Photo-induced Protonation of Polyaniline Composites and Mechanistic Study of the Degradation of Polychlorinated Biphenyls with Zero-Valent Magnesium

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PHOTO-INDUCED PROTONATION OF POLYANILINE COMPOSITES AND MECHANISTIC STUDY OF THE DEGRADATION OF POLYCHLORINATED BIPHENYLS WITH ZERO-VALENT MAGNESIUM

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of the Doctor of Philosophy in the Department of Chemistry in the College of Sciences at the University of Central Florida Orlando, Florida

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Major Professor: Cherie L. Yestrebsky
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ABSTRACT

As technology advances, a need for non-metal, conductive materials has arisen for several types of applications. Lithographic techniques are helpful to develop some of these applications. Such techniques require materials that are insulating and become conductive after irradiated. Composites of polyaniline in its emeraldine base form (PANI-EB) doped with photo-acid generators (PAG) become conductive upon photo-irradiation. This increase in conductivity is due to the protonation of PANI-EB. Such materials may be utilized to fabricate conducting patterns by photo-irradiation; however, the conductivity obtained by direct irradiation of PANI-EB/PAG composites is normally quite low (<10^{-3} S/cm) due to aggregation of highly loaded PAG. In this work, poly(ethylene glycol) (PEG), a proton transfer polymer, was added to PANI-EB/PAG. Results showed the addition of low molecular weight (MW) (550) PEG significantly enhanced the photo-induced conductivity to a level comparable to that of PANI-salt synthesized by oxidizing aniline in the presence of an acid. High MW (8000) PEG is less effective than PEG 550, and composites of PANI-EB and N-PEG-PANI showed conductivity as high as 10^{2} S/cm after treatment with HCl vapor. The photo-induced conductivity of the N-PEG-PANI/PANI-EB/PAG composite reached 10^{-2}-10^{-1} S/cm.

Polychlorinated biphenyls (PCBs) are a class of chemicals with 209 different congeners, some of which are known carcinogens, and are persistent organic pollutants in the environment.
After its synthesis, it was seen as a phenomenal additive in a multitude of different applications leading to the widespread use of PCBs and a need for a safe, effective, and inexpensive remediation technique. While it is known that magnesium can degrade PCBs, the mechanism of this reaction was not well-understood. In order for magnesium to be broadly used as a remediation tool, it is necessary to fully understand how the reaction is taking place and if the PCBs are able to be fully dechlorinated into biphenyl. This research focuses on the hydrodechlorination of PCBs with zero-valent magnesium in acidified ethanol. The degradation pathways of 2, 2’, 3, 5, 5’, 6- hexachlorobiphenyl were investigated to determine the identity of the daughter PCBs produced, how and if they continue to be dechlorinated into biphenyl. The proton source for this hydrodehalogenation reaction was also studied using both deuterated solvent and acid to give more detail to the mechanism of this reaction.
To my husband, Kevin
I am so grateful for your unwavering support. You have been there to make me laugh when I wanted to cry and to push me to do better when I needed it. I love you.

To my parents,
I could not have gone so far without your endless encouragement, faith, and pushing me to always go after my dreams. Thank you from the bottom of my heart.

To two of my best friends, Dr. Valentine and Jayme Johns
You two have helped make this journey fun, and a little easier. You have always been there to talk through any chemistry or personal problems.
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<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>EB</td>
<td>Emeraldine base</td>
</tr>
<tr>
<td>GC/ECD</td>
<td>Gas chromatogram with electron capture detector</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas chromatogram with mass spectrometer</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidinone</td>
</tr>
<tr>
<td>PAG</td>
<td>Photo-acid generators</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PANI-EB</td>
<td>Polyaniline in emeraldine base form</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated biphenyl</td>
</tr>
<tr>
<td>PCDD</td>
<td>Polychlorinated dibenzodioxins</td>
</tr>
<tr>
<td>PCDF</td>
<td>Polychlorinated dibenzofurans</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>Ph$_3$S$^+$OTf</td>
<td>Triphenylsulfonium triflate</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent organic pollutants</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>TSCA</td>
<td>Toxic Substances Control Act</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>UV-Visible</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>ZVM</td>
<td>Zero-valent metal</td>
</tr>
<tr>
<td>ZVMg</td>
<td>Zero-valent magnesium</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

Polyaniline

Conducting Polymers

Conducting polymers are organic polymers that can conduct electricity. Their conductivities can range widely from semi-conducting to near metallic, $10^5$ S/cm (H. Shirakawa 1977). In the 1950’s scientists discovered organic compounds can carry current as charge transfer complexes. Polycyclic aromatic salts formed with halogens (Naarmann 2000) were the first organic charge transfer complexes. This steered researchers towards polycyclic aromatic polymers. By 1963, Australian researchers reported conductivities as high as 12.5 S/m with polypyrrole (B.A. Bolto 1963). Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa were awarded the Nobel prize in 2000 for their work with iodine-doped polyacetylene.

![General structure of polyaniline](image)

Figure 1: General structure of polyaniline

Polyaniline (PANI) is a semi-flexible, conducting polymer discovered in the late 19th century (Letheby 1862). The general structure of PANI is shown in Figure 1. De Surville et. al. reported high conductivities for doped PANI in 1968. PANI is a unique type of polymer in its ability to be converted from a non-conducting polymer to a highly conducting polymer. PANI has been of great interest to scientists for the past few decades due its tunable properties, ease of
synthesis, low cost, and good stability. These properties have led to studies for a wide variety of electrical devices and functional materials (Zhang, et al. 2009) (Crompton 2011) (Moriuchi 2012) (Bendrea 2011) such as novel biosensors (Virji, et al. 2005) (Nemzer, Schwartz and Epstein 2010) and energy storage (Murugan, Muraliganth and Manthiram 2010).

![Diagram of polyaniline configurations](image)

**Figure 2:** Three different configurations of polyaniline, (a) pernigraniline (b) emeraldine (c) leucoemeraldine

The oxidation and protonation state dictate PANI’s electrical conductivity and color. Figure 2 shows the three different oxidation states of PANI. The pernigraniline state is fully deprotonated and appears blue/violet in color. While in its leucoemeraldine state, it is fully
protonated appearing white to clear. The emeraldine state has two colors, it is blue while in its base form and green in its salt form as seen is Figure 3. PANI only becomes conductive when protonated to its emeraldine salt form, otherwise the polymer is an insulator. The conductivity of PANI has been reported as high as $10^2$ S/cm (Cao, Smith and Heeger 1992) (Lee, et al. 2006) (Chiang and MacDiarmid 1986).

**Base form**

\[
\begin{array}{c}
H \\
N \\
H \\
\end{array}
\]

**Salt form**

\[
\begin{array}{c}
H \\
N \\
H \\
\end{array}
\]

*Figure 3: Emeraldine base form (above) and emeraldine salt form (below)*

Only after vapor doping with HCl have conductivities higher than $10^{-3}$ S/cm been observed with PANI. Strong acid treatments not only add a processing step, but also may be harmful to other parts of the devices. Therefore, a very desirable process is to achieve high conductivities using photo-irradiation alone.
Photo-acid generators (PAGs) in combination with PANI potentially could allow for the PANI to increase its conductivity to the desired levels without the use of vapor doping. The use of PAGs with PANI-EB would allow for only select sections of the polymer thin film to become conductive by simply irradiating. This would also allow for PANI to be used in photo-lithography making it a very useful material for a wide variety of applications and devices. Photo-lithography can be used to create nano-sized conductive patterns with materials of this nature without the need to expose any other components of the specific device to possibly harmful chemical processes.

Polyaniline Research Objectives

Theoretical calculations show that hydrogen bonding within the PANI polymer matrix could help to improve the electrical conductivity (Foreman and Monkman 2003). This hydrogen bonding network would facilitate the transfer of protons from a PAG to the PANI, increasing the efficiency of the doping process, and result in a higher conductivity after irradiation. Possible hydrogen bonding additives were studied, by incorporating them into the PANI/PAG matrix, to improve its conductivity after irradiation without decreasing the resistance of the non-protonated state. The resistance in its non-protonated state is important for later applications, allowing for only selected areas to be conductive while other areas remain non-conductive. These additives included sites capable of easily forming and breaking hydrogen bonds, to facilitate the transfer of protons from PAG to the imine group on the PANI, in solid state. A successful investigation of polyvinyl alcohol (PVA) as a hydrogen bonding additive to the PANI/PAG system was completed by us in 2011 (Shi, et al. 2011). PVA’s ability to increase the mobility of the protons from the PAG to PANI led to the notion of increasing the oxygen content to further increase both the proton mobility and electric conductivity. Polyethylene glycol (PEG) contains oxygen within the polymer as opposed to PVA, which only has an oxygen on the end of the polymeric chain. The amount of oxygen in the matrix, as well as the optimal length of the polymer chain, needed to be investigated for their proton transfer abilities in this PANI/PAG system. Grafting PEG directly onto the PANI was studied to determine whether this might further the proton transfer efficiency from the PAG to the PANI by increasing compatibility of longer PEG chains and
PANI  PEG-grafted PANI was synthesized and its conductive properties were studied for the PANI/PAG material.
Polychlorinated Biphenyls

History

The history of polychlorinated biphenyls (PCBs) dates back to 1865 when a “PCB-like” chemical was isolated as a byproduct from coal tar. Several years later, in 1881, the first PCB was synthesized in a German laboratory. Such large quantities of PCBs were released into the environment from 1881-1914 that there are still measurable amounts in bird feathers currently held in museums (Riseborough and Brodine 1971). In 1929, the largest commercial producer was Monsanto Company in the United States. The single largest producer of PCBs was the Monsanto Company, with over 600,000 tons produced between 1930 and 1977 (Breivik, et al. 2002). PCB production increased to supply the electrical industry with a less flammable cooling and insulating fluid for industrial transformers and capacitors to replace mineral oil. PCBs were also found to be useful in many applications and started to make their way into urban and industrial areas, they were used as plasticizers in paints and cements, stabilizing additives for PVC coatings, electrical wires, electronic components, pesticide extenders, cutting oils, flame retardants, lubricating oils, sealants in buildings, adhesives, wood floor finishes, water-proofing compounds, and other uses not listed for brevity.

![General Structure of PCBs](image)

**Figure 4:** General Structure of PCBs
PCBs are not naturally occurring compounds and the term is a general one describing over 200 man-made congeners of polychlorinated biphenyls (PCBs) with varying numbers of chlorine atoms at different positions on two benzene rings (Erickson 1997), as shown in Figure 1. Their physical appearance varies from clear to amber in liquid form and white solids with no smell or taste. PCBs have many properties leading to high stability such as non-flammability, good electric insulating properties, low water solubility (0.0027-0.42ng/L), low vapor pressure at room temperature, and high thermal stability (Novaes-Card 2013). These properties led to a wide variety of applications since the late 1920’s. In fact, the very reason PCBs were so useful for so many applications is the same reason they are so hard to remediate; they are very stable and resist most types of degradation. This extremely versatile additive was used in so many different construction applications that it made its way into most of the building materials in the time before it was banned. According to the EPA, every building in the United States built between late 1950s through 1976 is at risk of having PCB contamination.

In 1979 the United States banned PCB manufacture and started a five year plan to phase out most of the industrial uses of PCBs. In the UK, in 1981, using PCBs in closed systems such as in capacitors and transformers was banned in all new equipment. However, it was not until the end of 2000 that the use of existing equipment containing PCBs in excess of 5 liters was stopped.
Health Risks

The US EPA issued that a dose of 0.02 ug/kg/day is an acceptable daily intake of PCBs (Toxicity Summary for Aroclor 1254 1997). Acute PCB exposure has shown to mainly have long-term effects on humans. It is expected to increase risk of cancer and have neurodevelopmental, hormonal effects and cause immunosuppression (Priha 2005). Several peer-reviewed health studies have shown a link between exposure to PCBs and a fatal form of cancer, non-Hodgkin Lymphoma (Kramer 2012) (Bertrand, et al. 2010) (Hardell, et al. 2009).

The health risks of PCBs started to become apparent early on, but were ignored and even denied by the largest PCB manufacturers and producers. In 1937, a paper was published by Drinker, Warren and Bennet in the Journal of Industrial Hygiene and Toxicology describing the toxicity associated with PCBs. The health risks of PCBs were not limited to workers in the Monsanto Company and their families. PCBs were spreading out into the environment and surrounding areas through the widespread use of these contaminated products. The four main ways PCBs are emitted into the environment are through equipment use, thermal processes, incineration of municipal waste and food (Mukesh Kumar, et al. 2013). PCBs have been found in buildings, air, soil, and natural water sources such as lakes and streams. In 1964, a Swedish researcher, Dr. Soren Jensen found a unknown group of chemicals recurring in his human blood samples while trying to study DDT levels. The group of chemicals turned out to be PCBs. He found that even hair samples from his wife and three children showed traces of PCBs with the highest level being in his nursing infant daughter (Francis 1994). These results are evidence that
PCBs contaminated air and soil, spreading to plants and animals and making their way back into food supplies. In 1979, Ritewood Farms, one of the largest chicken farms in the US, found concentrations of PCBs in their chicken to be higher than the upper limit of detection on the test, resulting in almost $3 million in poultry products being destroyed (Robbins 1997). A study was published in 1988 in the Journal of Pollution revealing levels of PCBs in dolphins to be 833ppm, nearly 17 times the level requiring goods to be handled as toxic waste (Tanabe 1988).

Current Treatments Options

Currently the treatments for PCB contaminants are incineration, dredging and landfilling. Incomplete incineration of PCBs can release polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Wu, et al. 2012) which are detrimental to the environment and may be even more harmful than PCBs themselves. Dredging and landfilling (US Environmental Protection Agency n.d.) do not treat the contaminant, only isolate it. Removal of PCB contaminated building materials and disposal of the waste can be difficult and costly due to only 3 Toxic Substance Control Act (TSCA) incinerators and 8 TSCA landfills in the US.

Current PCB Remediation Research Methods

Researchers throughout the world have been studying new more efficient methods to remediate PCBs from contaminated areas. Many researchers have been looking into catalytic hydrodechlorination with transition metals such as iron (Fe), nickel (Ni) or palladium (Pd) and
hydrogen gas (H₂) as a heterogeneous catalyst. Coutts, et al showed that dechlorination of PCB’s with mechanically alloyed Mg/Pd containing 0.1059% Pd gives a degradation rate of 1.22x10⁻³ min⁻¹ g⁻¹ catalyst (Coutts, et al. 2011). Pd/C with triethylamine has also shown to convert PCBs to biphenyl. The triethylamine greatly enhances the catalytic ability of the Pd/C by acting as an electron donor and an HCl scavenger to reduce the adverse effects of the produced HCl (Sajiki, et al. 2002). Some methods involve high temperatures, such as reactions involving sulfided Ni-Mo/Y-Al2O3 in hexadecane or dielectric oil at 523K and 2MPa. The major product is bi-phenyl and HCl. The catalysts are more resistant to deactivation by HCl than noble metal catalyst (Murena 1997) (Murena and Schioppa 2000) (Murena and Gioia 2002). A rotating basket reactor was used to avoid comminution problems encountered with stirring and agglomeration of the sticky powdered catalyst (Tanabe 1988). Iron based reductive dechlorination is also a highly studied method for possible remediation of PCBs. At high temperatures zero valent Fe is able to dechlorinate PCBs without solvents (Chuang, Larson and Wessman 1995). Schreier and Reinhard were able to use alkyl halides at a much lower temperature of 323K (Schreier and Reinhard 1994). Base-catalyzed decomposition has also been studied as a hydrogenation process for remediating PCBs from soil. Soil was mixed with sodium bicarbonate and oil and heated to 473-673K in a rotary reactor, destroying a significant amount of PCBs by promoting hydrogenation of the chlorides (Hu, Zhu and Ding 2011). Researchers are still working on optimizing remediation techniques to achieve the most useful and cost effective methods possible for widespread use.
PCB Research Objectives

Techniques for the degradation of PCBs, using acidified ethanol and magnesium, have shown to be effective. The goal of this research is to gain a further understanding of the mechanism of this degradation, specifically on the lower chlorinated PCB congeners. The complete reduction of higher chlorinated PCBs was explored by focusing on the degradation of lower chlorinated congeners, and confirming the higher chlorinated congeners are not simply being reduced to a lower chlorinated state. GC/MS was used in the analysis of the degradation products of lower chlorinated congeners, allowing for the detection and identification of these lower and non-chlorinated products, which was confirmed with standard reference samples. This research explores the effects of the differing positions of the chlorine atoms in the PCB structure and in the dechlorination reaction of different PCB congeners on the kinetics. The dechlorination patterns of PCBs were studied to allow for more accurate product predictions. The source of the hydrogen was also determined. Understanding the kinetics, degradation patterns and hydrogen source will allow for continued enhancement of this remediation technique and other similar systems.

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CHAPTER TWO: PHOTONANTION AND CONDUCTIVITY OF POLYANILINE/POLYETHYLENE GLYCOL

Introduction

The ability to achieve high conductivities with PANI using photo-irradiation, without the aid of vapor doping, has many sought after advantages. This would have multiple benefits for applications including no harmful acids corroding other parts of a device and leaving the door open for possible lithography type processes. Additives with hydrogen bonding capabilities can increase the efficiency of the proton transport from the PAG, proton source, to the imino groups of the PANI forming the conductive salt. In previous studies, PVA was investigated due to its simple polymer structure with hydroxyl end-groups, available for hydrogen bonding, good solubility, and cost effectiveness. The addition of PVA increased the conductivity from $<10^{-9}$ S/cm to $10^{-3}$-$10^{-2}$ S/cm after irradiation (Shi, et al. 2011). The hydroxyl groups aided in the proton mobility and increased the amount of PANI imino groups protonated, therefor increasing the conductivity.

1 The following chapter is based on work previously published with the title of Photo-induced protonation and conductivity of polyaniline/poly(ethylene glycol) and polyaniline/[poly(ethylene glycol)-grafted polyaniline] composites by Alber, Candace; Shi, Zheng; Johns, Valentine K.; Lafave, Sarah; Liao, Yi in the Journal of Applied Polymer Science (2013), 129(6), 3546-3550.
Figure 5: The conducting salt form of PANI-EB when doped with hydrogen

Figure 6 shows the structure of PEG. This polymer has oxygens available for hydrogen bonding and is known for being a cationic conductive polymer (Ratner and Shriver 1988). This implies that PEG may be able to form a hydrogen bonding network to assist in proton transfer from the PAG in the same manner as PVA; while also having the ability to conduct an abstracted proton along the PEG chain increasing the efficiency of the proton transfer to PANI. The following research was conducted, investigating the use of PEG as an additive to increase conductivity of the PANI/PAG system.

Figure 6: General polyethylene glycol structure
Methods

Materials Characterization

PANI-EB (MW = 20,000), triphenylsulfonium triflate and poly(ethylene glycol) monomethyl ether (PEG MW 550) were purchased from Aldrich. PEG 8000 was purchased from Fisher. All of the solvents were used without further purification. Film thickness was measured by a profilometer. UV-visible spectroscopy was performed on a Varian Cary 50 spectrometer. ATR-IR spectroscopy was conducted on a Perkin Elmer Spectrum One spectrometer equipped with a Universal ATR Sampling Accessory (single reflection, Diamond/ZnSe). IR spectra were collected in the range of 1000-4000 cm\(^{-1}\) with resolution of 1 datum every 2 cm\(^{-1}\). Elemental analysis was conducted at Micro-Analysis, Inc.

Figure 7: Picture of a typical PANI sample spin coated onto a glass substrate with gold electrodes, used for conductivity testing
Preparation and Irradiation of the Thin Films

PANI and PEG were dissolved in \textit{N}-methylpyrrolidinone (NMP) and mixed with a solution of triphenylsulfonium triflate, the commercial photoacid generator (PAG) used in this study, dissolved in NMP. The overall solid to solvent ratio (weight) was \(~1:10\). The resulting solution was filtered through cotton. Thin films of the composites were prepared by spin casting on glass substrates with gold electrodes, Figure 7. Each thin film was placed in a vacuum oven at room temperature for 24h to remove the solvent. These samples were irradiated in a RPR-100 photochemical reactor equipped with 254nm UV lamps. The conductivity before and after irradiation was measured by I-V scan using a Keithley 2400 source meter. Given that the conductivity of the materials is relatively low and the major application of this type of material is patterning conducting circuits on thin films, I-V scan is a suitable method. Some samples were tested using the four point probe method. The conductivities of these samples were in the same order of magnitude as the values obtained by I-V scan.

Analysis

Results and Discussion

Composites of PANI-EB/PAG often result in low increases in conductivity upon photo-irradiation. The main factors that cause low conductivities are low proton transfer efficiency from the PAG to the PANI-EB and film quality. A previous study showed, adding PVA increases the final conductivity by introducing a hydrogen bonding network that assists proton...
transfer and by improving film quality (Shi, et al. 2011) (Foreman and Monkman 2003). This work shows the addition of a proton transfer polymer to PANI/PAG is an effective way of improving conductivity. Polyethylene glycol (PEG) is a well-known cationic conducting polymer and has been used for protonic conduction (Ratner and Shriver 1988) (Tang, et al. 2012) (Shukur, et al. 2012) (Ibrahim, et al. 2012). The weak basic ether groups of PEG can bind to protons, as shown in Figure 8. Protons can move from the binding oxygen to an adjacent ether oxygen and/or to the oxygens on a nearby chain segment. If there is sufficient segmental mobility the proton can migrate downfield with an applied external field (Barker 1976). Therefore, PEG may have the ability to increase the efficiency of protonating PANI with a PAG by increasing the mobility of the proton from the PAG. It should also be noted that PEG is commonly added as a plasticizer to avoid phase separation by hydrogen bonding with the glycol groups (Ratner and Shriver 1988) (Li, et al. 2012) (Hardy and Shriver 1984) (Hardy and Shriver 1985).
Figure 8: A schematic of low-MW PEG assisting in proton transfer to PANI. The oxygen groups of the PEG are capable of assisting in proton transfer via the formation of a hydrogen bonding network with the PANI and/ or conducting the cation into a closer position to the imino group of the PANI.

In this work, composites of PANI-EB, PAG and PEG were studied. The PAG chosen for these studies was triphenylsulfonium triflate, Figure 9, because of its high quantum yield of 50% (Dektar and Hacker 1990).

Figure 9: Triphenylsulfonium triflate
Theoretically to achieve maximum conductivity, at least 0.5 molar equivalents of PAG must be added to the aniline unit of PANI-EB. However, at this ratio the weight of the PAG is more than that of the PANI-EB. The heavily loaded low MW PAG tends to form macrophases, which lowers the film quality, and reproducibility as well as the photo-induced conductivity (Venugopal, et al. 1995). Previous work by Chiang and MacDiarmid showed that the conductivity does not increase significantly when the protonation of PANI increases from 25% to 50% (Chiang and MacDiarmid 1986). It was observed that lowering the molar ratio of PAG:PANI-EB to 25% significantly improved the film quality and reproducibility, and in most cases gave higher photo-induced conductivity than the samples with 50% ratio. (Molar ratio of the polymers mentioned refers to that of the corresponding monomers.) Figure 10 shows the effects in conductivity of different molar ratios of PEG added to a fixed 4:1 molar ratio of PANI-EB:PAG.
The quality of the thin films also contributes to the ability of a thin film to reach high conductivities. Low molecular weight PEG (MW=550) is a viscous liquid, which aided in the ability to make thin films with good quality and stability in air prepared from NMP solutions of the PEG, PANI-EB and PAG. No phase separation or pasty form was observed even when the weight ratio of PEG:PANI-EB is as high as 1:1. This result indicates that the low MW PEG has good compatibility with PANI-EB, which, as described in the IR analysis below, is at least partially due to the hydrogen bonding between PEG and PANI-EB. Several ratios of PEG:PANI-EB where tested from 1:10 to 1:1. After irradiation at 254nm, the conductivity of the thin films with a weight ratio (PEG:PANI-EB) of 1:2 increased from $10^{-9}$ S/cm to $10^{-1}$-$10^{0}$ S/cm. When the ratio was significantly higher or lower than 1:2, the conductivity decreased. The photo-induced conductivity is comparable to the conductivity of common PANI-salt synthesized
by oxidizing aniline in the presence of an acid. The value is also ~two orders of magnitude higher than that of the previously reported composite with PVA as the proton transfer additive (Shi, et al. 2011).

Figure 11: UV-Vis spectra of PANI-EB/PEG/PAG thin film (a) before irradiation, (b) after irradiation at 254nm

The color of the thin film showed obvious signs of protonation of the PANI-EB by changing from blue before irradiation to green after irradiation. A UV spectrum of the PANI-EB/PAG/PEG mixture shows the characteristic peaks of polyaniline in emeraldine base form before irradiation with a peak at 650nm attributed to an intermolecular and/or intramolecular charge-transfer process from the benzenoid to quinoid ring. After the thin film was irradiated with 254nm light this peak at 650nm disappeared indicating the absence of the exciton in the
polaron lattice formed with protonation of the imino groups (Natesan, Karan and Katiyar 2006) (Figure 11). Two more peaks also appeared centered at 420nm and centered at 850nm. These peaks are due to the polaron-π* and π-polaron transition (Quillard, et al. 1995).

ATR-IR spectroscopy was used to study the hydrogen bonding and the proton transfer in the material (Figure 12). The peak at 1258cm\(^{-1}\) appears due to the partial overlap of C-N stretching vibration from the PANI and the methyl end of the PEG chain. A new peak appears at 2880cm\(^{-1}\) also representing the C-H stretch of the PEG chain. A peak at 1160cm\(^{-1}\) is attributed to the ether bonds of the PEG. The characteristic peak located around 1590cm\(^{-1}\) represents the quinoidal ring stretches of C=C and C=N. Generally, shifts of this peak are due to interactions with the quinoidal nitrogen. The addition of hydrogen bonding networks will cause a slight shift and proton transfers cause a major shift in this peak. A film of PANI-EB alone showed a peak of 1590cm\(^{-1}\), which shifted slightly to 1597cm\(^{-1}\) with the addition of PEG. This slight shift is similar to the shift of 7cm\(^{-1}\) that was observed with the addition of methanol to PANI, which was attributed to the hydrogen bonding (Zhou, Wu and Kan 2007) (Patil, et al. 2011). Therefore the 7 cm\(^{-1}\) observed in this work is attributed to the hydrogen bonding between PANI and the hydroxyl ends of PEG. Once the composite thin film was irradiated, a classic shift to 1575cm\(^{-1}\) was observed indicating the protonation of PANI (Ghadimi, et al. 2002).
Figure 12: ATR-IR spectra of PANI-EB/PEG/PAG thin film (a) before irradiation, (b) after irradiation at 254nm

PEG with a $M_n$ of 8,000 was also studied as a proton transfer additive. Thin films of PANI-EB/PAG/PEG 8000 were prepared, in which the ratio of PEG:PANI was 0.5. After irradiation with 254nm UV light, the conductivity was $10^{-3}$-$10^{-2}$ S/cm which is much lower than that of the composite with low-MW PEG. It is well known that ion mobility in polymers is related to the segmental motions of the polymer (Barker 1976) (Ratner and Shriver 1988) (Fuoss 1941). Chains of the high-MW PEG are expected to be less mobile in the thin film than those of the low-MW PEG, which may lower the proton transfer efficiency. In addition, we noted that the film quality and reproducibility of the composite with PEG 8000 are worse than both the composite with PEG 550 and the composite with PVA, which indicate that the compatibility between PEG 8000 and PANI-EB is not good. As described above, compatibility between PEG
and PANI relies on the hydrogen bonding between them. Hydrogen bonding between the hydroxyl ends of PEG and the imino groups of PANI is much stronger than the one between the ether groups of PEG and the amino groups of PANI. PEG 550 has ~15 times more hydroxyl groups than PEG 8000, which makes it more compatible with PANI, and thus a better proton transfer additive. In fact, IR of the PEG 8000/PANI-EB composite did not show any positive shift of the quinoidal ring stretch at 1590 cm$^{-1}$ in contrast to that of PEG 550/PANI-EB (Figure 13).

![Figure 13: ATR-IR spectra of (a) PANI-EB, (b) PANI-EB/PEG 550, and (c) PANI-EB/PEG 8000 thin films](image)
Conclusion

This work shows that addition of low-MW PEG to PANI-EB/PAG can significantly increase the photo-induced conductivity to $10^{-1} - 10^{0}$ S/cm without post treatment with HCl. The improvement could be due to the formation of a hydrogen bonding network formed with the oxygens in the PEG structure. This network allows the protons to be more mobile than in the PANI/PAG system and reach more imino groups of the PANI and increases the overall film quality by reducing the amount of visible macrophases. The increase in conductivity is attributed to both the good proton transfer ability of PEG and good compatibility between low-MW PEG and PANI-EB. The higher MW PEG showed decrease in film quality and resulted in lower conductivity after irradiation. This was attributed to lower compatibility of the high MW PEG and PANI-EB. Grafting a higher MW PEG directly to PANI-EB may help decrease these issues.
CHAPTER THREE: PHOTOINDUCED PROTONATION AND CONDUCTIVITY OF POLYANILINE/[POLYETHYLENE GLYCOL-GRAFTED POLYANILINE]²

Introduction

Achieving maximum conductivity without the use of vapor doping is desired, to increase the applicability of PANI for lithography and many other applications. In the previous chapter, composites of PANI/PEG/PAG were observed to be able to increase the photo-induced conductivity of PANI to $10^0$ S/cm without vapor doping. Previous studies have shown that grafting short PEG chains to a polymer can increase its ion conductivity (Ratner and Shriver 1988) (Barker 1976) (Blonsky, et al. 1984) (Binks and Sharples 1968). Grafting PEG to PANI could avoid the potential compatibility issue (Wang, et al. 2001) (Ratner and Shriver 1988).

Methods

Materials and Characterization

PANI-EB (MW = 20,000), triphenylsulfonium triflate, and poly(ethylene glycol) methyl ether tosylate were purchased from Aldrich. All of the solvents were used without further purification. Film thickness was measured by a profilometer. UV-visible spectroscopy was performed on a Varian Cary 50 spectrometer. ATR-IR spectroscopy was conducted on a Perkin

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Elmer Spectrum One spectrometer equipped with a Universal ATR Sampling Accessory (single reflection, Diamond/ZnSe). IR spectra were collected in a range of 1000-4000 cm\(^{-1}\) with resolution of 1 datum every 2 cm\(^{-1}\). Elemental analysis was conducted by Micro-Analysis, Inc.

Synthesis of PEG-Grafted PANI Derivatives

The PEG grafted PANI derivatives were synthesized following literature procedures with some modifications (Wang, et al. 2001) (Hwang, et al. 1998). PANI-EB (50 mg) was reacted with (20 mg) sodium hydride in (5 mL) anhydrous dimethyl sulfoxide and allowed to stir for 6 h at 45°C. 1 molar equivalents of poly(ethylene glycol) methyl ether tosylate [PEG(1000)tosylate] was added and allowed to stir at room temperature overnight. The product was precipitated out using a brine solution and washed several times with water and dried overnight. Elemental analysis: %C: 56.7, %H: 7.32, %N: 4.88.
Figure 14: Synthesis scheme of PEG grafted PANI

Preparation and Irradiation of the Thin Films

PANI and PEG grafted PANI were dissolved in N-methylpyrrolidinone (NMP) and mixed with a solution of triphenylsulfonium triflate (PAG) in NMP. The overall solid to solvent ratio (weight) was ~1:10. The resulting solution was filtered through cotton. Thin films of the composites were prepared by spin casting on glass substrates with gold electrodes. Each thin film was placed in a vacuum oven at room temperature for 24h to remove the solvent. These samples were irradiated in a RPR-100 photochemical reactor equipped with 254nm UV lamps. The conductivity before and after irradiation was measured by I-V scan using a Keithley 2400
source meter. Given that the conductivity of the materials is relatively low and the major application of this type of material is patterning conducting circuits on thin films, I-V scan was found to be a suitable method as mentioned in the previous chapter.

Analysis

Results and Discussion

PEG grafted PANI was synthesized by attaching short PEG chains (Mₐ 1000) to the imino groups of PANI-EB (N-PEG-PANI) following a literature method. The only modification is that PEG(1000) tosylate instead of PEG halide was used due to availability. A 1:1 molar ratio of PANI(aniline unit):PEG(1000)tosylate was used in the synthesis of this N-PEGPANI. The synthesized polymer has an oxygen/nitrogen ratio of 6.37 based on elemental analysis, which indicated that approximate 1.1 out of every four nitrogen atoms in the polyaniline was linked to a PEG chain (Figure 14). To estimate the maximum conductivity of the polymer after being fully protonated, thin films of the polymer were treated with HCl vapor. Consistent with previous reports the doped N-PEG-PANI showed a lower conductivity than PANI salt (Wang, et al. 2001) (Li and Ruckenstein 2004) (Ma, et al. 2006). After vapor doping with HCl, the conductivity of N-PEGPANI was only 10⁻² S/cm. However, when the N-PEG-PANI polymer was mixed with PANI-EB at a weight ratio of 1:2, the composite showed a conductivity as high as 10² S/cm after treatment of HCl vapor. Therefore, thin films of PANI-EB/PAG/N-PEG-PANI composite were prepared for studying photo-induced conductivity. The weight ratio of PANI-EB:N-PEG-PANI was 2:1 and the molar ratio of PANI-EB:PAG was 2:1. The UV spectrum of the N-PEG-
PANI/PANI-EB/PAG thin film (Figure 15) shows the classic 650nm peak attributed to an intermolecular and/or intramolecular charge-transfer process from the benzenoid to quinoid ring is visible before irradiation. After irradiation, this peak at 650nm disappears and a peak at 420nm appears, similar to the PANI/PEG/PAG system, indicating the conducting PANI-EB salt formation. After irradiation at 254nm, a change in conductivity from \(<10^{-9}\) S/cm to \(10^{-2}-10^{-1}\) S/cm was achieved. Although the value is relatively high, it is lower than that of the composite with PEG 550. Given that N-PEG-PANI can also be protonated, the amount of PAG in the composite was doubled. However, the photo-induced conductivity was lowered by approximately an order of magnitude, which is attributed to phase separation of the heavily loaded PAG. It may also be important to note that the PEG 550 used in the previous study had a hydroxyl end group, while the grafted PEG had a methyl end group. It may be possible that the low MW PEG had an increased hydrogen transfer with these hydroxyl end groups, since a slightly lower conductivity can be achieved with PVA (Shi, et al. 2011).
Figure 15: UV-Vis spectra of N-PEG-PANI/PANI-EB/PAG thin film (a) before irradiation, (b) after irradiation at 254nm

**Conclusion**

This study has demonstrated that PEG grafted PANI-EB can also be used as an effective additive to PANI. The high conductivity ($10^2$ S/cm) of the HCl-vapor doped PANI-EB/N-PEG-PANI composite indicates that this is a promising system. Although the photo-induced conductivity of PANI-EB/PAG/N-PEG-PANI composite is lower than that of PANI-EB/PAG/PEG550, the system may be improved by developing PAGs with better compatibility.
CHAPTER FOUR: CONCLUSION: POLYANILINE

The goal of these polyaniline studies was to explore the effects of the addition of a possible hydrogen bonding network into a PANI-EB/PAG system. In this system the PANI is in its non-conductive EB form with a PAG dispersed throughout this thin film. When the system is irradiated the PAG acts as a Bronsted acid, releasing a proton. This proton must make its way to an imino group of the PANI-EB to form the conductive salt form of PANI. The two major issues in achieving high conductivities with a PANI/PAG system are the physical transfer of a proton to the PANI imino group in this solid, thin film state and the film quality being too low. Film quality can be highly affected by several factors such as the ratios of PANI to PAG and compatibility of the structures. Macrophases can be formed which block the protons from being able to transfer efficiently. The addition of a hydrogen bonding network helps improve the film quality and avoid the formation of macrophases. This network can also provide another route for the proton to transfer to the imino group on the PANI.

Low MW PEG was added to the PANI/PAG system increasing its photo-induced conductivity to $10^{-1}$-10$^0$ S/cm without post treatment with HCl. The PEG’s structure includes ether groups that can provide multiple hydrogen bonding sites in each strand. This network along with the cationic conductive capabilities of the PEG allows the protons to be more mobile and reach more imino groups of the PANI and increasing the overall film quality by reducing the amount of visible macrophases. The increase in conductivity is attributed to both the good proton transfer ability of PEG and good compatibility between low-MW PEG and PANI-EB.
The additional hydrogen binding sites of longer chains of PEG, theoretically, should increase to mobility of the proton from the PAG to the PANI. The ATR-IR of the longer chain (8000) PEG, Figure 13 in the previous chapter, showed a lack of quinoidal shift and a much lower resulting conductivity after irradiation in the PANI/PEG/PAG system. The incompatibility and low resulting conductivity of the PEG 8000 was attributed to the excessive length of the PEG chains, rendering the chains immobile within the thin film state. To increase the compatibility of a longer chain PEG to PANI a PEG grafted PANI was synthesized with a chain length longer than that of PEG 550 and shorter than PEG 8000. PEG grafted PANI-EB was also observed to be an effective additive to PANI. The high conductivity ($10^2$ S/cm) of the HCl-vapor doped PANI-EB/PEG-PANI composite indicates that this is a promising system. Although the photo-induced conductivity of PANI-EB/PAG/PEG-PANI composite is lower than that of PANI-EB/PAG/PEG550.

This research could be continued by looking into PEG with a MW larger than 550 and smaller than 1,000. This study of different MW PEG could also be extended into the PEG grafted PANI-EB. The low MW PEG shows good compatibility, but the efficiency of proton transfer could be increased. The system may be improved by developing PAGs with better compatibility. A PAG with high quantum yield and smaller size would be more ideal for proper dispersion into the thin film. A small PAG that could be grafted onto the PANI-EB may also solve the compatibility and dispersion problem and drastically increase photo-induced conductivities. The next major goal of this research would go into photo-lithography, studying
the resolution with either a mask or laser irradiation of specific patterns on the PANI/PAG system.
CHAPTER FIVE: SUBSTITUTENT POSITION EFFECTS ON PCB DEGRADATION

Introduction

PCBs are considered persistent organic pollutants (POP) due to their widespread presence in the environment and the inability of most biological systems to degrade them. There are 209 different congeners of this man-made chemical. The physical properties, such as low electrical conductivity, non-flammability and chemical inertness, made these chemicals very attractive as additives to many industrial products. The Monsanto company mass produced PCBs with an industrial scale reaction of biphenyl and chlorine gas. This process resulted in a mixture of several different congeners. These mixtures were sold under the trade name Aroclor 12XX. The 12 referring to the number of carbons in biphenyl and the XX number represented the mass percentage of chlorine by mass contained in the mixture.

Monsanto Company produced and sold over 600,000 tons of PCBs before their manufacture was banned by the United States Environmental Protection Agency (USEPA) in 1979. PCBs are labeled as a possible carcinogen and studies have shown increases in not only the risk of cancer, but also the risk of neurodevelopmental effects, hormonal effects and immunosuppression (Priha 2005) from PCB exposure. Ironically, the same physical properties that made these aroclors so attractive to industrial applications are the same properties that have made degradation so difficult. Over the decades, the widespread industrial use and careless disposal of PCB laden products have spread this particular POP worldwide. PCBs have been found contaminating most urban and commercial areas including most buildings that were
constructed between 1950 and 1976 as well as our oceans and food supplies. With the low water solubility of PCBs, they tend to concentrate in fatty acids of living animals and are not readily broken down by metabolic processes. The United Nations composed the *Stockholm Convention on Persistent Organic Pollutants* identifying 12 specific compounds, including PCBs, as the “dirty dozen”.

Halogenated aromatic compounds, such as PCBs, have long shown to be difficult to degrade in mild conditions requiring much higher temperatures (Chuang, Larson and Wessman 1995) and increased pressures (Yak 1999). Doyle et al used Fe and Fe/Pd systems, at room temperature and atmospheric pressure, which led to the idea of using zero-valent magnesium (ZVMg) with a much larger reduction potential of 2.37V, compared to zero-valent iron’s reduction potential of 0.44V (Doyle 1998). The reduction potentials of various PCBs ranging from 1.891V to 2.317V were published by Rusling and Miaw (Rusling and Miaw 1989). The higher reduction potential of the ZVMg implies the ability for the ZVMg to reduce PCBs without the aid of the more expensive Pd. This chapter focuses on the effects of the position of the substituent on the biphenyl ring in the degradation of PCBs with ZVMg in acidified ethanol.

Previous research, by the UCF Industrial/Environmental lab, has demonstrated that higher chlorinated PCBs such as PCB 151 (Maloney 2013) and aroclors (Novaes-Card 2013) can be dechlorinated into lower chlorinated PCBs with zero valent magnesium (ZVMg) and acidified ethanol. These studies did not focus on the dechlorination of lower chlorinated PCBs or the mechanism of this dechlorination reaction. This research focuses on the ability of ZVMg in acidified ethanol to dechlorinate the lower chlorinated homologs into biphenyl and on the
mechanism of this reaction. Biphenyl is classified by the USEPA as a group D chemical meaning that it is not a human carcinogen and can also be degraded further biologically into non-toxic compounds, unlike PCBs. While investigating the ability of the ZVMg to reduce mono and dichlorinated homologs, it was observed that the position of the chloride on the biphenyl ring played a large role in the rate at which the mono and dichlorinated PCBs could be dechlorinated into biphenyl. The preference of the dechlorination pathway of PCBs was the first step to the mechanistic investigation of this reaction. Gas chromatography mass spectrometry (GCMS) was used to identify PCB homologs and biphenyl, retention times of standard reference samples was used to positively identify individual PCB congeners.

Methods

Materials and Chemicals

PCB standard solutions were prepared by diluting the neat standards purchased from Accustandard with absolute ethanol. The absolute ethanol was obtained from Pharmco-AAPER and used without any further purification. Mirco-scale magnesium (4μm nominal diameter) was purchased from Hart Metals, Inc. and ball milled with the optimal parameters for PCB degradation (Aitken, et al. 2006) prior to use. Glacial acetic acid and toluene were purchased from Fisher scientific.
Experimental Procedure

PCB standard solutions were used to prepare 2.5ng/μL solutions for degradation tests. Ball milled Mg (250mg) was weighed into a 20mL borosilicate glass vial, with polytetrafluoroethylene (PTFE) cap, and 5mL of PCB solution was added followed by 50μL of glacial acetic acid. The vial was then capped and shaken by hand immediately before shaking continuously on a Cole Parmer EW-51401-06 shaker table with a set time period.

The extraction process was started by adding 5mL of toluene to the sample vial and shaken by hand for 2 mins before transferring to a centrifuge tube and centrifuging for 10 mins. The clear liquid aliquot was poured out and filtered through a syringe equipped with a Millipore 25-mm (0.45μm pore size) nylon syringe filter, to remove any remaining solid Mg. Deionized (DI) water was added (5mL), shaken vigorously and centrifuged for 20 mins, to separate the organic and aqueous layers. The addition of the DI water was repeated if the sample pipetted off of the top was cloudy and not clear. Samples were then analyzed by GC/MS. The lowest energy configuration calculations were estimated using Gaussian 09, Revision A.02 using method B3LYP with the basis set as cc-pVDZ for the optimization calculations.

Analysis

All lower chlorinated samples, PCBs with less than four chlorines, were analyzed using a Agilent 6850 gas chromatograph with a mass spectrometer detector (GC/MS) equipped with a Restek RTX-5 capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness). Degradation was confirmed by disappearance of the specific PCB peak and the corresponding appearance of
lower chlorinated congener peaks as well as a biphenyl peak. Identity of degradation products were determined by mass spectrometry and/or standard references.

**Results and Discussion**

**Monochlorinated PCB Degradation**

PCBs 1, 2, and 3 are the mono-chlorinated homologs, shown in Figure 16. PCB 1 (2-chlorobiphenyl) takes the longest time to dechlorinate, with this system of ZVMg and acidified ethanol, to concentrations below detectable limits. PCB 1 took four days to reduce to 55% of its original 5ng/µL concentration (Figure 17). While PCB 2 (3-chlorobiphenyl) is undetectable by GCMS in four days (Figure 18) and PCB 3 (4-chlorobiphenyl) is undetectable in approximately 5 hours, shown in Figure 19. The monochlorinated PCBs follow second-order rate during this degradation with respect to the decreasing concentration of the PCB.

![Figure 16: Structures of monochlorinated homologs.](image)

A) PCB1 (2-chlorobiphenyl)  
B) PCB 2 (3-chlorobiphenyl)  
C) PCB 3 (4-chlorobiphenyl)
Figure 17: Dechlorination of PCB 1 with zero-valent magnesium in acidified ethanol

Figure 18: Dechlorination of PCB 2 with zero-valent magnesium in acidified ethanol
Figure 19: Dechlorination of PCB 3 with zero-valent magnesium in acidified ethanol

This dechlorination system seems to follow an ortho/para preference. PCB 1, having a chloride in the ortho position, is much slower likely due to the steric hindrance of the neighboring phenyl group. This phenyl group is large and can impede the ability for PCB 1 to come into contact with the ZVMg surface in such a way that the ZVMg can react with the chlorine and the chlorinated carbon.

Ortho/Para Preference of a Dichlorinated PCB

The preference for the degradation reaction to occur at the ortho/para positions was further explored by looking first at a dichlorinated PCB. PCB 5 (2,3-dichlorobiphenyl) has a chlorine in the ortho and meta position to the phenyl group, shown in Figure 20. Due to the
ability of the ZVMg to replace one chlorine at a time from the biphenyl ring the degradation pathway of PCB 5 can be plotted out, shown in Figure 21.

![Structure of PCB 5 (2,3-dichlorobiphenyl)](image)

**Figure 20:** Structure of PCB 5 (2,3-dichlorobiphenyl)
Figure 21: Possible degradation pathways for PCB 5, dechlorinating to biphenyl.

Figure 22: Chromatogram from GCMS of PCB 5 degradation after 3 days in acidified ethanol and ZVMg
The first dechlorination step includes the removal of either the ortho or the meta position chlorine. The effect of the phenyl group indicates that the removal of the ortho position chlorine should be favored first. Figure 22, a chromatogram of PCB 5 after 3 days shaking in acidified ethanol and ZVMg, shows a peak for PCB 2 and no appreciable peak for PCB 1. This observation indicates that the ortho chlorine is favored to be taken first, when more than one chlorine is present on the ring.

**Torsion Effects**

The ability of the ZVMg to interact with the ortho chlorine first, in the case of higher than monochlorinated homologs, can be attributed to the change in conformation of the substituted biphenyl. Gaussian 09, Revision A.02 software estimates that the lowest energy conformation torsion of unsubstituted biphenyl to be 141.03° measured along the 2-1-7-12 position carbons, shown in Figure 23, using method B3LYP with the basis set as cc-pVDZ for the optimization calculations.

**Figure 23:** Gaussian torsion measurements were based on the angle between carbons 2-1-7-12, which are number differently than the numbering convention used for naming PCBs.
The chlorines on PCBs 2 and 3 change the torsion of the biphenyl structure conformation very little with estimations of 140.93° and 141.42°, respectively. This similarity in lowest energy conformation is also observed in the calculated $\Delta G_{aq}$ of 249.0 for PCB 2 and 250.0 kJ/mol for PCB 3 (Harrison 1993). The calculated $\Delta G_{aq}$ do not represent the exact system since these experiments were in ethanol, however, they do give an example of the trends of the molecules conformations. While the estimated torsion of PCB 1 is 125.29° and the calculated $\Delta G_{aq}$ is 259.6 kJ/mol. In a study of the substituents’ effects on the conformation of biphenyls it was observed that there is a gain in conformational stability with increasing ortho substituents on biphenyls, including chlorine substituents (Wolf 2007).

![Figure 24: The rotation of the biphenyl rings is hindered with the addition of ortho substituents](image)

Wolf also states that most ortho-sub biphenyls are conformationally stable with three to four ortho-substituents. Figure 24 shows the biphenyl ring rotated with two ortho substituents hindering free rotation in the biphenyl system. The Gibbs free energy values reported by Harrison are calculated values for the formation of PCBs in an aqueous system. Since these values are not under the same conditions as were used in these studies the exact values are not directly comparable, however the trends can be compared giving an indication of why one
product maybe favored over another. This implies that the favored products usually have a lower $\Delta G_{aq}$.

Effects of Direct Competition of the Ortho, Para, and Meta Positions

PCB 29 (2,4,5-trichlorobiphenyl) is a trichlorinated PCB with chlorines in the ortho, para and meta positions. The study of this PCB allowed for the observation of the direct competition of chlorines in ortho, para, and meta positions on the same ring. Figure 25 shows the possible routes for degradation. The ortho/para favored pathway is in bold in Figure 25, with the para position reacting first, then the ortho position, before finally taking the meta position to form the fully dechlorinated biphenyl species. The degradation pathway of PCB 29 proved to be more difficult to analyze the daughter PCBs (PCB 7,9 and 12) due to the relative speed at which each of the three possible dichlorinated daughter PCBs dechlorinate. PCB 29 degrades to concentrations below GCMS limits of detection in less than 24 hours. Only two dechlorinated daughter peaks, PCB 9 and 12, and PCB 2 were observed after 24 hours in acidified ethanol and ZVMg.
Figure 25: Possible degradation pathways for PCB 29 with the ortho/para preferred pathway in bold.
Figure 26: Structures of PCB 29 (2,4,5-trichlorobiphenyl) and its possible daughter PCBs, PCB 7 (3,4-dichlorobiphenyl), PCB 9 (2,5-dichlorobiphenyl), and PCB 12 (2,4-dichlorobiphenyl).

PCB 12, 9 and 7 were studied to compare their relative rates of degradation, structures shown in Figure 26. It was observed that PCB 12 dechlorinated the fastest, taking only 2 hours to reach undetectable concentration. PCBs 7 and 9 took 8 hours to dechlorinate into their daughter PCBs, see Figure 27 and Figure 28. This makes positive identification of the exact degradation pathway difficult for PCB 29.
Figure 27: The degradation of PCB 7 over 8 hours

Figure 28: The degradation of PCB 9 over 8 hours
When the study was repeated with a higher starting concentration of PCB 29 and with one hour time increments, after one hour a very small peak is visible for PCB 12 (Figure 29) and no peaks for PCB 3 or PCB 1 are observed in any of the time points. This indicates that the removal of the para position chlorine is the favored position in the first step of the dechlorination of PCB 29.

Figure 29: Chromatogram from GCMS for PCB 29 after 1hr in acidified ethanol and ZVMg. PCB 2, 9, 12, and 29 are labeled. The internal standard, PCB 151, appears at 43.5 mins is not labeled.

Ortho/Para Induction Effect Source

Literature resources often refer to the ortho/para directing strength of a phenyl group as moderately directing and a chlorine group as weakly directing. Hammet’s $\sigma$ constant does give an idea of the relative directing strength for a para chlorine and a para phenyl group. The para phenyl group has a $\sigma$ constant of 0.009 and a para chlorine is 0.227 (Hammett 1937). The more positive the $\sigma$ constant the more electron withdrawing the substituent is. The $\sigma$ constant takes the inductive and mesomeric effects into account and in the case of the halogens it causes a partial cancellation. The larger $\sigma$ constant of the para chlorine means that it has less of an inductive effect than the phenyl indicating that the phenyl group has a larger influence on the ortho/para
directing effects of this system. Halogens, such as chlorine, have a very similar electron donating effect to the ring and thus are also characterized as ortho/para directors.

![Reaction Scheme A](image1)

![Reaction Scheme B](image2)

Figure 30: Scheme A shows as magnesium reacts with the chlorine it induces a negative charge on the nearby carbon that can be stabilized by the resonance abilities of the ortho phenyl group. In scheme B the carbocation cannot be stabilized in the same manner.

The inductive effects cause specific positions on a phenyl ring to be more susceptible to nucleophilic attacks by stabilization of the intermediate species. Figure 30 shows two schemes of magnesium reacting with the ortho chlorine in scheme A and the meta chlorine in scheme B. In the meta position reaction, the phenyl group is unable to stabilize the carbanion as it can when the magnesium reacts with the ortho chlorine.
**Figure 31:** Ortho/para influence of the electron donating phenyl group for PCB 29. Each arrow is color coded and includes a letter corresponding to the letter near the position number with the phenyl group’s influence arrows as a.

The influence of both ortho/para directors can be examined with PCB 29. In Figure 31 the arrows are color coded representing the influence of the phenyl directing (black), the 2 position chlorine (blue), the 4 position chlorine (red) and the 5 position chlorine (green). The 5 position chlorine is being influenced by two chlorines, while, the 2 and 4 position chlorines are being influenced by two chlorines and the phenyl group. This reveals a competition between the ortho and para positions for dechlorination. It is proposed that the added availability of the para position versus the ortho position, hindered by the neighboring phenyl group, explains the observed abundance of PCB 9 instead of PCB 12 during the degradation of PCB 29.

Ortho position chlorines on higher chlorinated PCBs could also form a Meisenhiemer type complex, adding more stability to this specie. This intermediate is a pseudo 6 membered ring formed with an ortho hydrogen, the magnesium on the ortho position of the other phenyl
ring. Meisenhiemer complexes can be formed between an arene with electron withdrawing substituents and a nucleophile. The proposed intermediate forms a hydrogen bond between the magnesium and the hydrogen on the ortho position of the neighboring phenyl ring as shown in Figure 32. This figure depicts a negative charge forming on the carbon meta to the phenyl ring, then being delocalized around the biphenyl structure. The stability added by this ability to delocalize the negative charge not only makes the ortho position more reactive, but also can induce the formation of this pseudo 6-membered ring intermediate complex.

Figure 32: Proposed intermediate complex for ortho position dechlorination
Hexachlorinated PCB

In a further investigation of the ortho/para preferences of this system PCB 151 (2,2',3,5,5',6-hexachlorobiphenyl) was studied, shown in Figure 34. PCB 151 was found to rapidly dechlorinate in acidified ethanol and ZVMg, being undetectable in less than 25 mins, Figure 33.

Figure 33: Degradation of PCB 151 in acidified ethanol and ZVMg over 22mins
Using the ortho/para preference pattern and the $\Delta G_{\text{aq}}^{\circ}$, calculated by Harrison and Holmes, the favored degradation pathway was proposed, see Figure 35 and Figure 36. PCB 151 first forms PCB 92 by loss of either the 2 or 6, ortho, position chlorine. Then the next chlorine lost is at the 6, ortho, position of PCB 92 forming PCB 72. PCB 72 then loses the 2’, ortho, position chlorine to form PCB 36. PCB 36 can then form either PCB 11 or 14 with the $\Delta G_{\text{aq}}^{\circ}=222.5$kJ/mol and 225.2kJ/mol, respectively. Both PCB 11 and 14 will break down to PCB 2.

Figure 34: Structure of PCB 151 (2,2’,3,5,5’,6-hexachlorobiphenyl)
**Figure 35**: Proposed degradation pathway for PCB 151. (Top) PCB 151 loss of first chlorine, (Bottom) PCB 92 the loss of the second chlorine
**Figure 36:** Proposed degradation pathway for PCB 151. PCB 72 the loss of the third chlorine forming PCB 36.

**Figure 37:** Chromatogram of PCB 151 after reacting with magnesium in acidified ethanol for 22mins. Two pentachlorinated daughter peaks, PCB 92 and 95 are observed along with two tetrachlorinated PCBs, 72 and 52. PCB 36 is a trichlorinated biphenyl and PCB 11 is a dichlorinated biphenyl appearing as prominanted daughter peaks in the degradation of PCB 151.
Figure 37 is a chromatogram of the degradation product of PCB 151 after 22 mins in magnesium and acidified ethanol. PCB 92 and 95 are the PCBs observed when the first chlorine has been removed. PCB 92 is formed when either the 2 or 6 position chlorine is removed. In PCB 92 the 2 position is more sterically hindered, by another chlorine in the 2’ position, than the 6 position. This indicates that the 6 position chlorine is the chlorine removed to form PCB 92. Using Gaussian 09, Revision A.02 the torsion between the two phenyl rings can be estimated. This estimation reveals that PCB 151 in its lowest energy conformation has a 89.53° torsion between the phenyl rings. This position may allow the magnesium easier access to the ortho chlorines and may hinder the inductive effects of the phenyl ring. This would increase the inductive effects of the chlorines and would result in a higher probability of the 3 or 5 position chlorines to be removed in the first step instead of the 6 position. The removal of the 3 or 5 position chlorine results in PCB 95 which is also observed in Figure 37 as a penta daughter peak. It was also observed that the peaks for PCB 92, 72, and 36 change rapidly, lowering to almost undetectable peak areas within 30 minutes. While PCB 95 and 52 peaks did not significantly decrease in the same time frame. In Figure 38 a 3-D model of PCB 95 is shown with the 89.58° torsion. This amount of torsion between the two phenyl rings may cause the phenyl ring to have less ortho/para directing effects similar to PCB 151. This indicates that the chlorines have a stronger directing effect, however, does not eliminate the phenyl directing effect. The first daughter peak from PCB 95 is PCB 52 resulting from the 2 position chlorine being removed. Figure 40 shows the possible daughter PCBs from PCB 95. Due to the near 90° torsion angle of PCB 95 (Figure 38) the hydrogen on the ortho position has equal ability for a pseudo 6-
membered ring complex to be formed with either ortho chlorines. The appearance of PCB 52 indicates that this intermediate structure (Figure 39) is more thermodynamically favored than the intermediate formed with the removal of a meta position chlorine from PCB 95. It is also implied by the slower rate of degradation of PCB 95 compared to PCB 92, this intermediate (shown in Figure 39) is unable to form a planar molecule and delocalize the negative charge among both rings.

**Figure 38:** 3-D model of PCB 95 with a torsion of 89.58°

**Figure 39:** Proposed intermediate for ortho position in the degradation of PCB 95
Positions 3’ and 3 are sterically available, however both are in meta positions to the phenyl ring and this causes them to be less favored. The neighboring chlorine in the 3 position adds an inductive effect towards the 2 position chlorine. The appearance of PCB 52 verifies that the 2 position is the most favored for the first chlorine removal, shown in the chromatogram of the degradation of PCB 151 (Figure 37).
Figure 40: Proposed degradation pathway for PCB 95 a product from PCB 151.

- PCB 52 (2,2',5,5') \( \Delta G_{aq} = 186.4 \text{ kJ/mol} \)
- PCB 59 (2,3,3',6) \( \Delta G_{aq} = 192.8 \text{ kJ/mol} \)
- PCB 53 (2,2',5',6) \( \Delta G_{aq} = 188.2 \text{ kJ/mol} \)
- PCB 44 (2,2',3,5') \( \Delta G_{aq} = 192.6 \text{ kJ/mol} \)
- PCB 45 (2,2',3,6) \( \Delta G_{aq} = 195.4 \text{ kJ/mol} \)
Conclusion

This work shows the dechlorination of PCBs with ZVMg in acidified ethanol proceeds with a preference for ortho/para positions. The main ortho/para director is the phenyl group, although the chlorines themselves add a directing influence as well. The monochlorinated PCBs showed this preference with a fastest rate of dechlorination for PCB 3, with the chlorine being in the para position. PCB 1 was slower than PCB 2 due to the hinderence of the neighboring phenyl group. The directing abilities of the phenyl group were further observed with the di and trichlorinated homologs. PCB 151 was studied showing same continued pattern of ortho/para directing from the phenyl group. However, the study of PCB 151 also revealed that the torsion of the phenyl groups plays a role in the degradation pathway. The addition of ortho position chlorines increases the torsion of the lowest energy conformation and the relative stability of this conformation. The torsion of PCB 151’s phenyl groups are at a nearly 90° angle decreasing the effect of the phenyl group’s influence, but not eliminating it, and increasing the chlorine groups ortho/para directing effects. This resulted in multiple daughter peaks for some of the PCB homologs in the degradation of PCB 151.
CHAPTER SIX: MECHANISIC ASPECTS OF THE HYDRODEHALOGENATION OF POLYCHLORINATED BIPHENYLS BY ZERO-VALENT MAGNESIUM IN ACIDIFIED ETHANOL

Introduction

Halogenated aromatic compounds have long been shown to be extremely difficult to degrade under mild conditions, with most techniques. Few techniques have shown the ability to dechlorinated at room temperature, and even fewer without the aid of mechanical ball milling. However, ZVMg in acidified ethanol has been shown to dechlorinate PCBs at room temperature without mechanical ball milling. Due to the mild conditions required, this technique lends itself to field applications.

For the use in field applications, the mechanism of this technique needs to be understood to fully optimize this reaction. A mechanism for this reaction has never been fully studied before. In the previous chapter, the ability of this system to completely dechlorinate PCBs into biphenyl was explored along with the degradation pathway preferences. This chapter focuses on the study mechanistic aspects of ZVMg in acidified ethanol, allowing for a mechanism to be proposed.

Methods

Materials, experimental procedure and analysis were performed in the same manner as described in the previous chapter with the exception of the solvents use of deuterated in the hydrogen source experiments. Deuterated solvents were purchased from Cambridge Isotope
Laboratories. All solvents were used without any further purification. GCMS was used to analyze the products to determine if a deuterium was added to the biphenyl ring.

Results and Discussion

Hydrogen Source

The degradation technique studied is classified as a hydrodehalogenation reaction, removing one chlorine at a time from the biphenyl ring and replacing it with a hydrogen. The source of this hydrogen was investigated with a series of experiments using deuterated methanol instead of ethanol due to cost and availability of deuterated ethanol. PCB 151 was selected for these tests due to its relatively fast reaction rate allowing for several PCB homologs to be detected after reacting for 24 hours. Figure 41 is the mass spectrum of a di-chlorinated homolog product with a mass to charge ratio (m/z) of 222 from a degradation of PCB 151 in methanol and deuterated acetic acid. The m/z ratio of the dichlorinated daughter peak matches the reference m/z ratio of a dichlorinated homolog, this indicates that hydrogens were added to PCB 151 instead of deuterium and the acetic acid is not the source. Figure 42 shows a similar mass spectrum of the dichlorinated homolog product with the use of dried methanol and dueterated acetic acid. In both cases all the identified homologs match the reference m/z, as seen in Table 1.
Figure 41: Mass Spectrum of a dichlorinated PCB product from the degradation of PCB 151 in dried CH$_3$OH and CH$_3$COOD

Figure 42: Mass Spectrum of a dichlorinated PCB product from the degradation of PCB 151 in dried CH$_3$OH and CH$_3$COOD
Table 1: Mass Spectra m/z values for the PCB homolog products of the degradation of PCB 151 in methanol and acetic acid

<table>
<thead>
<tr>
<th>PCB Homolog</th>
<th>Reference</th>
<th>Dried CH$_3$OH + CH$_3$COOD</th>
<th>CH$_3$OH + CH$_3$COOD</th>
<th>CH$_3$OD + CH$_3$COOH</th>
<th>CD$_3$OD + CH$_3$COOH</th>
<th>CD$_3$OD + CD$_3$COOD</th>
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</thead>
<tbody>
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<td>188</td>
<td>188</td>
<td>192</td>
<td>193</td>
<td>193.1</td>
</tr>
<tr>
<td>Di</td>
<td>222</td>
<td>222</td>
<td>222</td>
<td>225.1</td>
<td>226</td>
<td>226.1</td>
</tr>
<tr>
<td>Tri</td>
<td>256</td>
<td>255.9</td>
<td>255.9</td>
<td>-</td>
<td>258.9</td>
<td>-</td>
</tr>
<tr>
<td>Tetra</td>
<td>292</td>
<td>291.9</td>
<td>291.9</td>
<td>294</td>
<td>293.8</td>
<td>294</td>
</tr>
<tr>
<td>Penta</td>
<td>326</td>
<td>325.8</td>
<td>325.9</td>
<td>326.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Partially deuterated methanol with acetic acid was tested, resulting in an increase in the m/z of all of the identified homologs, however, not all of the chlorines removed from the biphenyl where replaced with a deuterium (Table 1). The penta and the tetra homologs revealed an expected m/z. The di and mono homologs each showed one less deuterium added to the ring than expected. The mass spectrum of the dichlorinated homolog from the partially deuterated methanol and acetic acid is shown in Figure 43. In this test, the tri homolog did not have a high enough concentration to reveal a clear mass spectrum for comparison. To identify whether this hydrogen is from the methyl group of the partially deuterated methanol or an environmental condition, such as humidity, two more tests were completed with fully deuterated methanol. One test used acetic acid and the other deuterated acetic acid. Both tests revealed similar results.
showing the deuterium added to all the expected positions. The mass spectrum of the dichlorinated homologs from the fully deuterated methanol with acetic acid and fully deuterated methanol with deuterated acetic acid are shown in Figure 44 and Figure 45, respectively. The two fully deuterated tests reveal that the hydrogen added with partially deuterated methanol came from the methyl group and not the acetic acid or other experimental conditions. The hydrogen source experiments concluded that the hydrogens added in the hydrodehalogenation reaction are from the protic solvent, with the majority of the hydrogens coming specifically from the hydroxyl end of the methanol.

**Figure 43:** Mass Spectrum of dichlorinated PCB product from the degradation of PCB 151 in CH$_3$OD and CH$_3$COOH

**Figure 44:** Mass Spectrum of dichlorinated PCB product from the degradation of PCB 151 in CD$_3$OD and CH$_3$COOH
Figure 45: Mass Spectrum of dichlorinated PCB product from the degradation of PCB 151 in CD$_3$OD and CH$_3$COOD
The pH of the reaction was tested by wetting pH strips and then adding a few drops of the reaction solution, shown in Figure 46. It was observed that the pH of the ethanol goes from 7 to 4 with the addition of the acetic acid. The pH then goes from 4 to 11 in seconds after contact with the ZVMg. This provides further proof that the acetic acid is not the proton source due to the acetic acid existing in its conjugate base form during the extended reaction periods with PCBs.

![pH strips](image)

**Figure 46:** pH strip tests. The top strip is ethanol only giving a pH of 7. The middle strip is after 50uL of glacial acetic acid was added and the resulting pH was 4. The bottom strip is after the acidified ethanol was added to ZVMg resulting in a pH change to 11

**Mechanism**

The methanol providing the hydrogen in this hydrodehalogenation reaction implies that the protic solvent is the hydrogen source and also gives insight into the exact mechanism of the hydrodechlorination for this remediation technique. The generalized mechanism is Grignard-like and graphically shown in Figure 47 and a mechanism showing the dechlorination of PCB 5 is shown in Figure 48. The acetic acid cleans the surface of the magnesium and helps initiate the
surface Grignard formation. When a PCB gets into the proper position, near an activated site on
the ZVMg surface, an electron is accepted into the carbon-halogen anti-bonding orbital from the
magnesium surface producing an anion radical in close association with a univalent magnesium
cation (Walborsky 1990). The collapse of this tight radical pair (Figure 47 the upper path) or
dissociation (Figure 47 the lower path) forms a Grignard reagent. However, the lower path can
also form MgX₂. These two possible paths account for retention and racemization in this general
Grignard mechanism. In the case of the Grignard-like mechanism proposed graphically in
Figure 48, this formation of this cyclic bond-like association between the carbon, chlorine and
magnesium causes an induced partial negative charge on the neighboring phenyl carbon. This
induced charge is delocalized throughout the ring and influences preference of the magnesium
attack by stabilizing the intermediate. The dipole formation between the magnesium and the
phenyl ring causes the phenyl to immediately attack the hydrogen on the protic solvent. This
attack abstracts a hydrogen and results in the dechlorination of at least one chloride on the
biphenyl. This continues to repeat until the PCB has been reduced to biphenyl. The favored
hydrogen abstraction is from the alcohol in of the protic solvent, forming a charged oxide group.
However, the radical structure formed is very reactive, as discussed in a previous section, and a
hydrogen can be abstracted from the methyl end of the protic solvent. This methyl end hydrogen
abstraction is not the favored abstraction, as demonstrated by the experiments with deuterated
methanol.
Figure 47: The generalized surface radical mediated reaction mechanism for this Grignard-like reaction.
Figure 48: Surface radical mediated Grignard-like mechanism for the first step in the dechlorination of PCB 5

The hydrogen source tests not provided the confirmation that the protic solvent is the source, and also imply that this reaction involves a surface mediated radical (Walborsky 1990). It was also reported by Teerlinck and Bowyer, that a surface radical mediated Grignard is less affected by the presence of oxygen (Teerlinck and Bowyer 1996). However, the addition of a hydrogen when a partially deuterated methanol, CH$_3$OD, was used, implies that a hydrogen is sometimes extracted from the methyl group. This methyl hydrogen extraction is not the favored hydrogen extraction, but does indicate the production of radicals at the surface of the magnesium in this system as well (Walborsky 1990). It is clear that there is minimal methyl hydrogen abstraction.
and the favored mechanism includes a surface mediated radical, similar to the results observed by Walborsky.

The rapid change in pH also indicates that there is no more influence of the acetic acid after the first few seconds; this would lead to the question of how the Grignard-like reagents would continue to form. Silverman states that Grignard reagents can initiate new Grignard reagents to be formed (Silverman and Rakita 1996). This means that the ZVMg is initiated first by the acetic acid and then by the formed PCB Grignard-like reagents.

**Conclusion**

In the previous chapter, the substituent positions were studied with ZVMg in acidified ethanol revealing an ortho/para preference with the phenyl group as the strongest directing effect. To further investigate the mechanism of this dechlorination reaction the hydrogen source was studied using deuterated solvents. The deuterium was added to the PCB with the abstraction of the chlorine only when the deuterium originated on the protonated solvent. These observations indicate a Grignard-like reaction due to this magnesium insertion-like intermediate. The formed Grignard-like reagent is immediately quenched by the protonated solvent. A similar mechanistic conclusion was proposed by Volker Birke in his studies with a mechanochemical process in which the ZVMg is initiated with a mechanical process and the Grignard-like reagent formed immediately removes a proton from an amine (Birke, Schuett and Ruck 2009). The addition of the hydrogen from the hydroxyl end of the alcohol also indicates that the mechanism
for this reaction is a surface mediated Grignard formation as described by Walborsky and Bowyer’s groups. The mechanism proposed by this work is a Grignard-like reaction where the ZVMg is initiated by the acidic acid allowing a univalent magnesium radical to be formed with the donation of an electron to the carbon chlorine bond. These surface radicals form Grignard-like reagents that take a proton from the protonated solvent, removing the chlorine and adding a hydrogen in the same step.
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