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# Surge of Green: A Sustainable Approach to Conductive Polymers

**BETH MASTEN, SHEA SCHOLAR**

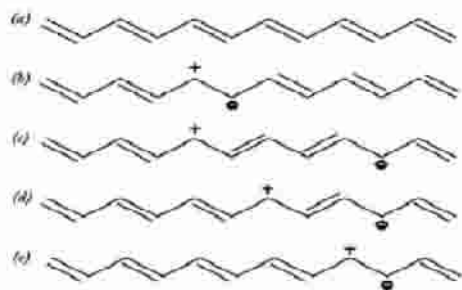
Beth Masten is currently a graduate student at Carnegie Mellon University working towards a doctorate in Chemistry. This paper was made possible thanks to the Adrian Tinsley Program and the Shea Scholar Program. Beth would like to extend her gratitude to her mentor, Dr. Ed Brush, and the Chemistry Department at Bridgewater State College.

## Introduction

Chemists are known for their ability to take natural resources and, through a series of chemical processes, convert them into useful materials ranging from agricultural chemicals to pharmaceuticals. Plastics are a unique subset of these materials in that they are polymers: substances composed of long chains of connected molecules, the chemical equivalent of a string of pearls. Polymers have unique properties that arise from the way the monomer subunits are strung together. Although some polymers are naturally occurring, such as skin, bones, wood, and fibers, a great deal of the others are synthetic (1). Following the emergence of the field of polymer chemistry in the 1920's came the booming use of polymers in the 1950's plastic industry. Long prized for their applications in the textile, pharmaceutical, agricultural, electronics, and automotive industries, polymers are used today in the largest quantity of all synthetic materials (1). Such was the history that 'set the stage' for the development of conductive polymers, according to Laureate Dr. Alan Heeger during his address upon receiving the 2000 Nobel Prize in Chemistry for his part in the development of conductive polymers.

Conductive polymers are a class of chemical materials characterized by the ability to conduct electricity along their long molecular chains - they are essentially plastics that can carry an electric current (2). Unlike conventional polymers, the ability of conductive polymers to act as charge carriers arises from the presence of extensive conjugation along the polymer backbone. This conjugation itself does not give rise to the conductive properties of polymers; rather, it is when the material becomes "doped," when negative charges (electrons) and positive charges ("holes") are introduced into the material. As electrons jump from neighboring positions to fill in holes, new holes are formed and charges can be carried along long distances (Figure 1).

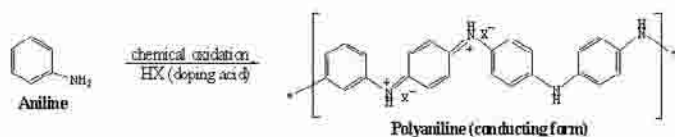
Figure 1. Schematic of Polaron Formation (a-b) and Migration (c-e) in Undecahehexane (3).



The development of plastics capable of conducting electricity has numerous and exciting potential applications. Among those listed in a 2003 *Business Week* article (3) are “smart tags” that can be cheaply processed and easily imprinted onto all manner of commercial goods, “video wallpaper” capable of turning entire walls into affordable television screens, ultra-tiny transistors, and even electronic newsprint. Additional applications are unique to biodegradable conductive plastics, including the potential to act as nerve guidance channels: conduits onto which two severed nerve ends can be attached for repair of nerve damage (4). Conductive polymers are currently used for electromagnetic shielding, as corrosion inhibitors, in electroluminescent and cellular phone displays, for static dissipation, and for various sensing devices (5).

**Polyaniline.** Current commercial conductive plastics are made from a chemical material called polyaniline. Among the properties that make polyaniline more useful than other conductive polymers are its good air and moisture stability in both its doped and insulating forms, as well as the simple acid-base chemistry required for switching between its conductive and nonconductive forms (6). Unfortunately, polyaniline is synthesized from aniline, a non-renewable feedstock obtained from petroleum resources (7). The chemical oxidation of aniline to form polyaniline can be achieved by electrochemical means utilizing organic solvents or in aqueous solution from aniline hydrochloride (Figure 2). Polymerization requires strongly acidic conditions and the conductivity and solubility of the resulting polyaniline depends in part on the choice of acid used for protonation (5).

Figure 2. Structures of Aniline (Monomer Unit) and Polyaniline.



In addition to its potentially harmful polymerization conditions, aniline is also problematic in that it is a hazardous chemical material with documented health risks; the health risks associated with *polyaniline* have not yet been studied (8). Although the use

of anilinium hydrochloride is preferred over liquid aniline from a hazards standpoint, there is still a real hazard to industrial plant workers, and a potential hazard to the consumer if polymer products are contaminated with raw materials. There is also an environmental hazard as aniline is a known environmental toxin (8). Finally, neither aniline nor polyaniline are readily biodegradable, and polyaniline would be expensive to reclaim and recycle once it has served its useful purpose (8, 9). The environmental stability of polyaniline is the property responsible for its extensive investigation as a potential conductive plastic (10). Before the commercial production and use of this class of conductive plastics becomes more widespread, it is critical that an environmentally sound alternative be found.

**Green and Sustainable Chemistry.** Environmental sustainability is one of the most pressing needs faced by the human race. The demands of human society for everyday materials, from plastics to medicines, have been met through unprecedented industrial production since the 18<sup>th</sup> century. Meeting these needs, however, consumes our planet’s natural resources and produces waste that is prohibitively expensive to recycle or reuse. This non-sustainable use of natural resources by our culture has created a real concern about the quality of life for future generations. Ensuring that the needs of today can be met without compromising the ability of future generations to meet their needs is the core of sustainability, as defined by the United Nations World Commission on Environment and Development in their report, “Our Common Future” (11).

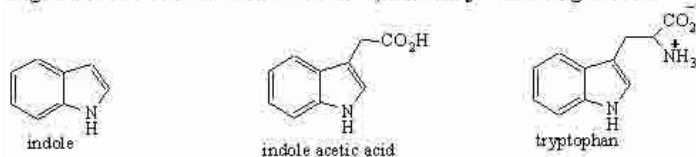
The field of Green and Sustainable Chemistry (GSC) seeks to make the chemical industry’s practices more environmentally benign, such that value-added goods can continue to be made for years to come. The goals of GSC are pursued through the use of a set of guiding “principles” that seek to reduce hazard and environmental impact by designing chemicals and chemical procedures to be benign from the start, and the use of environmentally benign materials. Current conductive polymer production contradicts GSC principles in many ways and therefore there are ample opportunities for improvement. Current conductive polymers, like polyaniline, are made from nonrenewable feedstocks, which could be replaced with naturally-occurring, renewable substances. Toxic raw materials are employed leading to the hazardous processing conditions that could be eliminated if a non-toxic feedstock was employed instead. Finally, current conductive polymers are persistent in the environment. If natural, biodegradable materials are substituted as starting materials, then the potential is very good that nature will also be able to degrade the resulting polymers. This project seeks to develop “greener” indole-derived conductive plastics to help remedy these problems.

**Recent Progress.** Green Chemistry principles have already

been successfully incorporated into the synthesis of conductive polymers through the use of environmentally-friendly catalysts employed in polymerization. These include enzymes such as horseradish peroxidase (HRP) and iron-based biomimetic catalysts like hematin (12). GSC encourages the use of a catalyst, a reusable substance that lowers the amount of energy required for a reaction to occur without being consumed by the reaction. With polyaniline, enzyme catalysis allows for environmentally benign reaction conditions, more control over the reaction rate, and a higher product yield (13). The oxidation can occur at a pH closer to neutral while also allowing for manipulation of the reaction's progress and generation of more polymer.

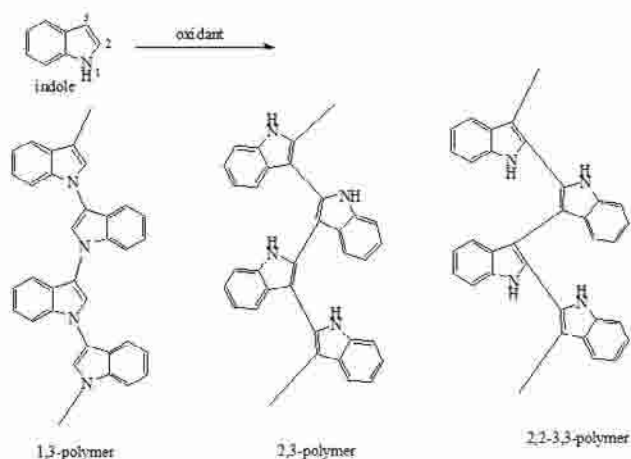
Although structurally similar to the starting materials of many known conductive plastics, indole, along with its derivatives, has not been extensively investigated as a feedstock for potential conductive polymers (14). These chemical materials are naturally occurring: indole is found naturally occurring in feces, indole acetic acid is a plant growth hormone, and tryptophan is an abundant amino acid (Figure 3). In general, indoles are non-toxic, found in a variety of plants, consumed in foods, widely used in medicine, and are known to readily biodegrade (8). Indoles are already in use in the dye, perfume, and pharmaceutical industries (8).

**Figure 3. Structures of Some Common, Naturally Occurring Indoles.**



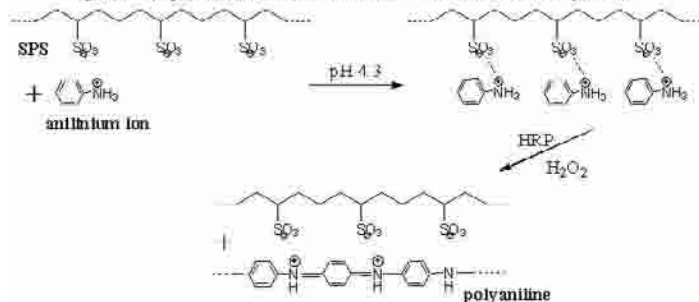
Preliminary investigative work was conducted on polyindoles (PINDs) as possible conductive polymers, but PIND was abandoned for the more easily characterized polyaniline. Recently, the presence of multiple polyindole products was proposed as the reason for difficulty in characterization (10, 15). Polyindoles can exist in at least three distinct, non-planar arrangements and this heterogeneity is believed to result in PINDs lower polymerization efficiency and conductivity compared to other polymers (Figure 4) (15). Thus, while polyindole films have been synthesized by chemical methods, the highly-branched products have been poorly investigated. In particular, no enzyme-catalyzed syntheses have been published to date.

**Figure 4. Proposed Structures for the Conducting Form of Indole Polymers.**



Advances in technology, especially the use of polymeric “scaffolding” as a template for building polymers with well-defined structures and properties, have reduced the heterogeneity of commonly synthesized conductive polymers (13, 16). The use of a template in the synthesis of conductive polymers can have multiple advantages, including electrostatic alignment (providing a more linear and thus more conductive film); supplying counter ions for the doping process; and allowing for water solubility (13). One commonly-used template for the synthesis of polyaniline, sulfonated polystyrene (SPS), is of particular interest for use in producing conductive polyindoles. SPS can be made to hold a negative charge that attracts positively charged ions, such as the monomers used for construction of conductive plastics. This electrostatic interaction helps build linearly arranged polymeric films known to have desirable electrical conducting properties. Without the scaffold, aniline still polymerizes, but the polyaniline formed has a “branched” structure, leading to poor conductivity. This reaction is shown in Figure 5.

**Figure 5. Template-Based Reaction Scheme for the Generation of Polyaniline.**



The synthesis of conductive polymers that utilizes enzymatic catalysis and a molecular template allows for the additional ease of “one-pot” synthesis, essentially creating a “nanoreactor” (12). Within this nanoreactor, it is necessary to oxidize the individual monomer ions and cause them to bond, or link together, to form

polymers. One way of achieving this is to use hydrogen peroxide and an enzyme called horseradish peroxidase. In the field of GSC, these are both considered to be “green” reagents: hydrogen peroxide forms benign water and oxygen when it reacts, and the naturally-occurring enzyme acts a catalyst that can either be reused or safely thrown down the drain when done.

**Goals and Objectives.** The goal of this project was to employ the principles of Green and Sustainable Chemistry to investigate a naturally-occurring and renewable group of chemicals known as indoles as a new and unique class of potential conductive polymers.

The objectives of this project were to:

- Study template-based synthetic methods of generating polyaniline to establish proficiency working with conductive polymers employing Green and Sustainable Chemistry techniques;
- Develop polymeric indole films using Green and Sustainable Chemistry synthesis schemes, and to characterize their chemical and conductive properties;
- Investigate naturally occurring substances as possible replacements for the undesirable and non-renewable molecular scaffolds currently used in conducting polymer synthesis.

**Experimental.** For detailed experimental procedures, please contact ebrush@bridgew.edu.

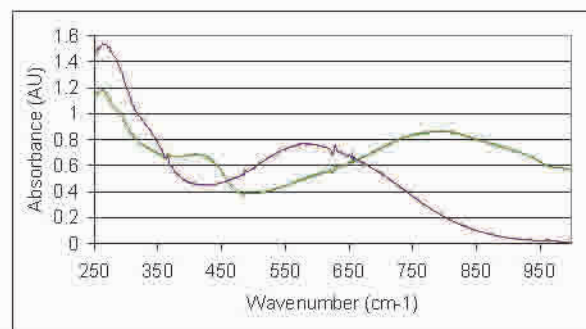
**Results and Discussion - General.** This project represents the preliminary phase of a long-term investigation into the relatively young field of Conducting Organic Polymers (“plastic electronics”). The main goal of this project was to investigate novel experimental methods toward the synthesis of sustainable conductive polymers. This work required investigations into numerous experimental approaches and has generated an enormous amount of synthetic data; discussion is focused only on those synthetic products that showed significant potential to be electrically conductive.

In general, the properties associated with conductivity were determined through a detailed, preliminary analysis of the known conductive polymer, polyaniline, synthesized enzymatically using the SPS anionic template (PANI-SPS) (Figure 5). PANI prepared in this manner was found to exhibit properties comparable with commercially produced PANI (13). The synthesis of conductive PANI-SPS is most obvious through simple visual inspection, as the material is a very dark emerald green color, and undergoes a reversible pH dependent color change upon “doping” (Figure 6). This color change corresponds with a shift in the UV-vis spectrum as seen in Figure 7.

Figure 6. Photograph of PANI-SPS Solution in 1 M HCl (green) and 1 M NaOH (blue).



Figure 7. UV-vis Spectra of PANI-SPS in 1 M HCl (green) and 1 M NaOH (purple).



The term “doping” is borrowed from a similar process associated with inorganic semiconductors in which materials are switched to either an insulating or a conducting state (17). This change is often referred to as a reversible redox reaction, although it is more accurately thought of as an acid-base reaction; the PANI-SPS can be titrated between acid and base forms (Figures 8 and 9).

Figure 8. PANI Redox Reversibility Data Titrating From pH 3 to pH 11.

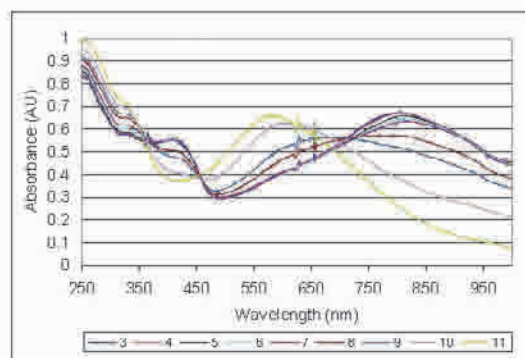
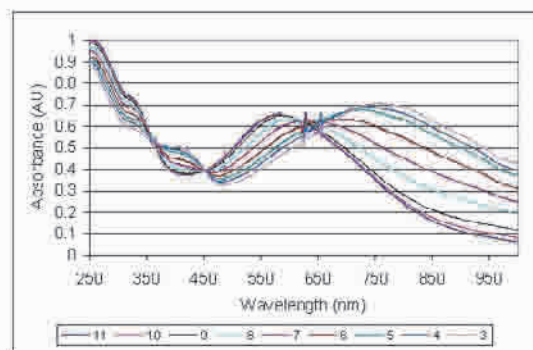


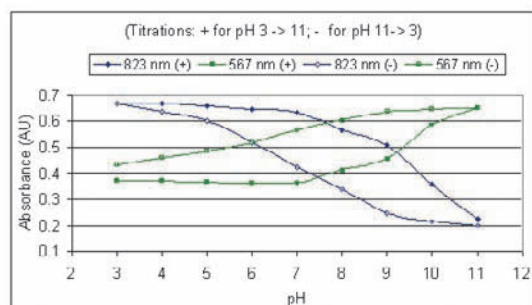
Figure 9. PANI Redox Reversibility Data Titrating From pH 11 to pH 3.





The isobestic points at 353 and 457 nm further confirm the presence of electroactive PANI-SPS (13). As seen in Figure 10, if the absorbances of PANI-SPS at 823 and 467 nm are plotted against pH when titrated with sodium hydroxide, the absorbance from pH 3 to 6 is constant, indicating that the free protons in solution are neutralized first, unlike chemically synthesized PANI that is dedoped by pH 4; the high concentration of protons in the vicinity of the PANI backbone, provided by the template, is responsible for this higher pH retention of the doped state (13). The strong interaction between the template and the PANI causes a pronounced delay in the redox process and is the basis for the formation of a hysteresis loop presented by the absorbances at 823 and 567 nm (13).

Figure 10. UV-vis Data for PANI Showing Variations of Absorbance at Various pH Values.



This behavior is well documented for PANI-SPS: at a high pH, PANI-SPS exists in its non-conducting, emeraldine base form, while a decrease in pH increases the conjugation of the polymer chains and converts the PANI-SPS to its doped, emeraldine salt conductive form (13). Spectroscopic analysis of conducting PANI-SPS at acidic pH reveals strong absorption bands at 414 and 843 nm, these are known to be polaron transition bands, as found in chemically synthesized PANI (13). For conductive polymers, polarons are defined as radical ions associated with a lattice distortion while the localized electronic bands in the gap are referred to as polaron states (17). These electronic bands are formed through the interactions of polymer subunits with their neighbors, just as in a crystal, and consist of the valence band (highest occupied level, HOMO) and conduction band (lowest unoccupied level, LUMO). The energy difference between these two levels is referred to as the band gap (17). The oxidation of PANI and other conductive polymers is akin to p-type doping, and is associated with a change in geometry that causes an upward shift in the HOMO and a downward shift of the LUMO (17). When the polymer is then ionized through an acid-base change, a hole (unfilled level) is created on the top of the valence band, that allows electrons to "hop" along the polymer from hole to hole and leads to the metallic, conductive character of doped conductive polymers (Figure 1).

The IR spectrum of PANI-SPS, summarized in Table 1, is also well documented and was used as another basis for comparison. Experimental results are consistent with these known values, indicating that a para-substituted, doped, conductive complex of PANI-SPS was formed (13). Our assessment of the electrical conductivity of other synthetic polymers prepared through this project was based on the initial visual observation of water solubility, dark emerald green products, and observation of characteristic UV-vis and IR spectra. Polymer products that did not show these key characteristics were assumed to be non-conducting, and were not subjected to further characterization.

Table 1. Summary of PANI-SPS FT-IR Spectra.

Wavenumber (cm <sup>-1</sup> )	Assigned Vibration (12)
1584	Quinone ring deformation
1484	Benzene ring deformation
1310	C-N stretching of a 2° aromatic amine
830	C-H out-of-plane bending
1584, 1484	Relative intensities indicate doped state
1034	Asymmetric S=O stretching
1008	Symmetric S=O stretching

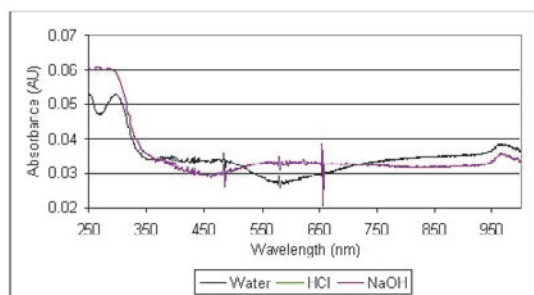
**Mechanochemical Synthesis - General.** Based on the knowledge that liquid aniline monomer forms salts with the doping acids during polymerization, it was hypothesized that a room-temperature, solid-state synthesis of polyaniline should be possible if a solid anilinium salt was used as the monomer (6). Kaner and co-workers found the resulting polyaniline to be chemically equivalent to that synthesized by traditional methods, with a yield of 65% and conductivity measurements in the range of traditional semiconductors, 10<sup>-2</sup> S/cm. This polymerization method is considered advantageous to both the chemical and electrochemical oxidations because no solvents are required; hence hazards associated with solvent use are eliminated.

Throughout this project, greener methods were consistently investigated to make the polymer syntheses more sustainable. It was, therefore, very exciting to discover a solid-state route to make these conductive polymers. Mechanochemical synthesis essentially involves grinding together the required chemical reagents which completely eliminates solvents from the experimental procedure (9). Elimination of solvent use, especially the use of hazardous solvents, is one of the goals of Green and Sustainable Chemistry; hence this method was extensively investigated (18). Promising mechanochemical products included polyaniline (PANI), polyaniline-sulfonated polystyrene complex (PANI-SPS), polyindole (PIND), polyindole-sulfonated polystyrene complex (PIND-SPS), and polyaniline-alginate complex (PANI-AA). Experimental attempts aimed at producing poly(indole acetic acid) (PIAA) and poly(indole acetic acid)-sulfonated polystyrene complex (PIAA-SPS) were not promising, as the products did not exhibit the characteristic conjugation, and possessed UV-vis spectra of a highly-branched, non-conducting polymer. Other products, including polyaniline-poly(styrene

sulfonic acid) complex (PANI-PSSA), polyindole-poly(styrene sulfonic acid) complex (PIND-PSSA), and polyindole-alginate complex (PIND-AA) did possess a weak absorbance band at 800 nm ( $A_{800}$ ), and thus may be slightly conductive, but they were not investigated further because the UV-vis did not indicate a strong polaron band and the solids were not significantly water soluble. Only those products with high potential for conductivity were pursued, as discussed below.

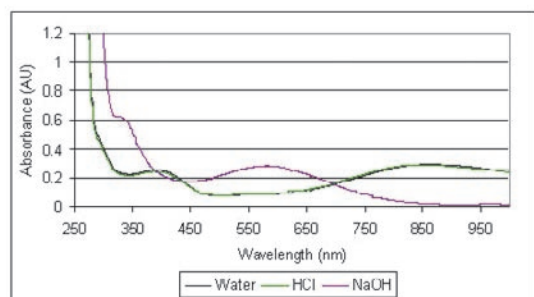
**Mechanochemical Synthesis - Polyaniline (PANI).** Attempted enzymatic synthesis of PANI in aqueous solution, but without the SPS template, leads to the formation of a highly-branched, nonconductive polymer. This product was characterized by UV-vis spectroscopy, and although a strong  $A_{440}$  absorbance band was present, there was no observable polaron band at  $A_{800}$ . As such, conductive PANI must be generated in another manner, and the mechanochemical method served to produce a green solid in high yield. This PANI, however, had poor water solubility and thus exhibited low absorptivity, it was difficult to characterize by UV-vis spectroscopy as a result (Figure 11).

Figure 11. UV-Vis Spectra of Mechanochemical PANI.



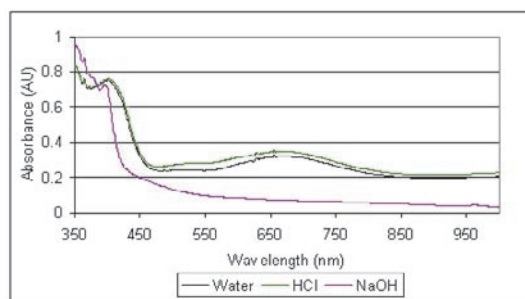
A sample is awaiting conductivity measurements, and will be used as a standard against which any conductivity increases due to presence of template will be observable. In particular, the PANI will be compared to the mechanochemical PANI-SPS, which exhibits significantly higher water solubility than the non-coordinated PANI. The PANI-SPS was produced in a very low yield, but did exhibit the entire range of UV-Vis behaviors characteristic of enzymatically synthesized PANI-SPS (Figure 12).

Figure 12. UV-Vis Spectra of Mechanochemical PANI-SPS.



**Mechanochemical Synthesis - Polyindole (PIND).** Indole has low aqueous solubility in the pH range through which the horseradish peroxidase catalyst is active, thus it was determined early on that the enzymatic synthesis of PIND would not be possible without significant alterations to the procedure. The mechanochemical route to PIND, however, produces a yellow-green solid in good yield. The product is slightly water soluble, and UV-vis spectroscopy indicated that the polaron band at  $A_{800}$  is present, though not as strong as the band possessed by mechanochemical PANI. The mechanochemical PIND-SPS also had a greater  $A_{800}$  than the PIND, perhaps indicating that the template was serving to align indole monomers to produce a more linear chain (Figure 13). Regardless, the presence of the template definitely served to impart water solubility onto the PIND-SPS complex. These results are exciting, as both PIND and PIND-SPS have characteristics of conductive polymers, and will be characterized further to determine conductivity and the effect of the template on conductivity.

Figure 13. UV-vis Spectra of Mechanochemical PIND-SPS.



**Conclusion.** The objectives of this study were all fulfilled during the duration of this project: (1) to establish proficiency working with conductive polymers, (2) to develop and characterize polymeric indole films using Green and Sustainable Chemistry synthesis schemes, and (3) to investigate naturally occurring substances as possible replacements for petroleum-derived templates. My initial investigations into known conductive polymers were very enlightening. I successfully synthesized new complexes with both polyaniline and polyindole, utilizing the mechanochemical synthetic route. Future work should include an evaluation of the oxidizing agents used with the mechanochemical route to conducting polymers, to determine the most benign method of synthesis, optimize the mechanochemical route, and evaluate the environmental impact of different purification procedures. Physical characterizations of the mechanochemical products all indicate great potential for conductivity. These results suggest that Green and Sustainable Chemical Technologies are indeed capable of producing conductive polymers that not only possess identical physical properties to known polymers, but that have significant environmental benefits over known polymers. Such a "Surge of Green" should be welcomed by the field of Conducting Organic Polymers for the benefits it offers for today's products and tomorrow's world.

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