Synthesis of Polyaniline by Bulk Polymerization

Nicholas Belgau, Chemical Engineering

Mentor: Dr. Floyd F. Klavetter

Kellogg Honors College Capstone Project

CAL POLY POMONA

1. Background Chemistry

The conductive nature of polyaniline and other intrinsically conductive polymers is due to the conjugated backbone along the main chain[1]. Alternating pi bonds are placed throughout the structure that contain a less localized pair of electrons compared to the nearby sigma bonds. Conjugation allows electrons to flow seamlessly along the main chain once a dopant is introduced[2]. Vacancies of charge are then created, allowing charge carriers to redistribute electrons along the polymer[3].

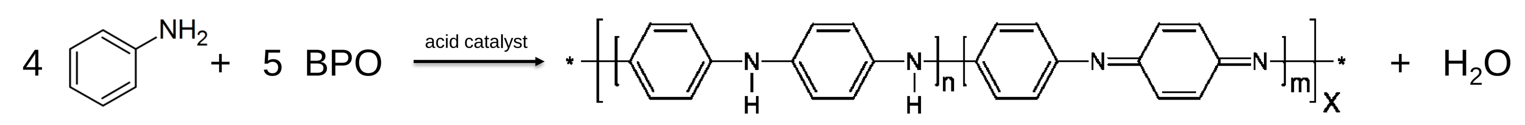


Figure 1: Polymerization reaction of aniline. Aniline and BPO are acid catalyzed to form of polyaniline of the emeraldine oxidation state (n=0.5, m=0.5).

Bulk polymerization of polyaniline utilizes benzoyl peroxide (BPO) as the oxidant and dodecylbenzenesulfonic acid (DBSA) that is both a polymerizing agent and a dopant[4]. Emeraldine is easily distinguishable from the other oxidative states due to its waxy green appearance and high conductivity.

2. Objective

The objective of this research was to understand how conductivity changes with varying reagent concentrations for the synthesis of polyaniline through bulk polymerization. Furthermore, the stability of doped polyaniline was to be analyzed.

This has economic and practical advantages in industry as well as possibly leading to technological developments in the study of polyaniline. Conductive polymers have demonstrated the ability to replace metal components in some applications.

3. Materials and Method

Aniline and dodecylbenzenesulfonic acid were weighed out in 4:4 stoichiometric molar ratios, and mixed in a 30mL glass beaker. Varying benzoyl peroxide concentrations were added to each sample mixture with less than 1mL acetone to help dissolve the BPO. Since the mixing of aniline and DBSA was exothermic, mixing was required for 5 minutes so that the beaker was not warm. Adding BPO after the heat had dissipated minimized the risk of explosion. Metal scoopulas were not used when transferring reagents since metal ions from rust can also trigger rapid decomposition of BPO[6].

Each sample mixture was then manually stirred for 10 minutes before being spread evenly between two glass slides. Two 2-inch nickel chromium resistance wires were places in parallel to each other protruding from the sample. Digital calipers were used to accurately record sample dimensions that are presented in Appendix A. Figure 3 exemplifies the dimensions measured in reference to the Appendix A values. The multilog ammeter leads were connected to the wires. Initial resistance measurements were recorded in addition to measurements taken at 1 hour and again at 24 hours. This process was repeated for each sample trial.

4. Calculating Conductivity

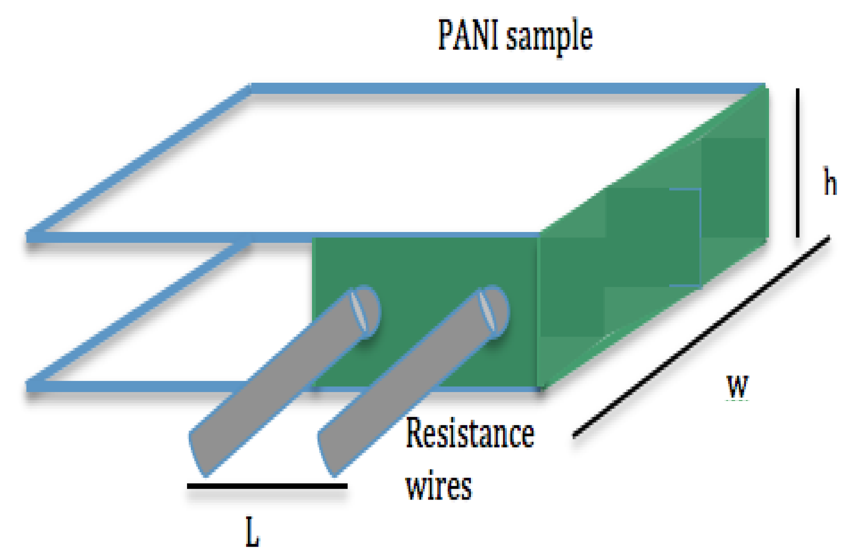


Figure 2: Conductivity measurement setup with multilog meter.

The resistance of the PANI samples were measured using the multilog meter as shown in Figure 2. The configuration required the distance between the electrodes and the cross sectional area to be known in order to calculate resistivity. Conductivity could then be determined because it is inversely related to resistivity.

$$R = \frac{\rho L}{A}$$

$$\sigma = \frac{1}{\rho}$$

5. Benefits of Bulk Polymerization

Figure 3 outlines the comparative conductivities of polyaniline and similar conductive polymers. Metals such as silver and copper provide a baseline at 10^8 S/m to compare these conductivities to. Doped polyacetylene has been known to have the highest conductivity out of the various polymers of interest.

However, synthesizing polyaniline using bulk polymerization has several benefits over traditional methods of synthesizing PANI. The most notable being that PANI from bulk polymerization becomes doped without any additional steps, and remains stablent[5]. Additionally, bulk polymerization instantly produces a green wax that can be readily molded and used. Aniline, DBSA, and BPO are all liquids at room temperature, so the hazards of handling flammable acetylene are mitigated. These rapid processing techniques and moldable characteristics allows for several industrial applications that are not possible using other methods of polymerization and other monomers.

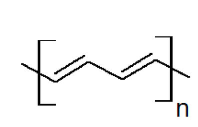
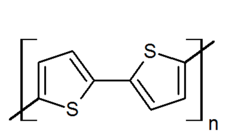
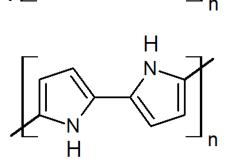
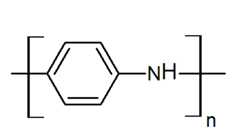
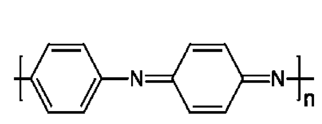
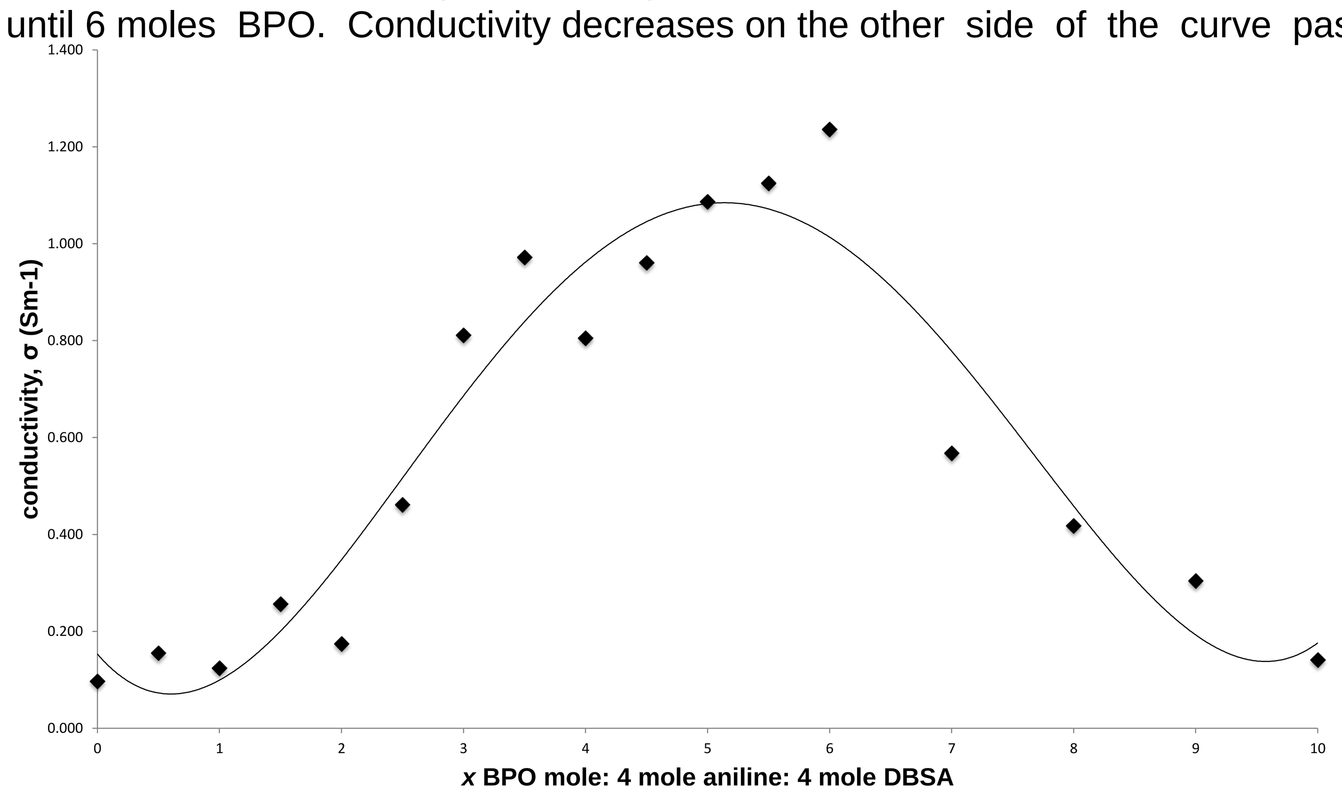
Compound	Repeating Unit	Conductivity (S/m)
Silver & Copper		10^8
Polyacetylene		10^5
Polythiophene		10^3
Polypyrrole		10^3
Tradition Polyaniline		10^2
Synthesized Polyaniline		10^0

Figure 3: Comparison of PANI conductivity to other conductive polymers.

6. Results & Discussion

Effects of BPO Concentration on Conductivity

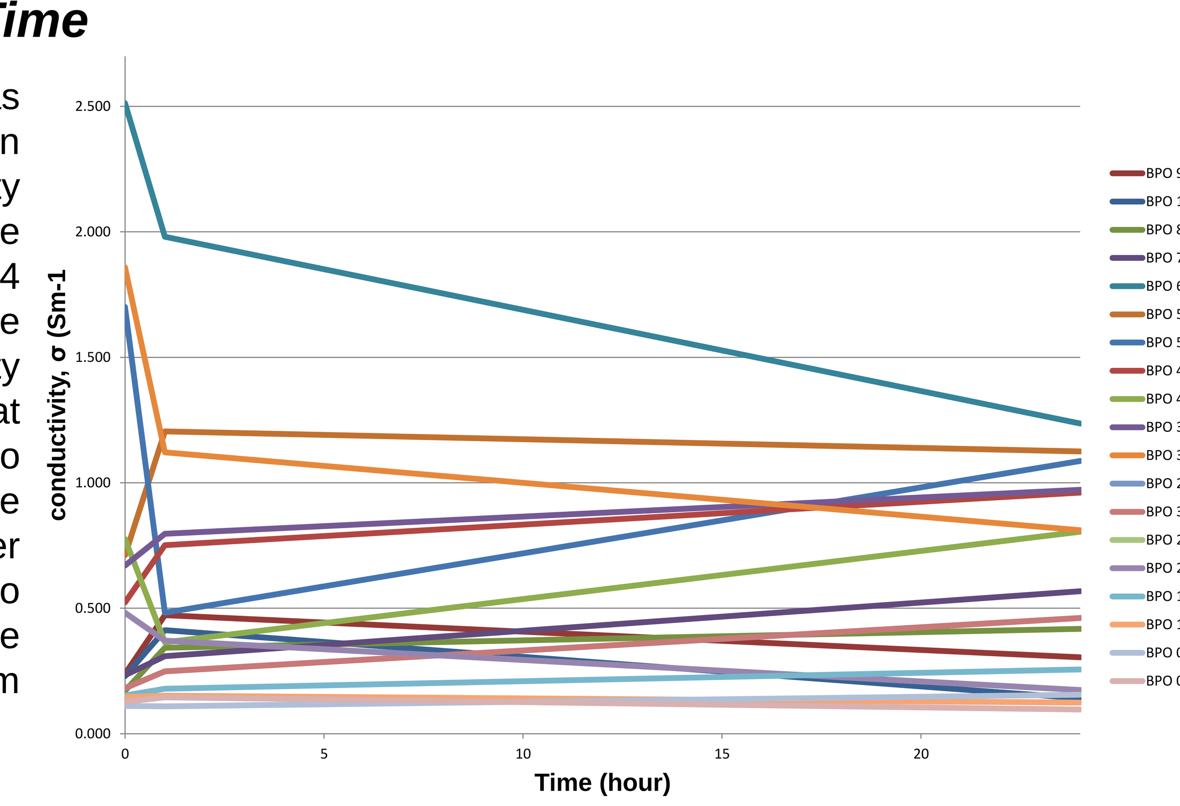
Literature suggested that a 5 molar ratio of BPO yields conductive emeraldine base[16]. With a single target value in mind, trials between 0 and 10 molar ratios of BPO were analyze this effect of conductivity from varying BPO concentration. After measuring conductivities, a unimodal curve was used to fit and verify this assumption. This sample set displayed the BPO molar ratio of 6 as having the highest conductivity at 1.236 S m^{-1}. The data displays a clear trend of increasing conductivity for BPO ratios 0, 0.5, 1, and 1.5, and conductivity continues to increase until 6 moles BPO. Conductivity decreases on the other side of the curve past 6 moles BPO as the reagent.



The trend observed conflicts with literature, since it appears that 6 moles of BPO results in a higher conductivity. This higher reagent requirement to maximize conductivity may be explained by inadequate mixing, as the gradual formation of wax inhibited the reaction from reaching completion. This could be fixed by mechanical mixing or using a more finely-grounded BPO reagent.

Change in Conductivity Over Time

The stability of the polyaniline wax was analyzed by measuring the change in conductivity over time. Conductivity measurements were taken directly after the mixing of BPO, 1 hour later, and again 24 hours later. The data reflects that 10 of the 16 data points decreased in conductivity over the span of 24 hours, suggesting that the wax reacts with moisture in the air to eliminate some of the double bonds in the polymer chains. Evaluation of this trend over the span of several days would be helpful to determine the extent of disrupting the conjugated chain, or to see if an equilibrium value can be achieved.



7. Conclusions

Polyaniline was synthesized, and conductivity measurements were successfully plotted against varying oxidant concentrations for a bulk polymerization reaction of dodecylbenzenesulfonic acid, benzoyl peroxide, and aniline. A bell curve fit the data points provided for BPO concentrations, and 6 moles of BPO to 4 moles of aniline provided the highest conductivity at 1.236 S m^{-1}. The reaction progress was also examined with conductivity measurements taken at 0 hour, 1 hour, and 24 hours. It appeared that the polyaniline wax reacted with moisture in the air to gradually decrease in conductivity. This study provided insight into how the conductivity of bulk polymerized polyaniline is affected by oxidant variations.

8. Works Cited

1. "Noble Prize in Chemistry, Conductive Polymers." (2010): The Royal Swedish Academy of Sciences.
2. Shumaila, G.b.v.s. Lakshmi, Masood Alam, Azher M. Siddiqui, M. Zulfequar, and M. Husain. "Synthesis and Characterization of Se Doped Polyaniline." *Current Applied Physics* 11.2 (2011).
3. Hammo, Shamil M. (2012). "Effect of Acidic Dopants properties on the Electrical Conductivity of Poly aniline". *Tikrit Journal of Pure Science*.
4. Macdiarmid, Alan G. "Polyaniline and Polypyrrole: Where Are We Headed?" *Synthetic Metals* 84.1-3 (1997): 27-34.
5. Goorskey and Klavetter, "Polymer Preprints." 44 (2008).
6. Sarpong, Richard. "Chemical Class Standard Operating Procedures: Potentially Explosive Compounds (PEC)." June 3, 2013. Cal Berkeley Department of Chemistry.
7. Pinto, N.j., P.d. Shah, B.j. Mccormick, and P.k. Kahol. "Dependence of the Conducting State of Polyaniline Films on Moisture." *Solid State.*

9. Future Work

The weight of this study could be improved if a greater extent of independent variables were measured. Obtaining a set of data that holds BPO concentration constant while varying DBSA and Aniline molar ratios would be conducive to understanding the full story of how conductivity is affected by reagent concentration. Varying the DBSA concentration was attempted, but the high viscosity of mixtures below 4 moles of DBSA to 4 moles of aniline lead to inconsistent dimension measurements and placement of the resistance wire. Glass slides would need to be replaced by ceramic enclosures to maintain shape of the polyaniline samples. Enclosed structures would increase the accuracy of dimension measurements as well. Additionally, obtaining more data points of the polymerization would increase the accuracy of the stability trend observed in this study. A Kithley 487 picoammeter could eliminate manual data collection.

Exposure to moisture has been thought to affect the conductivity of many conductive polymers[7]. Water molecules are introduced by diffusion from the atmosphere, so humidity and vacuum conditions should be considered if this variable is to be analyzed in future studies. Moisture was also introduced from the benzoyl peroxide moistened 25% from Acros. The viability of providing a coating on the PANI wax should be explored if this material is to be considered for industrial applications.

10. Acknowledgements

The research conducted through the synthesis of polyaniline was made possible by a few notable departments and individuals. The first acknowledgment goes out to the Kellogg Honors College for encouraging students to follow their own interests in route to complete the Capstone project. In addition, the patience and guidance provided by my mentor and advisor, Dr. Klavetter, allowed me to pursue my fascination with conductive polymers. Lastly, I would like to acknowledge the chemistry department and Dr. Klavetter's graduate students for helping me find the answers to any questions that arose when conducting this research, and for promoting a safe research environment. I hope that my work inspires other students to pursue research in conductive polymers as there is great potential for breakthroughs in this field.