track-etch rates and the radial etch rates at both of the etch temperatures used. We have also found that membrane roughness increases with etch time and etch temperature. This causes the gold cones deposited in pores etched at long times and high temperatures to have very rough surfaces (Figure 1E). Surface roughness was explored quantitatively using AFM.

We also discovered an interesting etching phenomenon that results from the lamellar morphology of the PET membranes used here. Preferential penetration of the etch solution between the PET strata cause planar projections to form on the gold cones. These projections can be quite large for cones deposited in pores etched for long times at the higher temperature (Figure 6).

4. Experimental Section

Materials: Ion-tracked PET membranes (12-μm thick, 10⁶ tracks cm⁻²) were obtained from GSI, Darmstadt, Germany. Membranes that were not tracked were also obtained from GSI. The PET membrane (Hostaphan RN, biaxial stretched) was purchased by GSI from Hoechst. Purified water was obtained by passing house-distilled water through a Barnstead E-pure model D4641 water purification system. All other chemicals were of reagent grade and used as received.

Pore etching: Conically shaped pores were etched into the tracked PET membrane using a method similar to that described by Apel et al.[21] The general strategy is to place the tracked membrane between a solution that etches the track and a solution that neutralizes the etchant. Pore etching begins at the face of the membrane in contact with the etch solution and the large-diameter openings (bases) of the conical pores are present at this face of the membrane. In all prior work on etching conically shaped pores[8–10,21,30] etching was continued until the etchant propagated through the entire thickness of the membrane and broke through to the stop solution at the opposite face of the membrane. The small-diameter openings (tips) of the conical pores are present at this face of the membrane. The key difference in the new etching procedure described here is that etching is stopped before the etchant breaks through to the stop solution on the opposite side of the membrane (Scheme 1). In this way, conically shaped pores that do not propagate through the entire thickness of the membrane are obtained. As shown in Figure 2, the distance that the etchant propagates through the membrane (the length of the conically shaped pore) can be controlled by varying the etch time and temperature. Prior to etching, the PET membrane was exposed to UV radiation (254 nm) for 1 h on each side.[9] The membrane was then sandwiched between the two halves of the Kel-F plastic cell described previously.[30] One of the half cells was filled with ~3.5 mL of 5 M KOH in absolute methanol, the etch solution. The other half cell was filled with the same volume of aqueous 1 M KCl and 1 M HCOOH, the stopping solution. Membranes were etched either at room temperature (20 ± 1 °C) or at 30 ± 1 °C for durations between 50 and 500 s. For the 30 °C etching, the etch and stopping solutions were preheated in a water bath (Isotemp 3016H, Fisher Scientific) and the cell was also preheated using a hotplate (Isotemp stirring hotplate, Fisher Scientific). The preheated etch and stopping solutions were then added to the preheated cell and a temperature probe was inserted into the etch solution. The probe was continuously monitored by the hotplate to maintain the etch solution temperature at 30 ± 1 °C. After the desired etch time, the etch solution was replaced with the stopping solution. The membrane was exposed to the stopping solution on both sides for 10 min[9] and then rinsed with water and stored in water until the subsequent gold-plating step.

Electroless deposition of gold cones within the pores: Gold cones were deposited in the conically shaped pores using an electroless plating method described in detail previously.[5,9,31] A plating time of 15 h was used.

Scanning electron microscopy: Electron micrographs were obtained using a Hitachi S-4000 FESEM. FESEM was used to image the conically shaped pores in the PET template as well as the gold cones deposited within these pores. In order to image the gold cones, the PET template had to be removed. This was accomplished, as described previously, by dissolving the PET in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).[9] Image J software from NIH[32] was used to obtain the dimensions of the gold cones. The images used for these measurements had the same focal distance at the tip and at the base of the gold cone. This was done to make sure that the cones were not tilted toward or away from the focal plane.

Atomic force microscopy: AFM was used to investigate the change in surface roughness of the PET membrane with etch time. Non-tracked PET membranes etched as described above at 30 °C were used and the surface exposed to the etch solution was imaged. AFM experiments were performed using a Multimode NanoScope IIIa AFM (Digital Instruments, Santa Barbara, CA). AFM images were obtained in a tapping mode under N₂ gas. The scan rate was kept constant at 0.5 Hz. MPP-11200 Si tips (Veeco, radius r <10 nm) were used.

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