The focus of this project was to determine the dielectric constant of polypropylene doped with various ethynol porphyrins at different concentration levels in order to determine if the degree of conjugation within ethynol porphyrin oligomers would increase the capacitance of naked polypropylene films. The research procedure for this study began by forming a capacitor with a film of polypropylene as the dielectric material. The capacitance was then measured and the dielectric constant was calculated. In order to deposit the film, polypropylene was spin-cast. Over the course of this study the capacitance values for polypropylene films doped with the compounds ZnTPP, ZnO1, ZnO3, Zn 3,5 and Zn 2,6 were studied. The capacitance values have shown a significant increase, roughly one million times greater than naked polypropylene although this value is inherently flawed due to inaccurate measurements of film thickness.
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1. INTRODUCTION

As the world attempts to wane its dependence on fossil fuels, the flexibility of electricity as an energy source has become increasingly important. The most efficient way for small amounts of high-voltage energy to be quickly stored and released is through the use of a capacitor. Of the many available capacitor designs those using thin-film technology are considered the best because they are capable of storing energy at high density levels. Amongst the many available films, polypropylene is considered the dielectric of choice [1] Nonetheless, there are still many properties of polypropylene films which, with fine tuning, could be improved upon in order to make such thin-film capacitors more readily usable in many possible applications. One way of adjusting the properties of polypropylene is by using dopants, additives that are added in small amounts to a pure substance to change its physical properties. [2] The dopant used in this experiment is porphyrin. Porphyrins are tetapyrrolic conjugated macrocycles with large π–conjugated ring systems and heteroatoms that give rise to porphyrin-porphyrin π–interactions. [7] This effectively makes for a highly polarizable substance which is ideal for this experiment.

This paper will cover many aspects of the thin-film polypropylene capacitor technology including its fundamental design and response to various doping agents. Section Two will cover a brief background of the classic capacitor and explain the transition from such capacitor designs to those of thin-film capacitors. Section Three will discuss design, implementation, and evaluation of the experimental thin-film capacitors. In Section Four final analyses of the experiment and results will be made.

2. BACKGROUND

2.1 Modern Day Applications

As mentioned earlier, thin-film polypropylene capacitors have immediate use in various industrial and military applications. For instance, industrial strength lasers and other pulse power equipment require high voltage power that can be quickly released. This characteristic of energy is one which capacitors can best provide. Moreover, this same kind of energy storage and release is desirable for a variety of other applications, notably, military weaponry. The most obvious of all applications would include refinement of the stun gun, which releases large doses of electrical charge in extremely short periods.

2.2 Parallel Plate Capacitor
The parallel plate capacitor is a capacitor which consists of two parallel capacitor electrodes. When these electrodes are equally and oppositely charged, they have an ability to store charge which is known as capacitance. The charge placed on the capacitor electrodes and the potential between the two plates are proportional according to the equation [3]:

\[ Q = VC \]

In this equation Q represents charge, V represents voltage, and C represents capacitance. Although in this equation the constant C plays a special role since it has no dependence on Q or V. The value of capacitance is determined by the geometry of the capacitance electrodes which comprise the capacitor. In the case of a parallel plate capacitor capacitance is evaluated using the equation [3]:

\[ C = \varepsilon_0 \cdot \frac{A}{d} \]

In this equation C is again capacitance while \( \varepsilon_0 \) is the permittivity constant \( 8.85 \times 10^{-12} \) F/m, A is the area of the two capacitor electrodes, and d is the distance between the two plates of the capacitor.

![Figure 1-A charged parallel plate capacitor](image)

These equations are of great importance for even at the thickness of microns they govern the design of thin-film capacitors.

### 2.3 Parallel and Series Capacitance
When connected in parallel $n$ number of capacitors have an equivalent capacitance of [3]:

$$C_{equiv} = C_1 + C_2 + ... + C_n$$

Capacitors in series have an equivalent capacitance of [3]:

$$1/C_{equiv} = 1/C_1 + 1/C_2 + ... + 1/C_n$$

The equation for equivalent series capacitance was very important in the experimentation process because this was the only method available to evaluate the polypropylene film capacitance using the capacitance bridge available.

2.4 Dielectrics

A dielectric is a material which sits between the two plates of a parallel plate capacitor. [3] Furthermore, a dielectric material must be polarizable because a capacitor stores electrical energy by polarizing its dielectric resulting in an electric field. [3]

2.5 Porphyrins

As stated earlier, porphyrins -- the core components of this research project -- are tetrapyrrolic conjugated macrocycles with large $\pi$-conjugated ring systems and heteroatoms that give rise to porphyrin-porphyrin $\pi$–interactions. [7] Each pyrrole subunit is linked to each other by way of a methine bridge. [4,5] The great appeal of porphyrins -- a natural pigment -- stems from the fact that freebase porphyrins can easily be manipulated by adding metal ions to the center of their structures. [6] This allows the properties of a porphyrin to be manipulated. In this experiment the metal ion selected was zinc. This choice was made because zinc porphyrins are commonly known to be one of the easier and more stable porphyrins to prepare.

3. EXPERIMENTAL METHODS

3.1 Shadow Mask Design

A shadow mask was employed to create an assortment of capacitors using one slide a shadow mask was used. This allowed for evaluation of the capacitance of numerous
smaller capacitors with plate areas varying from \(0.03516 \text{ cm}^2\) to \(1.43 \text{ cm}^2\). The shadow mask used was designed using AutoCAD LT 2005 and fabricated with a CNC milling machine. Seen below, the mask was approximately 2.6 cm by 2.6 cm.

![Shadow Mask](image)

Figure 2-A picture of the shadow mask used

### 3.2 Slide Preparation

The original design proposed for this experiment called for plating glass slides with 100 nanometers of gold. This process proved too difficult to implement. Thus, it was decided that the slides would be purchased already plated from the company GenTel BioSurfaces.

![Glass Slide](image)

### 3.3 Polypropylene Preparation

Preparation of the polypropylene was done with the assistance of doctoral student Paul Frail of Dr. Michael Therien’s research group which is part of the Chemistry Department at the University of Pennsylvania. A variety of undoped solutions of polypropylene were prepared in order to: 1) better understand the spin-cast process, 2) determine the best concentration of polypropylene to use for the experiment, and 3) determine a background value to evaluate ethynol porphyrin oligomer’s ability to increase the capacitance of polypropylene film. These solutions were heated to reflux, approximately 150 degrees
Celsius. This is the approximate melting temperature of polypropylene. At this point, drops of the solution were placed upon a contained area of the slide marked off using Teflon tape. The slides were then placed in a spin-casting machine where they were spun so that the solution would form a film on top of the slide. Once the film was deposited it was taken to a sputter-coat machine where anywhere from 600 to 1000 angstroms of gold were deposited through the shadow mask. Upon completion the slide was taken to a LCZ meter where the capacitances of the areas formed by the shadow mask were measured using micromanipulating electrodes. After evaluating solutions of five different concentrations, it was determined that 1 gram of polypropylene in 50 mL of Decalin (solvent) formed the most reproducible and best measurable capacitance values.

3.4 Dopants

Dopants are additives added in small amounts to a pure substance in order to alter its properties. [2] In this experiment dopants were added to polypropylene with the intention of increasing the capacitance per area of the thin-film capacitors created. The amount of dopant added was determined via percent relative to weight. The quantity was varied in order to determine the most effective loading.

3.4.1 ZnTPP

The first and simplest dopant to be added to the polypropylene was tetraphenyl porphyrin (ZnTPP). Doped solutions were prepared from 200 mg of polypropylene in 10 mL of Decalin. Solutions with four different loadings were made including 1%, 5%, 10%, and 15% by weight. After assessment of the slides it was determined that the 1% and 5% doping levels produced films which were too thin. In some instances the capacitance produced caused measurement overflows in the LCZ meter. Thus, it was decided that according to the various films consistency, and lateral homogeneousness, 10% doping would be sufficient for taking capacitance measurements. In order to further increase film thickness it was decided that multiple layers of film would be deposited. The concept was implemented as such: first a layer of undoped polypropylene was spun on top of the slide. Then a second layer of polypropylene containing the dopant was spun onto the slide. Lastly, a third film of undoped polypropylene was spun on top of the doped film. Based on the results of the preceding steps and the new film technique, a new set of more complex dopants were tested.
3.4.2 ZnO₃

In the second round of trials a set of dimer porphyrins were assessed. ZnO₃ was the first to be evaluated. Once again, doped solutions were prepared from a polypropylene-based solvent. In this set of slides all dopants were added at a proportion of 10% by weight. The compound ZnO₃ is characterized by its relatively high level of interaction with similar porphyrins. Increased capacitance values for the film doped with this substance suggest that the relatively high level of interaction of ZnO₃ may be attributed to polypropylene’s increase in capacitance relative to solutions doped with ZnTPP.

3.4.3 ZnO₁

The porphyrin ZnO₁ was the next dopant evaluated. It is similar to ZnO₃ yet has four less oxygen molecules. This makes for a slightly less interactive, however more bulky molecule. No fair predictions could be made about whether this characteristic would aid in increasing or decreasing the capacitance of polypropylene. Interestingly, results showed a negligible difference in capacitance values for similar capacitors at 100 Hz frequency AC current when compared to ZnO₃. Nonetheless at the 1 kHz frequency the capacitance values for ZnO₁-doped film were significantly less and on average, were almost half that of ZnO₃-doped films.
3.4.4 Zn (3,5) & Zn (2,6)

The next two dopants that were tested have structures significantly different from the previous porphyrins. The first of these is Zn (3,5) which contains two phenyl groups on opposite sides of the structure. Furthermore, both phenyl groups have bulky alkoxy side chains at the 3 and 5 positions. Capacitance values for the film to which this dopant was added were significantly greater than films doped with ZnO1 and ZnO3. In fact, the capacitance values recorded were on the order of roughly 1.5 to 3 times greater.

The last dopant to be thoroughly evaluated was Zn (2,6). Even bulkier than Zn (3,5) this porphyrin also contains phenyl groups on opposite side of the structure. In addition alkoxy side chains are attached at positions 2 and 6. This orientation makes for a larger angle between the alkoxy side chains than the positions 3 and 5 occupied in Zn (3,5) and the result is an even bulkier molecule which takes up more space. Nonetheless, there was a negligible difference in capacitance values for Zn (3,5) and Zn (2,6). These results suggest that positioning of the alkoxy side chains has no effect on the capacitance values of the polypropylene film.
3.4.5 Trimmers

The last group of porphyrins tested was trimers. These porphyrins included ZnO3, ZnO1, Zn (3,5) and Zn (2,6). The capacitance of films doped with these compounds was significantly greater than that of films doped with any previous porphyrins. In fact, the differences were immeasurable. Even when run in series with capacitors of 5 and 6 mF the capacitance values could not be accurately measured. From the few values that could be obtained it is estimated that the capacitance of polypropylene film doped with trimers is somewhere between 200 and 1000 mF.

4. DISCUSSION AND CONCLUSIONS

Preliminary results have shown that porphyrins are most certainly a proper agent for increasing the capacitance of polypropylene film. With a metal-coated slide, a spin-caster, and a sputter-coating machine capacitors can be prepared to evaluate the dielectric film in question. The technique used in testing various porphyrins is still being refined yet is certainly a fruitful area for future research. It is also essential that researchers keep in mind that the technique which was used for testing requires numerous pieces of rather expensive and highly delicate machinery that are vulnerable to mechanical failure. Nonetheless, the experimental capacitor is a great way to record the capacitance values of a dielectric film and its use is only limited by the accuracy of the measuring equipment used.

5. RECOMMENDATIONS

Overall the technique used in this experiment worked reasonably well. However, there were two factors that hindered the pace of this research project. These were the availability and the precision of working equipment. Obviously these issues were of great importance when carrying out the experiment; they also became critical when doing calculations. A resulting problem was that measurements could not be taken for the later films because their capacitance values were too large for the capacitance bridge available. In many cases the meter simply read “overflow”. Additionally, no calculations could be completed on \( \varepsilon_0 \) for any of the films used because thickness could not be measured precisely. The instrument used was an ellipsometer and it is recommended that this instrument not be employed for any similar experiments because of its limited utility.

6. ACKNOWLEDGMENTS
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7. REFERENCES

8. APPENDIX

![Graph showing capacitance (microfarads) vs. doping level (% by weight) with a regression line and $R^2 = 0.7146$.](image-url)
Doping Level (% by weight) vs. Capacitance (microfarads)

Capacitance decreases as the doping level increases. The graph shows a linear trend with an $R^2$ value of 0.7686.

$0.1057 \text{ cm. }^2 - 100 \text{ Hz}$
The graph shows the relationship between capacitance (in microfarads) and doping level (% by weight). The equation of the line is given by:

\[ R^2 = 0.8871 \]

The graph indicates a negative correlation between capacitance and doping level.