

Testing different polymers and boron nitride nanotube properties in fabrication of ion-selective membranes

Joshua Yi¹, Jerry W. Shan²

¹East Brunswick High School, East Brunswick, New Jersey

²Fluid Hydrodynamics Laboratory, Rutgers University, New Brunswick, New Jersey

SUMMARY

One largely untapped source of clean energy is the use of osmotic gradients where freshwater and saltwater are mixed, for example at estuaries. To harness such energy, charge-selective membranes are needed to separate the anions and cations in saltwater, establishing an electric potential like a battery. The objective of this study was twofold: to investigate the creation of the polymer matrix and test the properties of boron nitride nanotubes, as both are essential in the creation of an ion-selective membrane. The proposed polymer layer has many attractive properties: controllable thickness allowing nanotubes (typically 5-10 microns long) to pass through, being rapidly curable with a UV lamp, easy mounting on other substrates, resistance to O₂ and SF₆ plasma gas etching, and structural strength to prevent tears. The hypotheses for this study are that the Soltech 704 (SU704) will prove to be the best polymer in terms of both etching and curing results, in addition, the relationship between the magnetic dipole moment and the length of the nanotubes is predicted to be linear. The Soltech 704 is trifunctional, compared to the other difunctional polymers tested, which is why it is predicted to have the highest strength. The dipole moment was hypothesized to be linear with nanotube length, since a longer nanotube allows for more iron oxide particles to attach to it. Out of three polymer samples tested in this study, the mixture known as Soltech 704 showed the best resistance to etching, as well as the highest UV cure rate. These two traits are desirable since they lead to a sturdier membrane and one that is created more quickly. To allow such nanotubes to be aligned, we attached magnetic iron oxide particles and then applied a magnetic field. We then recorded the magnetic dipole moments of nanotubes and compared it to the length of the nanotube. The relationship between dipole moment and length can thus be discovered. Such results can be used to optimize the alignment procedure for the nanotubes, as well as the procedure for curing the polymer.

INTRODUCTION

Clean energy has been one of the most pressing issues in recent years. Most of the current energy generating methods rely on non-renewable resources, such as coal, oil, uranium, and natural gas. This is neither sustainable nor environmentally friendly, as many pollutants from combustion are released into the atmosphere (1). Although some other methods are currently being developed to generate energy such as solar or wind power, these sources are expensive, intermittent, and have limited efficiency in their power generation.

An alternative method to fix this issue is to harness the osmotic gradient between freshwater and saltwater in estuaries or the mouths of rivers. This is a better alternative energy source compared to existing sources, as it is cheaper to build than solar or wind farms, more available as facilities can be built at any coastal location with brackish water, and it provides constant non-intermittent power (1). Globally, it is estimated that over one terawatt of this unused energy can be successfully harnessed, roughly equivalent to the power of 1,000 nuclear reactors (1). Although there are many methods to harness such an energy, one of the most efficient methods is known as reverse electro-dialysis (1).

Reverse electro-dialysis works by driving ions across a series of cation- or anion-selective membranes (Figure 1). This diffusion of the ions across a membrane is caused by the large ion concentration gradient between freshwater and saltwater. Unfortunately, if the ions can freely diffuse, no power will be generated since both types of ions will pass across the membrane. However, if the saltwater and freshwater are separated by an ion-selective membrane, then only positive or negative ions will be allowed to flow across. Since only one type of ion is crossing to the freshwater, this will lead to a difference in electric charge and potential across the two reservoirs, as the positive and negative ions become separated (2). This potential energy can then be harnessed with electrodes to create current similar to a battery (2). The membrane created needs to be small and selective enough to only let specific ions through, as if both cations and anions are moved through the membrane, no potential difference will be created (1).

Nanotubes allow for the creation of these ion-selective channels (3). Such nanotubes are hollow cylinders one atom thick, through which ions may pass. The membrane in this study is one with boron-nitride nanotubes as pores,

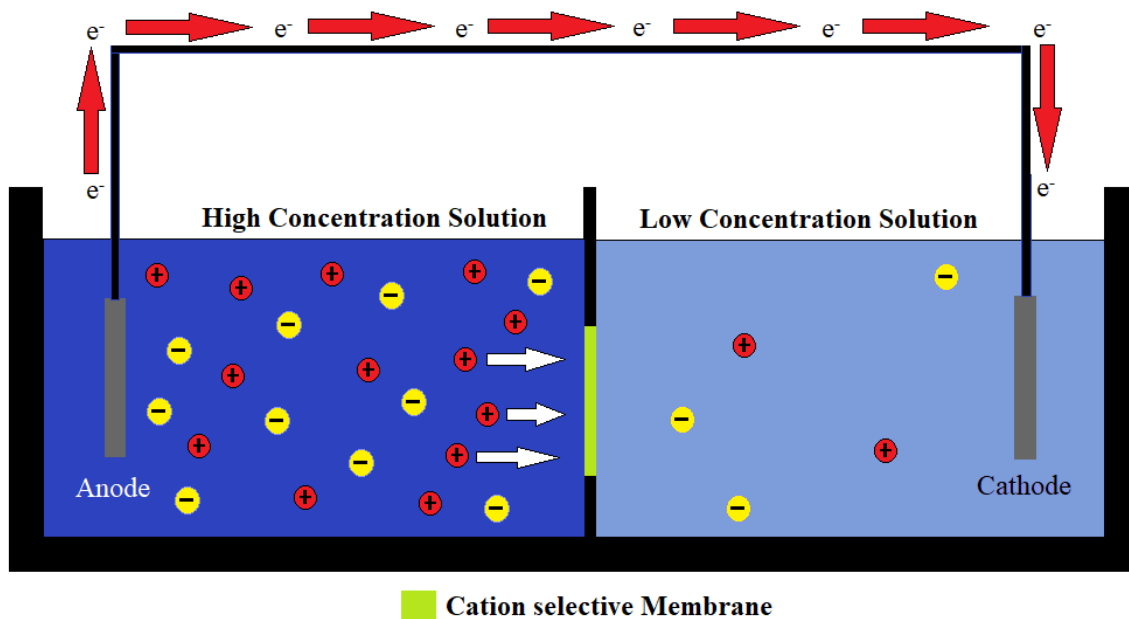


Figure 1. Diagram explaining how power might be generated by such a reverse electro-dialysis, current may be generated via the ion concentration difference between brackish and fresh water. Only one type of ion is allowed to pass, which enables a potential difference to be created.

embedded in a polymer matrix. In such a membrane, the nanotubes will act as open channels for the ions to flow through while they are surrounded by a polymer matrix that provides structural support (1). Boron-nitride nanotubes are used because they have a negatively charged inner surface (4). This negatively charged inner surface not only allows for ion selectivity of positive cations, but also leads to increased flow speed through the membrane as the negative surface attracts positive charges (4). However, there are many problems that need to be addressed to create power-generating membranes, as they are not commercially viable yet and have only produced high power densities at very small scales (measurements of one nanotube) (1). Ultimately, our research found three problems that needed to be solved to produce efficient and economically viable construction of ion-selective membranes. First, the nanotubes need to be aligned to allow them to traverse the entire length of the membrane. Otherwise, the nanotubes would not form an open channel through both ends. Second, the nanotubes must be concentrated to have the membrane with enough pore density to produce an economically viable amount of energy. Finally, agglomerations in the nanotubes must be removed, as this would lead to holes or defects in the membrane.

There are many desirable characteristics associated with the polymer layer of the membrane. First, it must be curable in a reasonable time, as long curing times would make creating the polymer unfeasible for mass production. This was achieved by mixing a photo-initiator into the polymer that would cure when exposed to ultraviolet (UV) light. Second, it must be resistant to plasma etching, as each membrane in our work is etched to remove the caps on the

nanotubes, this is a necessary step to open the nanotubes to be channels, as seen in previous carbon and boron-nitride nanotube studies (5). Third, it must be a thin thickness of around 5-10 microns, as the relatively short nanotubes must pass all the way through the membrane. Finally, it also has to have mechanical strength, as it cannot rip or tear, which would render the membrane useless, as the saltwater and freshwater would simply mix. The first objective of this study was to test for these characteristics.

We aligned and concentrated the nanotubes by attaching iron oxide particles to the nanotubes in suspension, and then applying a strong magnetic field, as has been shown effective in previous studies (6-7). However, the details of this process are not well understood or documented, although such magnetic alignment has been performed in the past, notably on boron nitride platelets (7). The second objective of this study, therefore, was to investigate the relationship between the magnetic field and length of the nanotubes.

We hypothesized that the Soltech 704 (SU704) will prove to be the best polymer in terms of both etching and curing results, out of the three urethane acrylates we tested. In addition, we predicted the relationship between the magnetic dipole moment and the length of the nanotubes to be linear. These hypotheses were based on the fundamental chemistry of the components: Soltech 704 is a tri-functional polymer compared to the di-functional Soltech 710 (SU710), another polymer used in the study, with three attachments to nearby subunits compared to two (8). Trifunctional and difunctional simply refer to the amount of attachments each polymer subunit has to others, which was the only significant difference between the two polymers. This led us to predict

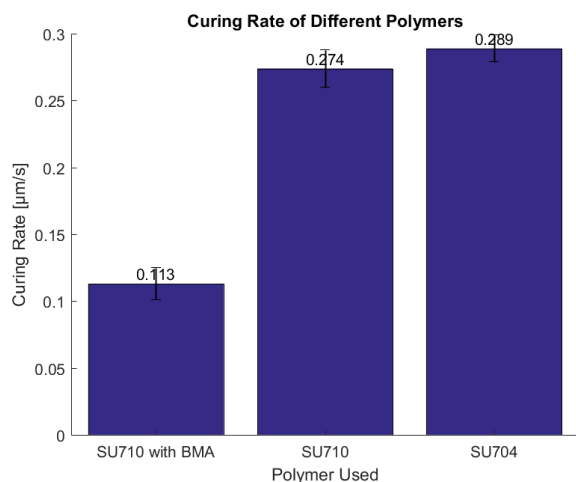


Figure 2. SU704 has the fastest curing rate. Average curing rates ($\mu\text{m/s}$) of SU704, SU710, and SU710 with BMA (10 different samples tested). Error bars represent standard deviation.

that 704 would be stronger and thus more resistant to plasma etching, while curing faster. The relationship with dipole moment and length is predicted to be linear, due to similar effects with carbon nanotube alignment (5), as well as the fact that a longer nanotube leads to a greater amount of iron oxide units attached. The impact of our study will be to create more durable and efficient membranes, which may be more effective at generating power.

RESULTS

The first of our results are the average rates of curing, given in microns per second (**Figure 2**). The curing rates we calculated were an average taken of 10 membranes. The curing rates were found by curing several membranes for fixed amounts of time, then measuring the thickness. In this study, three polymer materials were tested: SU704, SU710, and SU710 mixed with butyl methacrylate (BMA), an additive that allowed the polymer to be more easily mixed, as well as being more resistant to etching. Only these three polymers were used because they have shown strong chemical resistance in previous studies (9).

The curing rates of the pure SU704 and SU710 membranes were almost the same, with that of the SU704 being slightly higher; however, t-test analysis found no statistical difference between the two. Both of these showed a thickness of roughly $17 \mu\text{m}$ after a 60 second cure time, with an average rate of $0.27 \mu\text{m/s}$ for the SU710 and $0.29 \mu\text{m/s}$ for the SU704 and standard deviations of $0.014 \mu\text{m/s}$ and $0.010 \mu\text{m/s}$, respectively. However, the curing rate of the SU710 mixed with BMA was significantly lower than the rates of both of the other polymers, at $0.11 \mu\text{m/s}$ with a standard deviation of $0.012 \mu\text{m/s}$. We found that SU710 with BMA cured at a rate significantly lower than the other two polymers (Student's t-test, p -value = 0.032). No intervals above 60 seconds were chosen as after 60 seconds, many of the membranes were

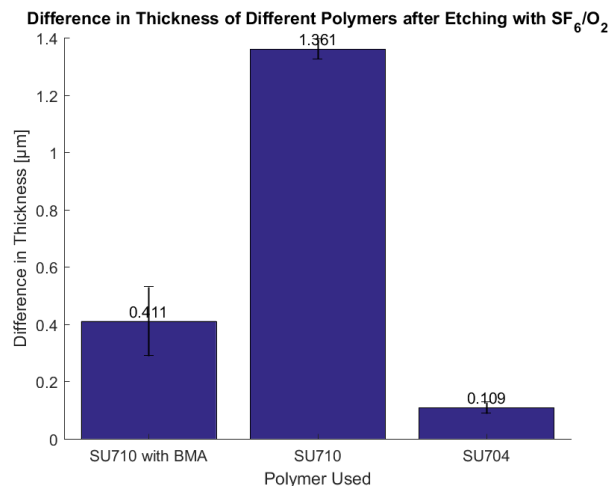


Figure 3. SU704 has the lowest etching rate, thus it is the most resistant. The difference in thickness of polymers (μm) under a 50/50 mixture of SF_6 and O_2 after etching for a given amount of time (three minutes). Error bars represent standard deviation.

too thick and exceeded the desired range of 5-10 microns.

This test showed that the better membranes were either SU704 or SU710, as they could be created faster. A faster cure was desirable for this test because that would mean the membrane requires less time and energy to make.

We then performed experiments to find the etching rates of the three polymers, which is a measure of how much of the polymer was etched away by the plasma after a given amount of time. We found that plasma etching caused the polymer thickness to decrease since the plasma etching removes part of the upper surface of the polymer. When SF_6 was used for etching, the polymer with the most resistance was SU704, as it had the lowest average thickness change from the initial thickness ($0.109 \mu\text{m}$, $0.020 \mu\text{m}$ standard deviation) (**Figure 3**). Both SU710 and SU710 mixed with BMA had thickness decreases nearly an order of magnitude higher than the SU704 ($1.361 \mu\text{m}$, $0.035 \mu\text{m}$ standard deviation and $0.411 \mu\text{m}$, $0.120 \mu\text{m}$ standard deviation, respectively). Moreover, SU704 had a significantly lower etching rate (Student's t-test, p -value = 0.041).

The thicknesses of the membranes decreased from the initial in the SF_6 and O_2 mixture etching as well (**Figure 4**). Those two gases were chosen due to their ability to etch open the boron nitride nanotubes compared to the pure SF_6 . Similar to the SF_6 etching, the most etch-resistant polymer was SU704 again, as there was the least average change between the initial and final thicknesses for this polymer ($0.067 \mu\text{m}$, $0.015 \mu\text{m}$ standard deviation). Again, the SU710 and SU710 with BMA had much higher average etching thickness differences ($0.888 \mu\text{m}$, $0.027 \mu\text{m}$ standard deviation, and $0.556 \mu\text{m}$, $0.023 \mu\text{m}$ standard deviation, respectively) (Student's t-test, p -value = 0.025. The t-test results also showed that the SU704 had a significantly lower etching rate, at a 5% confidence level.

The relationship between the magnetic dipole moment

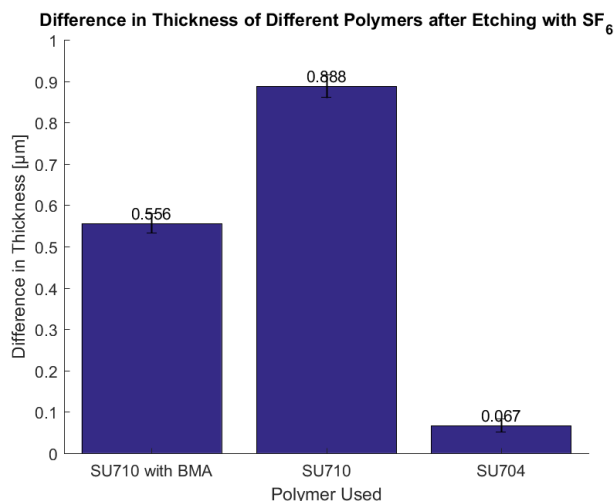


Figure 4. SU704 has the lowest etching rate, thus it is the most resistant. The difference in thickness of polymers (µm) under SF₆ plasma gas after etching for a given amount of time (three minutes). Error bars represent standard deviation.

and the length of the tube was linear, with a longer tube corresponding to a generally larger magnetic dipole (**Figure 5**). This data was collected by video recording nanotubes of different lengths in a microscope under a magnetic field. This correlation had a very high correlation coefficient of 0.962 (**Figure 5**). Since magnetic field multiplied by the magnetic dipole moment is equal to the torque, this relationship means that longer nanotubes experienced a greater torque when placed into a magnetic field of a certain strength. As torque is rotational equivalent of force, the greater torque on the nanotube would be expected to make the longer nanotubes align more quickly.

DISCUSSION

We conclude that the best polymer material out of the three tested was the SU704 membrane. This is because it performed significantly better than SU710 with BMA in both the curing rate test and significantly better than all the other polymers in the etching resistance test. SU704 displayed all four of the desired characteristics for nanotubes: reasonable strength, etching resistance, fast curing time, and 5-10 µm thickness. This investigation showed that by adopting this polymer, the resulting membranes created will not only have a stronger resistance to etching and therefore have fewer defects, but can also be produced more quickly in large quantities due to the faster curing rate. One plausible explanation for such results is that the BMA prevented the crosslinking of the photoinitiator and inhibited the curing. This would account for the much lower SU710 with BMA curing rate.

In addition, it can be concluded that the length does have a large positive relationship with the magnetic dipole moment of the nanotube. This investigation supported this

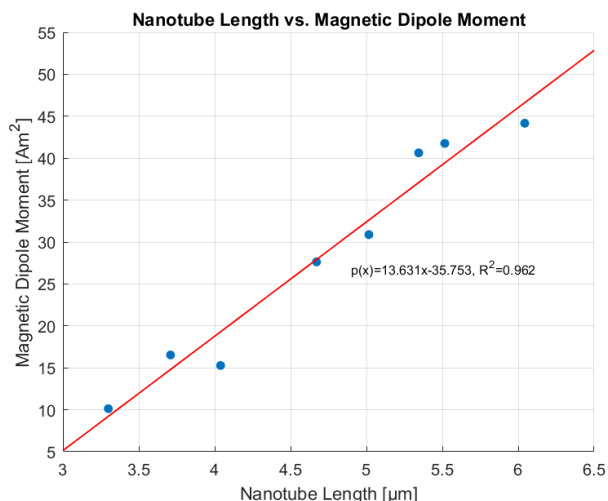


Figure 5. Nanotube length and magnetic dipole moment are linearly correlated. Graph showing the relationship between the nanotube length (µm) and the corresponding magnetic dipole moment (Am²), giving a linear relationship with a r coefficient of 0.962.

by analyzing several nanotubes under a magnetic field and microscope. The results will be used in our future work to optimize the magnetic field alignment time for membranes with different thicknesses.

This study is innovative as it was one of the first to analyze how boron nitride nanotubes and the membranes that can be created with them (1, 8). Previous studies have shown the mechanics of the fluid and ion transport through the nanotubes (4), but none have investigated polymer properties for the creation of membranes. Similarly, some studies have investigated the thermal properties produced by using a magnetic field to achieve alignment for boron nitride platelets (8), but this study was one of the first to investigate the mechanics of how boron nitride nanotubes will align, and what relationships might be found between length, magnetic field strength, and magnetic dipole moment. This study may help to fill in those gaps in our knowledge by illustrating a viable way to create nanotube membranes, as well as giving insight on the alignment process.

Future research will investigate the relationship of the nanotubes with a variable magnetic field. I have already started this work with the creation of a Helmholtz coil to create a uniform but variable magnetic field on the microscope. This means that a variable magnetic field can be produced at will by altering the current, which will allow for more detailed studies of the nanotubes.

Although mostly speculation at the current stage, results of this study may be used to create global networks of clean electricity by producing more efficient ways to create ion-selective nanotube membranes. In addition, these membranes can be used for other applications, such as filtration or desalination.

METHODS

Membrane Preparation

There are many steps to creating the polymer layer of the nanotube (Figure 6). The first step was to prepare each of the polymer solutions by mixing them thoroughly with a stirring rod with a 7.8% by volume concentration of Darocur 1173 (2-hydroxy-2-methylpropiophenone, Sigma-Aldrich, Inc.). Darocur 1173 is a specific photoinitiator used in this procedure because it cross-links and hardens when exposed to UV light, allowing the mixture to cure properly (10). This specific concentration of photoinitiator was chosen as it allowed for even curing throughout the mixture, as well as not compromising the structural strength of the polymer, and was determined by numerous tests.

The second step was to place the solution in a vacuum chamber for 24 hours. This was done to remove air bubbles that formed during the mixing of the photoinitiator and the polymer. This is necessary, as air bubbles interfere with the cross-linking during curing and lead to an uneven cure, which would cause decreased structural strength of the resulting polymer.

The third step was to place one drop of the mixture on a glass slide, which acted as a substrate. A quartz slide was placed on top of the drop, which compressed the drop into a thinner sheet, as well as limiting its exposure to air. Quartz was used for the upper glass slide, as it was more transparent than glass to UV light. After the quartz slide was placed, a UV lamp was shone onto the polymer for a specific amount of time. This allowed the thickness of the membrane to be controlled as a longer time allowed more of the polymer to be cured.

The fourth step was to remove the polymer off the quartz slide. The quartz slide was taken out and sprayed with acetone to remove excess polymer. Acetone was used for this application as it is a good solvent of the liquid polymer and is relatively cheap and available. Ethanol and distilled water were tested as solvents, and they did not work as well. Then, the remaining cured polymer on the glass slide was coated in more acetone to cause the membrane to swell. This swelling occurred because the acetone collected in large pockets underneath the cured polymer. This swelling was induced because it allowed the membrane to be more easily washed away with distilled water, as less area of the polymer was adhered to the quartz slide.

The final step was to mount the polymer onto a new plastic substrate. After the membrane was washed off the quartz slide, it was then carefully picked up with tweezers and dropped into a dish of ethanol. This intermediate step was done to remove folds in the membrane that may have occurred as it was washed off the quartz slide. Ethanol was used, as the surface tension of the ethanol slowly unfolded the cured polymer to its original state. Then, the unfolded membrane was picked up with tweezers and placed in a dish filled with distilled water. The distilled water was used to clean excess ethanol or acetone off of the polymer. Then, the polymer was placed onto a flexible plastic ring that allowed for mobility and easier testing, while still providing enough structural strength.

Curing Rate Test

This test was done by creating several membranes but changing the amount of time that the UV lamp was turned

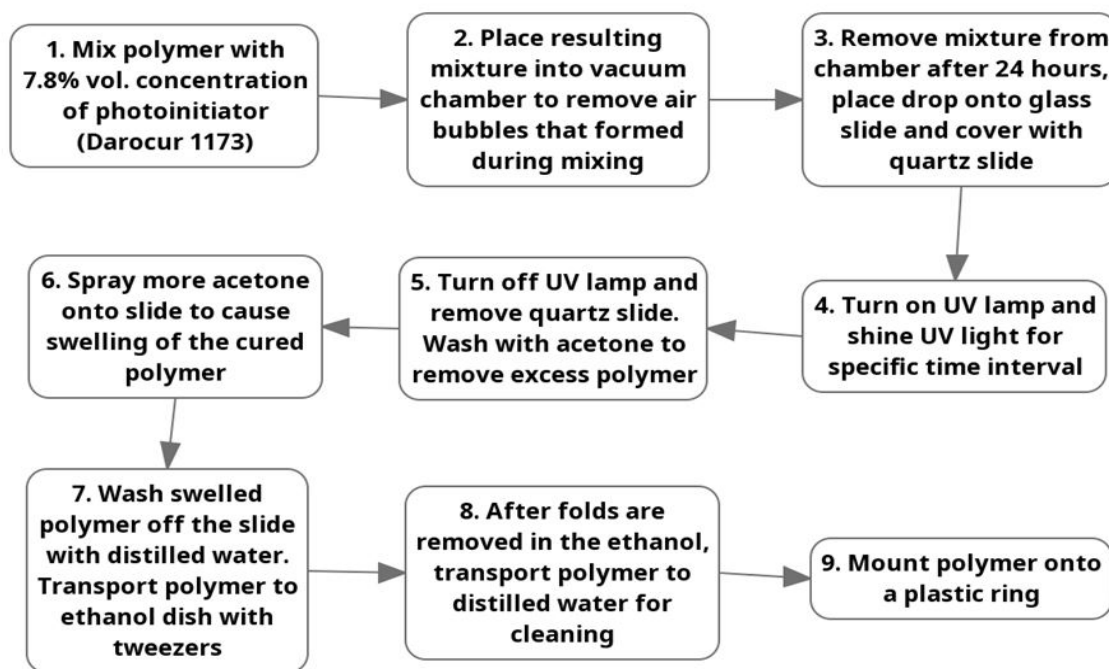


Figure 6. Chart explaining how cured polymer was created for this study. Polymer is first mixed, the cured with the UV light for a given amount of time, then washed with acetone to remove from a quartz slide.

on for each of them. For each different type of polymer, 4 different types of membranes were produced: one with the UV lamp on for 5 seconds, one with the UV lamp on for 10 seconds, one with the UV lamp on for 20 seconds, and one with the UV lamp on for 60 seconds.

The thicknesses of the finished membranes were then measured with a Filmetrics F3-sX series reflectometer. This device measured the thickness of the membrane by comparing the wavelengths of light reflected from top and bottom edges of the membrane. Three separate measurements were taken for each membrane, which were then averaged to find the thickness. The thickness could then be plotted against amount of time the UV lamp was curing the polymer for to find the curing rate of the polymer.

Etching Tests

The second test was the etching resistance test. This test was done to find which of the polymers was the most resistant to plasma etching. A more resistant polymer was desired as this would decrease the chances of etching causing a defect such as a hole or tear in the polymer.

First, polymers of the three chemicals were cured and each of their average thicknesses were measured with the reflectometer. Then, six of the membranes were etched by pure sulfur hexafluoride (SF_6) in a RF plasma etcher for three minutes, with two of each type of polymer: SU704, SU710, and SU710 with BMA. Another six membranes with two of each type were etched by an oxygen-sulfur mixture of 50% of each gas for three minutes. These gases were used because they have been proven to be capable of etching boron nitride nanotubes (10).

After the etching was finished, the thicknesses of each of

the membranes were measured again with the reflectometer. By comparing the difference in thickness of the membranes before and after the etching process, both the amount of polymer etched away and the etching rate for each of the polymers could be calculated.

Nanotube Alignment Analysis

The nanotubes were first functionalized by attaching iron particles to them, and then analyzed while aligning in a set magnetic field. The procedure for this is explained below.

The nanotubes used in the experiment were boron nitride tubes purchased from Naieel Co. These tubes had a diameter of 30-50 nm and a variable length of at least 10 μm (12). Initially, the tubes were suspended and dispersed in isopropyl alcohol (IPA) at concentrations of about 0.1 mg/mL. IPA was chosen as an initial solvent for the nanotubes since they are both nonpolar and easily miscible (11). After mixing, the nanotubes were sonicated for five minutes in a bath sonicator to create a better dispersion and to break up clumps of nanotubes. After being dispersed, the IPA was evaporated and replaced with water and re-sonicated for 15 minutes. Water was used as a solvent since IPA was not compatible with the iron particles. After sonication, the iron particles were added at a concentration of 0.01 mL of the particle suspension for every 5mL of the nanotube suspension. This concentration was tested to be an optimal concentration, as it ensured that enough iron attached to each nanotube. After three hours of mixing, the particles clumped and attach to the nanotubes, turning them into magnetic dipoles able to be aligned by outside fields. Finally, the excess iron particles were centrifuged out, leaving only the nanotubes with iron particles attached to them. This relatively dilute solution of

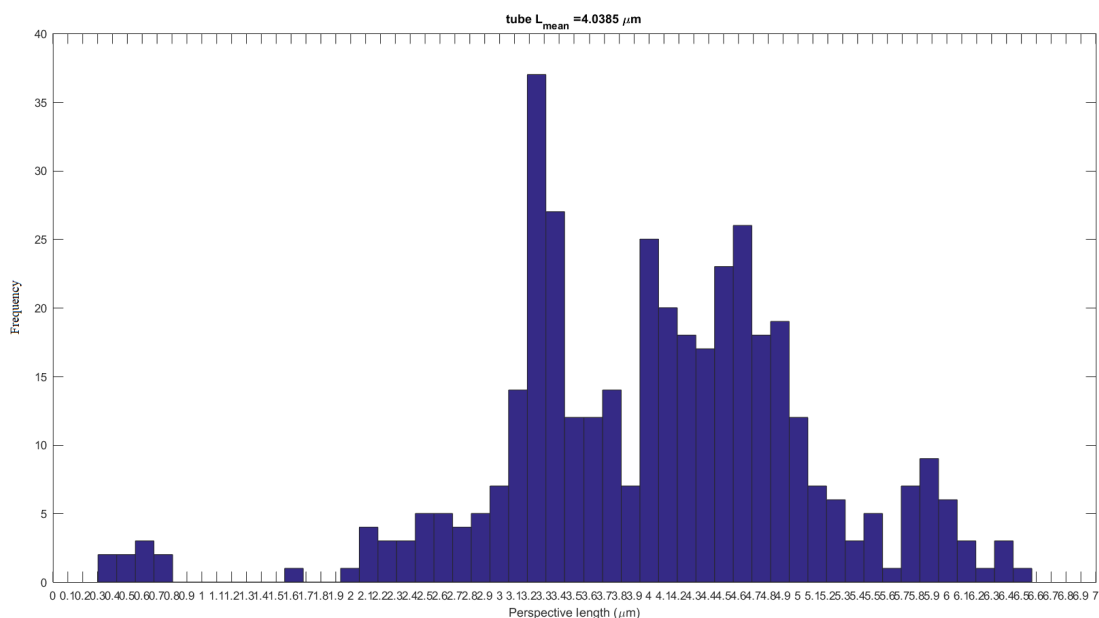


Figure 7. An example histogram representing the nanotube lengths (μm) recorded from each frame of the video of the nanotube under the microscope. The calculated length was the average from this distribution.

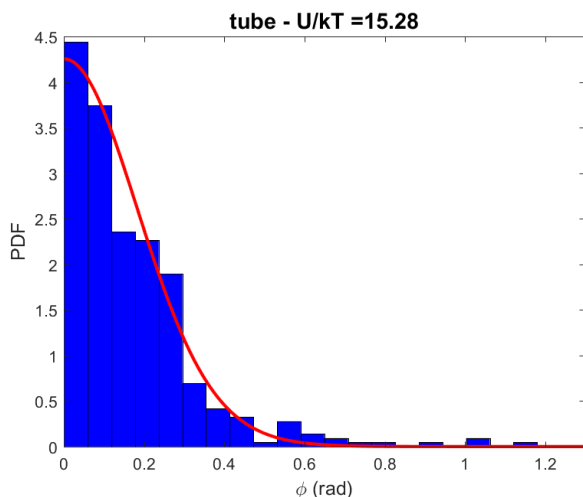


Figure 8. An example histogram representing the angle probability distribution from the recorded video of nanotubes under the magnetic field. Angle of the nanotube is measured with respect to the magnetic field direction.

functionalized nanotubes was ideal for investigating under a microscope.

The nanotubes were then analyzed using the microscope with a 40x objective lens. They were placed under a set magnetic field created with permanent magnets. This field could be varied with magnet placement and was 150 Gauss strong. Because of the magnetic iron particles attached to the tubes, this magnetic field aligned the tubes in one direction. To analyze the results, a camera was turned on to record the tubes' motion by recording a short video of the tube for up to one minute. After recording the video, individual frames of the video were analyzed by a MATLAB program that found the length of the tube and the angle it was at, relative to the angle of the magnetic field. The video was taken at 20 frames per second, amounting to 1200 frames of data for each nanotube.

These values were plotted on separate histograms. The histograms showing the length of the tube in each frame were plotted and averaged to find a length (**Figure 7**). The angle distribution is similarly plotted for each frame (**Figure 8**). After recording the values, the histogram of the angle distribution is fitted (**Figure 8**). This fit is used to calculate the dipole moment of the tube - the strength of the induced magnetic field of the tube. This dipole moment was then plotted against the length of the tube to see the relationship.

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