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Nanostructured Conducting Polymers for Applications in Water Treatment and Aerospace Coatings

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Nanostructured Conducting Polymers for Applications in Water Treatment and Aerospace Coatings

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry

by

Thomas Potapenko Farrell

2013
ABSTRACT OF THE DISSERTATION

Los Angeles

Nanostructured Conducting Polymers
for Applications in Water Treatment Membranes
and Aerospace Coatings

by

Thomas Potapenko Farrell
Doctor of Philosophy in Chemistry
University of California, Los Angeles, 2013
Professor Richard Kaner, Chair

Nanostructured conducting polymers have been synthesized by chemical oxidative polymerization, where the nucleation conditions have been intentionally modified to produce materials with high processability. These materials have been blended with conventional polymers and incorporated into polymer membranes via nonsolvent-induced phase separation. The membranes produced show tunable hydrophilicity, pore structure, and separation properties. Pure polyaniline membranes are super hydrophilic and have unusually high permeability.

The pore structure and resultant separation properties of polyaniline ultrafiltration membranes have been modified by the use of 4-methylpiperidine (4MP) as a gel-inhibiting agent. Bovine serum albumin (BSA) rejection for polyaniline membranes is improved from 0% to over 90% when 4MP is included in membrane casting solutions. Membranes cast with 4MP are hydrophobic until an appropriate post-treatment method is applied. Treatment with
camphorsulfonic acid recovers the hydrophilicity in these membranes through induction of the
expanded coil conformation of polyaniline, where hydrophobic 4MP molecules can now diffuse out
of the polymer matrix.

Polypyrrole nanospheres have been produced by rapidly initiated chemical oxidative
polymerization and used to produce nanocomposite membranes with polysulfone. The
nanocomposite membranes have high BSA rejection (>80%) and have permeabilities up to 5 times
greater than pure polysulfone. Fouling experiments were performed on these membranes by
monitoring the flux upon introduction of BSA and subsequent washing steps. Membranes
containing as little as 2% PPy nanospheres were resistant to both reversible and irreversible fouling
by BSA proteins.

Copolymer nanofibers of poly(aniline-co-ethylaniline) have been produced by rapidly-
initiated chemical oxidative polymerization using the initiators p-phenylenediamine and N-phenyl-
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conductivity than the parent polyaniline nanofibers. Conductivity is highest in copolymer samples
where p-phenylenediamine is used as an initiator.

Carbon nanotube/polyurethane composites have been produced as static dissipative coating
materials by using polyaniline/dodecylbenzenesulfonate (DBSA) as a matrix and dispersant. While
chloroform and DBSA were unable to disperse non-functionalized carbon nanotubes, the
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materials were combined with solvent-based polyurethane to produce composite coatings. With as
little as 20% loading of these polyaniline-based conducting materials, the composites fall within the
static dissipative regime and maintain a high transparency.
The dissertation of Thomas Potapenko Farrell is approved.

________________________________
Omar Yaghi

________________________________
Eric M.V. Hoek

________________________________
Richard B. Kaner, Chair

University of California, Los Angeles

2013
This dissertation is dedicated to my mother, Vera Potapenko,
and to the memory of my father, Thomas B. Farrell.
Love you
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Chapter 1. Introduction to Nanostructured Conducting Polymers

1.1 Introduction

Conducting polymers have garnered a great deal of attention since the discovery of metallic conductivity in polyacetylene in the 1970’s by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid, a feat leading to their 2000 Nobel Prize in Chemistry. Since then, guided inquiries of electrical conductivity in organic systems have produced a massive library of organic compounds with varying conductivities, solubilities, functionalities, and utility. The emergence of nanoscience in recent years has rejuvenated the field of conducting polymers with potential applications ranging from wearable electronics to transparent solar cells.

The unique electrical properties of conducting polymers arise from the chemical structure of their polymer backbone. The common feature in all conducting polymer systems is alternating single and double bonds along the backbone as can be seen in Figure 1. This creates a conjugated system of $\pi$ molecular orbitals derived from the overlap of $p_z$ atomic orbitals. Conjugation in polymeric systems leads to increased electron delocalization with corresponding electronic and structural effects. Unlike most polymeric materials, conjugated polymers are
highly colored due to their low energy $\pi$ to $\pi^*$ electronic transition. Delocalization also results in a rigid and generally planar structure as the lamellar conformation allows for the greatest extent of $\pi$ orbital overlap. This rigidity allows for polymer chains to pack together efficiently even though they are held together only by Van der Waals forces. While these non-covalent forces are generally quite weak, the large number of interactions present in the extended $\pi$ system of conjugated polymers produces relatively strong inter-chain interactions. This effect manifests itself in the extremely poor solubility of conjugated polymers. Additionally, whereas many conventional polymers can be melted and formed into desired shapes, almost all conjugated polymers are thermosets due to their unsaturated polymer backbones and accompanying propensity to crosslink. However, sulfonic and phosphonic acid dopants with extremely bulky hydrophobic side-chains can be used to melt-process polyaniline at temperatures of up to 160°C [1].

The electronic properties of conjugated polymers vary widely due to the structure of their backbone, functional groups, morphology, and oxidation state. Conjugated polymers undergo redox transformations from chemical or electrochemical oxidation or reduction that take the polymer from an electrical insulator to a metallic-like conductor. In analogy with inorganic semiconductors, this process is called “doping.” Doping in organic systems differs from traditional inorganic systems in that the doping level is extremely high (often >20%), whereas doped silicon has a doping fraction ranging from parts per billion to parts per thousand ($<10^{-5}$%). The doping process can change a conjugated polymer’s electrical conductivity by many orders of magnitude, e.g. from the insulating state $<10^{-10}$ S/cm to the metallic regime $>10^2$ S/cm. Doping of conjugated polymers including polyacetylene, polypyrrole, polythiophene and their derivatives involves partial oxidization (p-doping) or partial reduction (n-doping) to increase conductivity.
Oxidative doping produces p-type materials that conduct electricity primarily through hole-transport, while reductive doping produces n-type materials that are primarily electron conductors. Doping can also be accomplished electrochemically by applying an anodic or cathodic potential to a conjugated polymer in the presence of an appropriate electrolyte. Since polyaniline in its emeraldine oxidation state is already partially oxidized, p-doping can be carried out simply by chemical treatment with either Brönsted or Lewis acids and reversed with strong bases.

The distinction between conjugated polymers and conducting polymers is not immediately obvious. All conducting polymers are conjugated, but not all conjugated polymers are conducting. For a polymer to conduct electricity efficiently it must have charge carriers (electrons or holes) along with an obstacle-free path for them to travel. The first requirement is accomplished through doping, which adds electrons (n-type) or holes (p-type) that can flow through the band of states created by the overlapping of π orbitals. Charge carriers in conducting polymers are unique in that each charge is associated with a local geometric distortion in the conjugated backbone of the polymer. These charge/distortion features are known as solitons, polarons, and bipolarons, depending on the material and the level of doping [2]. The second requirement, creating a clear path for charge carrier transport, describes mobility (μ) just as in inorganic semiconductors. The planar nature of conjugated polymers provides a relatively uninterrupted path for charge carrier transport along the polymer backbone and thus a high mobility. The major bottleneck in conductivity is when charge carriers reach the end of a polymer chain and are forced to hop to a nearby chain. In fact, conductivity in conjugated polymers is generally described by a hopping mechanism [3]. Therefore, the largest
improvements in conductivity in conducting polymers are achieved when the packing of polymer chains is optimized.

Once an insoluble material has formed, there is not much further manipulation that can occur. In this light, efforts have been made to solubilize conducting polymers by incorporating substituents onto the polymer backbone that both prevent strong interchain interactions and also allow for interactions with solvent molecules. The structures of several conducting polymer derivatives are shown in Figures 1.2 and 1.3. The bulky aliphatic groups found in P3HT (Fig. 1.2) enable it to be processed from chloroform and chlorobenzene, while the sulfonic acid groups present in PMAS (Fig. 1.3), allows this polymer to be dissolved in water. Both polymers receive additional benefits from these functional groups in addition to their processability. P3HT, when synthesized in a regioregular fashion, self-organizes upon gentle heating under high solvent vapor pressure to form fiber-like morphologies on the nanoscale [4]. The polymers reorganize to form a lamellar structure that improves charge transport in two dimensions. PMAS, in addition to solubility, gains a counter-anion that can act as the dopant for polyaniline.
This self-doped conducting polymer’s conductivity is less sensitive to environmental conditions compared to polyaniline, which requires a low pH to become electrically conductive.

The initial discovery of conductivity in polymers spurred tremendous excitement as scientists and engineers envisioned using lightweight inexpensive plastics for all sorts of applications from aircraft wiring to batteries for electric vehicles where high conductivity metals and fast redox reactions, respectively, were required. As the library of materials matured, it became clear that conducting polymers failed in comparison to metals in terms of magnitude of conductivity, chemical stability and/or energy density. This realization shifted the focus to applications where a lower mobility semiconductor was acceptable or where the electronic properties of interest were the electrical transitions that give conducting polymers their intense color, such as light emitting diodes (LEDs) and solar cells.

1.2 Conducting Polymer Synthesis

Conjugated polymers can be synthesized by either chemical or electrochemical methods. Polyacetylene was first synthesized using a Ziegler-Natta catalyst from acetylene gas (Figure 1.4). Other conjugated polymers including polypyrrole, polythiophene and polyaniline have been synthesized chemically from their monomer and an oxidizing agent in the presence of a suitable counter-ion. Common oxidizing agents include ferric chloride and ammonium peroxydisulfate. The oxidizing agent strips an electron from the monomer, initiating a radical polymerization that
proceeds until the reagents are used up. Another straightforward synthetic method is electrochemical oxidation of a conjugated monomer, resulting in the deposition of a conducting polymer film onto the working electrode. This technique avoids the difficulty in processing conducting polymers by depositing them directly onto a desired substrate. It is limited, however, to conducting substrates. As both chemical and electrochemical oxidation strategies are radical processes, they can be difficult to control. Another synthetic method for conjugated polymers is the precursor route, where a soluble precursor polymer is synthesized in an unaromatized form, then is post-modified to produce the desired conjugated polymer [5]. Multiple-component conjugated polymers can be synthesized by carbon-carbon bond formation strategies used in organic synthesis such as Stille, Suzuki, and Ullman couplings.

1.3 Synthesis of Nanostructures

There are several ways to produce nanostructured conducting polymers using either physical or chemical methods. Due to the difficulty in processing most conjugated polymers, the large majority of synthetic strategies reported produce nanostructures during polymerization, as once the polymer has formed it becomes difficult to manipulate. Some derivatized conjugated polymers with bulky side chains can be processed from common organic solvents like chloroform. If the functional group present on a conjugated polymer backbone is charged (e.g. –SO₃⁻ or –NR₃⁺), the polymer can often be dissolved in aqueous media. For these examples of processable conjugated polymers, the technique of electrospinning is an attractive way to form nanowires. Nanostructured conjugated polymers can also be produced in situ during polymerization, which has been extensively studied [6]. Control over nanostructure is accomplished by either using a template that confers its morphology onto the resultant polymer or by careful control over nucleation conditions during synthesis.
**Hard Template**

The growth of conducting polymers within a porous membrane is a straightforward way to produce nanostructured materials. Anodic aluminum oxide is an example of a hard-template that is commonly used in the synthesis of nanowires of both organic and inorganic materials. First, the pores of the template are filled with a monomer. Next, the monomer is polymerized using chemical or electrochemical methods. The alumina template can then be etched away leaving the desired nanowires behind. A main advantage of using a hard-template to synthesize conducting polymer nanowires is the ability to control the nanowire composition along the wire axis. By electrochemical methods, one material can be deposited first, then another via the same mechanism, producing a nanowire with different chemical compositions at each end.

**Soft Template**

Nanostructures of conducting polymers can also be synthesized using molecules that self-assemble into micellular structures. Soft-templates are typically surfactants such as cetyltrimethylammonium bromide (CTAB) or hexadecyltrimethylammonium (C\textsubscript{16}TMA). Chemical oxidative synthesis of polypyrrole using ammonium persulfate in the presence of CTAB produces nanowire/ribbon-like morphology, whereas synthesis in the absence of a surfactant results in an agglomerated polymer morphology.

**Template-Free Methods**

Conducting polymer nanostructures can also be grown in the absence of any external templates by several methods. Polyaniline has featured prominently in these nanoparticle formation strategies, as its polymerization has been extensively studied since the starting material
aniline is inexpensive. Polyaniline nanofibers can readily be synthesized at the interface of two immiscible solvents where one solvent contains the monomer and the other solvent contains the oxidant. The nanofiber diameter can be controlled by the choice of acid used during the synthesis. Alternatively, combining a stoichiometric amount of aniline, with an acid and oxidizing agent at room temperature can be used to directly produce nanofibers. Adding an initiator such as bipyrrrole or terthiophene can be used to speed up reactions to produce nanofibers of polypyrrole or polythiophene, respectively [7].

1.4 Applications

Due to the strong interchain interactions present in conjugated polymers, these materials are difficult to process in most solvents traditionally used for polymers. High surface area nanomaterials open opportunities in the processing of conjugated polymers in the form of stable dispersions as opposed to solutions. A high surface area material possesses a high surface charge to mass ratio where the electrostatic repulsions between nanoparticles allow them to stay suspended despite gravity. The ability to process conjugated polymers in this manner opens up many opportunities for using these materials in a wide range of applications including anti-static coatings, corrosion protection, radio frequency shielding, bioimaging, batteries, supercapacitors, light emitting diodes, transistors, and solar cells.

Nanotechnology-Enabled Sensors

The high surface area of conducting polymer nanostructures combined with their unique oxidation-reduction chemistry and associated changes in properties provide an exciting platform for chemical sensing. In such devices, a conducting polymer is deposited onto a substrate such as a metal electrode or a quartz slide. The material is then connected to a transducer that detects
changes in electrical current, potential difference, mass change, color change, etc. The signal leaving the transducer is amplified or otherwise modified using measuring circuitry and then output to a computer, which displays results. The simplest type of sensor that can be constructed is a chemiresistor. These devices undergo a change in electrical resistance upon exposure to a particular analyte. The high surface area of nanostructured conducting polymers allow the analyte to diffuse through the material rapidly, enhancing the sensor’s time constant often to <2 seconds, as well as the overall magnitude of the response [8].

**Bio-Imaging**

Depending on the particular polymer, undoped conjugated polymers can exhibit strong fluorescence due to a direct band gap [9]. When excited by an incident photon, an electron is excited from the highest occupied molecular orbital (valence band) to the lowest unoccupied molecular orbital (conduction band). When the electron recombines with the vacant state it left behind it releases a photon of energy corresponding to the band gap energy of the conjugated polymer. The novelty in using conjugated polymers for this purpose is that their band gap can be tuned by the choice of polymer backbone and the functional groups present. The full range of the visible spectrum has been reproduced by systematic variation of polymer chemistry. Additionally, conjugated polymers are relatively biocompatible when in their undoped state.

**High Surface Area Electrodes**

The combination of high surface area, lightweight materials, and reversible oxidation/reduction reactions makes nanostructured conducting polymers very appealing for energy storage applications such as batteries and supercapacitors. Although conducting polymer batteries do not require a high surface area to store large amounts of charge, supercapacitors
require both a high capacitance as well as rapid charge/discharge characteristics. As the charge is stored in the form of an electrical double layer at the electrode surface, a higher surface area material will produce a higher capacitance. While the conductivity of most conducting polymers is too low to achieve the high charge and discharge rates required by high power applications, composites with inorganic carbons or graphenes are an attractive option.

**Transistors**

Conducting polymers such as P3HT can be used as the active material in field-effect transistors (FETs) for electrical circuitry. One-dimensional conducting polymer transistors using P3HT are of great interest because the self-assembled nanofibers are known to stack well together and produce high field-effect mobilities. Studying the structure-property relationships in these devices can help to elucidate the intrinsic transport properties of these materials and potentially aid in the development of high performance conducting polymers [10].

**Polymer Photovoltaics**

With increased concern over anthropogenic sources leading to climate change in recent years, renewable energy technologies are receiving considerable attention in the materials science community. Photovoltaic devices utilizing conjugated polymer/fullerene active materials are an attractive target due to a solution-based fabrication process that allows for roll-to-roll production. The efficiency of these devices is low when compared to commercial solar cells where high-mobility semiconductors such as silicon are used as the active material. Polymer photovoltaics offer the advantage of flexible, lightweight, low-cost materials and the potential to use the devices in locations where it is either not possible or not practical to use high efficiency materials. Continuing research on nanostructured electrodes has opened the possibility of producing solar
cells that are transparent throughout most of the visible spectrum by using low-bandgap conjugated polymers with absorption primarily in the near-infrared region [11].

*Polymer Light-Emitting Diodes*

Another exciting application for semiconducting conjugated polymers is the production of light through the application of an electric field across the material. Essentially the reverse process of photovoltaic power generation, light emission from these materials was first demonstrated in 1990. Early devices had very low efficiencies, but progress in polymer engineering has produced light emitting diodes bright enough to be seen in daylight. In addition, modification of polymers through chemical derivatization allows for the color of light emission to be tuned by changing the polymer's electronic structure. Just as with polymer photovoltaic devices, solution processing of these materials offers the possibility of producing large-area devices for lighting and display applications [12].

*Electrochromics*

The electrochemical switching of conjugated polymers can result in a dramatic color change. The oxidation and reduction of these materials changes the band structure of the polymer and the corresponding electronic absorptions. This effect can be used to produce back-lit displays as well as smart windows and memory storage devices. Tuning the polymer chemistry through chemical derivation and copolymerization creates materials with colors spanning the entire visible spectrum [13].
1.5 Conclusions

Conducting polymers have come a long way since their discovery in the 1970’s. With continuing advances in synthesis and processing, applications in electronics, energy and lighting should improve our world.
1.6 References


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Chapter 2. Introduction to Nanostructured Polyaniline

2.1 Introduction

The birth of the field of conducting polymers is normally associated with the discovery of high conductivity in doped polyacetylene in the 1970’s, but the polymer of aniline (aminobenzene) has appeared in the scientific literature as far back as the 1860s[1]. These highly colored oligomers and polymers of anilines were originally used as the blue dyes for denim and other types of clothing. Their structures were unknown and the concept of electron delocalization in organic molecules had yet to be understood. When organic metals became a target for synthesis in the 1980’s, the chemistry of polyaniline became relevant again, and materials’ chemists pursued many avenues in attempting to produce an air-stable version of polyacetylene that might one day replace expensive metals and semiconductors in electronic devices. The advent of nanoscience in recent years has expanded the potential use of these conducting plastics and polyaniline’s proclivity to form nanostructures has made it one of the most widely studied nanostructured conducting polymers.

![Figure 2.1: The repeat unit of polyaniline. Aromatic rings are linked in the para-positions by either amine or imine functional groups. The oxidation state shown above, with two imine nitrogens and two amine nitrogens per tetrameric repeat unit is known as the emeraldine oxidation state.](image)

A major limitation to the use of metallic materials is the difficulty in manipulating them under ambient conditions. Usually high heat, large electrical potentials, or large amounts of force
are required to deposit traditional conductors into a desired shape or location. As polymers are readily processed by solution or in melts, this appeared as an obvious advantage for polymeric conductors. Unfortunately, the initial results with polyacetylene and early studies of the other major conducting polymer families including polyanilines, polythiophenes and polypyrroles, indicated that these materials were essentially infusible and insoluble. Systematic studies, however, demonstrated that with careful control over the polymer chemistry and creative use of solvents and surfactants, some of these conducting materials could be deposited like conventional polymers from solution. Nanostructured conducting polymers further expanded the processing options of conducting polymers through the formation of charge-stabilized colloids, where the high surface area of nanomaterials and their tunable surface functionalities allowed scientists to form thin films of conducting materials from highly colored aqueous “inks”. The leading conducting polymer from a commercial perspective is poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) known as PEDOT/PSS. Essentially the PSS dopant for this polythiophene derivative both imparts conductivity and enables this nanostructured conducting polymer to disperse in water. Polyaniline is also commercially available and its nanostructured forms are dispersible in water.

Polyaniline is synthesized from the inexpensive aniline monomer through a simple oxidative process in aqueous media, meaning the overall process is scalable and relatively inexpensive. The impurities produced are easily washed away with water and alcohols and the resulting material takes on a brilliant green color, making it a visually appealing material to investigate. One of the most interesting properties of polyaniline is the dependence of its resistivity on the local pH environment, where a small amount of acid or base can produce a resistivity change of 10 orders of magnitude or greater. While polyaniline in its undoped state displays resistivity in the insulating regime, doping with different acids has led to highly conductive materials with recent reports of essentially metallic
polyaniline [2]. The combination of highly tunable electronic properties with a facility for nanostructure formation through relatively simple synthetic methods ensures that polyaniline will continue to be of great interest to the materials science community.

2.2 Synthesis of Polyanilines

Whereas many organic syntheses involve multiple steps and difficult purifications, the synthesis of all-organic polyaniline is a one-pot reaction that occurs rapidly, with purification steps that are straightforward and require minimal effort.

![Chemical structure of polyaniline](image)

Figure 2.2: The chemical (or electrochemical) oxidation of aniline at low pH produces the doped, conductive form of polyaniline, depicted in the green emeraldine salt form.

The reaction is initiated when aniline is exposed to an oxidizing agent and an electron is stripped from the aniline monomer, generating a radical cation that is very reactive. This aniline radical searches until it finds an equivalent molecule and the two link together. After losing two protons, the dimer re-aromatizes and the coupling process continues until a long chain polymer is produced [3]. The oxidant that initiates this reaction can be either a chemical oxidant or the working electrode of an electrochemical cell. The scheme shown in Figure 2.2 depicts aniline being oxidized by ammonium peroxydisulfate in the presence of a strong acid (HA) which could be something as simple as hydrochloric acid. The resultant material is a chain of aromatic rings, connected through the para-positions, via amine functional groups. The most appropriate way to depict the repeat unit in polyaniline is by showing the tetrameric unit, where three of the aromatic rings are benzenoid and ...
the fourth is quinoid (on the far right). This is indicative of the so-called emeraldine oxidation state, which is naturally occurring in wet-air conditions and appears either blue or green. As radical processes are known to be rapid and hard to control, initially there was uncertainty about the true structure of polyaniline and whether the oxidative process really produced such a homogeneous backbone structure. Confirmation of the structure was made through a very clever synthetic strategy where a condensation reaction was used to synthesize the ideal head to tail polymer poly(1,4-phenyleneamineimine) and characterization of the material showed an identical spectroscopic signature to polyaniline [4].

![Figure 2.3: The Wudl-Honzl approach to make poly(para-phenyleneamineimine). Condensation polymerization at 60 °C produces the carboxylated polyaniline, which can be thermally de-protected to produce the leucoemeraldine analog of polyaniline. Exposure of this material to atmospheric oxygen converts the light gray product to a deep blue/black material via reflected light, similar in spectroscopic signature to conventionally synthesized polyaniline.](image)

As mentioned earlier, purification of polyaniline is straightforward since the product is insoluble in the polymerization media as well as in most common solvents. This allows for simple washing steps using various solvents to remove salts or short-chain oligomers that arise from chain termination steps, e.g. when two short chains link together and precipitate. Further purification and isolation of the material may involve a drying step so that the polymer can be further manipulated as a solid. Note that due to the hydrophilic nature of the basic functional groups on polyaniline’s backbone, polyaniline is extremely hygroscopic, picking up over 5 wt% water from the air even in
low humidity. Additionally, subtle modifications in the synthetic parameters can have a drastic affect on the resulting structure and properties of the material produced.

The traditional chemical method for making polyaniline consists of drop-wise addition of an oxidizing agent to an acidic solution of aniline at low temperature (1-5°C)[5]. This low temperature and slow oxidant addition is meant to slow down the rapid oxidative polymerization in order to produce a more well controlled, regular structure. A variation on this method involves performing the reaction at extremely low temperatures by suppressing the freezing point of the aqueous solution by adding a large quantity of salt (sometimes over 5 M) [6]. This method is generally accepted to produce a relatively high molecular weight polymer, approaching 160 kDa. Conversely, performing the reaction at room temperature causes the reaction to proceed rapidly, resulting in a lower molecular weight polymer, often less than 20 kDa [7]. Further modification of the polymerization conditions by including immiscible solvents or other additives as well as controlling mass transfer in the solution provide additional tools for tuning the structure, morphology, and resulting properties of the polymer.

2.3 Nanoparticle Formation

Many conducting polymers, including the original polyacetylene produced via Ziegler-Natta catalysis, possess interesting morphologies on the nanoscale. The emerging applications of nanomaterials make understanding the mechanisms and methods that produce these materials of great importance.

Most nanoparticle formation strategies are categorized primarily into two methods: top-down, and bottom-up. Since the individual polymers comprising conducting polymer nanomaterials
are at most a few nanometers, all of the techniques for nanoparticle formation in polyaniline can be described as bottom-up. A better way to distinguish between these methods relies on the presence or absence of an external template to confer nanostructure. Templated-synthesis requires a sacrificial nanomaterial such as a porous aluminum oxide, so that when polyaniline is synthesized, it occupies all of the pore space within the template. Removal of the template then affords polyaniline in the inverse morphology; nanowires in the case of aluminum oxide [8]. A clever technique using vanadium oxide nanowires as oxidant and hard template produces a coating of polyaniline around the inorganic nanowires. Dissolution of the oxide then produces nanotubes of polyaniline [9]. Organic materials can also be used as templates and removed in similar fashion. Molecular surfactants, capable of producing micelles of aniline within an aqueous phase, can confer their morphology upon the resulting polyaniline and are easily washed away [10]. Additionally, amphiphilic block copolymers or terpolymers can be used to produce various micro-porous morphologies where polyaniline nanostructures can deposit within the void space [11].

While templated methods of nanoparticle formation are attractive in that the homogeneity of the resulting polyaniline nanomaterials are as regular as the sacrificial template, the additional steps required in template removal can make the synthetic process cumbersome. One of the most versatile techniques for producing long nanowires for most polymers is electrospinning [3]. In this technique, a concentrated polymer solution is extruded through a small nozzle by the application of a high electric field strength. This technique relies on the ability to form concentrated solutions of polyaniline, which is not a trivial endeavor. The strong pi stacking and hydrogen bonding interactions present in polyanilines make them notoriously insoluble in common organic solvents. The insulating emeraldine base form of polyaniline can be processed from N-methylpyrrolidone at high concentrations, but is only metastable in solution unless secondary or tertiary amine cosolvents
are used [12]. In order to process the conducting emeraldine salt form of polyaniline, the emeraldine base form must be combined with a Brønsted acid that confers solubility unto the polymer by behaving both as a dopant and a surfactant. Acids such as camphorsulfonic acid and dodecybenzenesulfonic acid are known for their ability to solubilize polyaniline in solvents such as m-cresol, chloroform, toluene, xylenes, and some concentrated organic acids [2].

![Figure 2.4: The repeat unit of poly(methoxyaniline sulfonate) (PMAS) shown in the emeraldine oxidation state. The sulfonic acid groups along the polymer backbone protonate the imine nitrogens to produce the conducting emeraldine salt form of polyaniline. The methoxy groups are required to increase electron density in the 4-position on the ring during synthesis, as the sulfonic group is highly electron withdrawing.](image)

The alternative strategy in solubilizing polyaniline is chemical derivation, where different functional groups are attached to the polymer backbone. These functional groups have the dual purpose of preventing strong interchain interactions and improving interactions with solvent molecules. Alkylated polyanilines can be processed from low-polarity organic solvents and sulfonated polyaniline can be processed from aqueous systems. The structure of the water-soluble polymer, poly(methoxyaniline sulfonate) is shown in Figure 2.4.

The other primary template-free method is in situ nanostructure formation during the polymerization process. This method takes advantage of the intrinsic morphology of these semi-rigid-rod polymers and their propensity to form nanostructures. First, the electrochemical oxidation
of aniline in hydrochloric acid has been shown to produce “spaghetti-like” materials on the electrode surface when the potential and current density at the working electrode is sufficient [2]. This straightforward process makes an excellent utilization of materials and deposits the polymer directly onto the substrate, eliminating the requirement for post-synthetic processing. Limitations of this technique include the requirement of the substrate to be electrically conducting as well as prospective complications in large-scale nanomaterial production.

Careful control over the chemical synthesis of polyaniline can also produce nanostructures. Analogous with electrochemical synthesis, the deposition parameters during synthesis are the determining factor as to whether a nanostructure will be produced. Although the monomer, aniline, is soluble in the polymerization media, as the reaction proceeds the oligomeric species reach a critical size and concentration, causing oligomers to stack together and form insoluble materials within the aqueous phase. The process of forming a new phase in an otherwise homogeneous system is referred to as nucleation. If the nucleation process occurs in a consistent manner for all nuclei, nanoparticle formation predominates [11]. The goal then is to select parameters that favor homogeneous nucleation. One of the first techniques developed in this light was the interfacial synthesis of polyaniline in an aqueous/organic system, where the oxidant is dissolved in the acidic aqueous medium and the monomer is in the organic phase. Oxidation and chain growth occur at the interface of the two liquids where monomer and oxidant interact. Presuming the right solvents are chosen, doped polyaniline nanofibers are produced, dispersing into the aqueous phase as a charge-stabilized colloid. Performing the synthesis in the presence of different acidic dopants produces nanofibers with controllable diameters [13]. Another technique for producing a homogeneous nucleation condition is by rapidly mixing two aqueous phases, one containing the monomer and the other, the oxidant [14]. If the two solutions are rapidly combined and then
allowed to sit under diffusion-limited conditions, all of the oxidant is consumed at the same time and a homogeneous dispersion of nanofibers result. It is worth noting that external forces such as shearing and agitation disrupt the nucleation conditions and nuclei form sequentially and eventually result in agglomerated structures [15].

2.4 Aniline Oligomers

Although not technically “polymeric materials,” oligomeric anilines are proving to be very useful model materials for determining the relationship between the packing arrangement within nanostructured polyaniline and the resultant electronic properties [16]. In analogy with oligoacenes commonly used in small molecule organic semiconductor applications, oligoanilines offer another method to process semiconductors from solution where the related polymeric material is difficult to process. Additionally, the fact that these oligomers can be produced as pure materials as opposed to polymers with varying polydispersity means less variability in batch-to-batch syntheses. There now exist many strategies for producing oligomers of aniline, ranging from oxidative coupling [17] to organometallic-catalyzed coupling [18] to the Moore-Honzl approach described earlier for the synthesis of poly(para-phenyleneamineimine) [4].

These well-defined oligomeric materials were previously found to be electrically insulating, lacking the long conjugation lengths that are generally associated with the long chains in conducting polymers. This was surprising, because when aniline oligomers reach a degree of polymerization of 8 (i.e. an octamer), the spectroscopic signatures are nearly identical to polyaniline and show the same reduction-oxidation peaks under cyclic voltammetry studies [19]. The limiting factor in conductivity in these materials turns out to be charge carrier hopping between conjugated segments [16]. Polyanilines have poorly defined structures/conformations in the solid state as they rapidly and
irreversible precipitate during synthesis. If the stacking of these materials in the solid state can be improved, so then will the mobility of charge carriers. Recently it has been shown that the tetramer of aniline can be crystallized into well-defined nanowires, nanobelts, and nanoflowers that have unprecedentedly high conductivities. Whereas the mobility in these oligomers in the direction of the polymer chain is limited by the oligomer length, the mobility in two dimensions (charge hopping) is drastically improved due to the long-range ordering of these crystalline materials [16].

2.5 Applications of Polyaniline Nanomaterials

Charge-stabilized colloids

When polyaniline is placed in an acidic environment, the basic functional groups along the polymer backbone become protonated and positively charged quaternary nitrogen groups are produced. These positive charges are accompanied by the counter-anion of the protonic acid. Nanostructured polyaniline, a high surface area material, carries this charge on its surface, producing a high charge to mass ratio. The electrostatic repulsive effect of these like charges between nanofibers allows the nanofibers to stay dispersed in solution despite their density being higher than the aqueous system they are dispersed in. This charge-stabilized colloid enables the processing of conducting polyaniline in aqueous systems where polyaniline is normally completely insoluble [20]. This innovation has opened the possibility of using aqueous-based coatings for a large range of applications where high surface area semiconductors offer operational advantage over more dense organic solvent-based analogs.

Immediate applications that arise from the water processability of these materials include coatings that previously could only be done using the organic solvents required for dissolving counter ion-solubilized polyaniline. As mentioned earlier, the common organic solvents for
processing the conducting form of polyaniline are toluene, chloroform, m-cresol, xylenes, and some halogenated organic sulfonic acids. All of these solvents will swell or dissolve most plastics. Therefore, an aqueous dispersion can be used to produce conductive coatings for anti-static applications where the insulating nature of plastics makes them vulnerable to charge build up followed by short-circuiting or dielectric breakdown. Moderate levels of conductivity also can be used for electromagnetic interference shielding. With an increasing trend toward environmentally friendly water-based polymer coating systems, this aqueous dispersability opens the door to conducting polymer composites that leverage the conductivity of polyaniline and the bulk mechanical properties of conventional polymers.

*Nanotechnology-Enabled Sensors*

Since the doping process in polyaniline produces a change in resistivity over many orders of magnitude, polyaniline nanofibers may be an ideal active material for resistive-type sensors, known as chemiresistors. Although the most obvious method of detection in polyaniline resistive type sensors is the doping/dedoping reaction, other processes such as reduction or oxidation, swelling by certain organic compounds, or polymer chain decoiling have been shown to affect the resistivity of polyaniline to a discernible degree [21]. In addition to being easily deposited upon an electrode array from an aqueous dispersion, these organic nanomaterial sensors can be operated at room temperature, whereas many inorganic semiconductors require elevated temperatures for efficient analyte detection [22].
The main physical advantage to using nanostructured polyaniline as opposed to conventional bulk polyaniline for sensing is that the nanostructured polyaniline has a high porosity that is easily accessible to gas molecules. When polyaniline is cast into a dense film from an organic solvent to be used as a sensor, the target analyte is required to dissolve and diffuse into the dense polyaniline active material before any sensor response is observed. For nanostructured polyaniline, the highly accessible pore space allows for much better mass transfer and access to the polymer/electrode interface that in turn produces a much faster response time. A typical nanostructured polyaniline with a diameter of 50 nm will have a surface area of around 50 m²g⁻¹ whereas its dense film counterpart is limited to just the area of the film surface [14]. The effect of this surface area and porosity is dramatic. Upon exposure to acidic or basic vapors, a nanofiber chemiresistor has a response time over ten times faster than a conventional dense film chemiresistor. In addition to detecting strong acids and bases, chemical reactions can be used to generate strong acid byproducts such as converting hydrogen sulfide to HCl using CuCl₂ that can dope polyaniline and register a significant response [21].

Figure 2.5: The imine nitrogens on the polyaniline backbone become protonated upon exposure to strong acids. This produces the emeraldine salt form of polyaniline that is conducting.
High Surface Area Electrodes

The same high surface area that makes polyaniline nanofibers useful for sensors can also make it useful in energy storage and conversion devices. While batteries do not require high surface area to achieve high energy storage density, supercapacitor energy storage density is largely influenced by the surface area of the electrode materials. Likewise, pseudo-capacitors benefit from high surface area, but now can take advantage of the reversible oxidation-reduction reactions present in the underlying chemical structure of polyaniline. Unlike other conducting polymers, polyanilines possess two reversible oxidative transformations as shown in Figure 2.6.

![Chemical structures of polyaniline oxidation states](image)

**Figure 2.6:** The repeat unit of the three major oxidation states of polyaniline. Top to bottom: Leucoemeraldine (fully reduced), emeraldine (half-oxidized, water and air-stable), pernigraniline (fully oxidized). The chemical structures each depict a deprotonated base form of polyaniline.

This can be seen in the cyclic voltammogram of polyanilines, where instead of a single oxidation-reduction peak, two will be observed. A “pseudo-capacitive” device, using polyaniline
nanomaterial electrodes will therefore store charge both through the electrical double layer on the electrode surface as well as in redox reactions within the bulk of the electrode material itself.

**Inorganic-Organic Nanocomposites**

Another application of these high surface area materials is to act as functional scaffolds for inorganic nanoparticles. The facile and reversible oxidation and reduction of polyaniline allows the polymer to behave as either an oxidizing agent or a reducing agent when combined with different materials. Treatment of polyaniline nanofibers with metal salts allows polyaniline to act as a reducing agent that donates electrons to the oxidized metal ion, causing deposition of metallic particles on top and within the polyaniline nanofiber network [21]. The resulting inorganic-organic nanocomposite materials maintain the high surface area and dispersability of the original polyaniline nanofibers and thus can be deposited and used as sensor materials or other electronically active materials. Gold-decorated polyaniline nanofibers have been explored for use in bistable memory devices [23].

Polyaniline nanofiber composites with metal nanoparticles can also be used in heterogeneous catalysis. Reduction of palladium(II) salts by polyaniline produces very small particles of palladium(0), the catalyst used for carbon-carbon bond formation between aromatic molecules in Suzuki coupling reactions [24]. Since polyaniline nanofibers form dispersions and not solutions, centrifugation can be used to pull the dense fibers out of the dispersions in order to recover the product of coupling reactions without time consuming extraction steps.
**Flash-Welding**

Polyaniline nanofibers are known to undergo a morphological transformation upon exposure to an intense pulse of light such as a camera flash. Examination of the polymeric nanostructure prior to and after exposure to a camera flash shows the disappearance of nanofibers due to a photo-thermal phenomenon. The process is believed to be a result of the low fluorescence efficiency of polyaniline and its propensity to crosslink. Figure 2.7 shows how the morphology of polyaniline nanofibers are altered by flash-welding. This technique can be used to create patterns and to form simple actuators [25]. While melt induced flash welding appears to be unique to conducting polymers, understanding this technique may allow its application to other nanostructured organic materials.

![Figure 2.7: Scanning electron micrographs showing the morphology of polyaniline nanofibers synthesized by the rapid mixing synthesis in the presence of the aniline dimer (left). If exposed to an intense flash of light, polyaniline nanofibers weld together and lose their high surface area and nanofibrillar morphology (center). Opaque materials can be used to form a patterned photomask. Upon exposure to high intensity light such as a camera flash or laser, exposed areas form a dark, welded, insulating material, and shaded areas remain conductive and nanofibrillar (right).](image)

### 2.6 Conclusions

Strategies for producing and implementing nanostructured polyaniline continue to be investigated within the materials community. Properties such as high-surface area and processability
from aqueous systems allow these materials to be implemented successfully into a wide range of applications. Further innovation and fine-tuning of chemical structure and morphology may see polyaniline replacing traditional materials in certain places or even opening the door to new, yet to be discovered applications.
2.7 References


Chapter 3. Pore-structure, Hydrophilicity, and Particle Filtration Characteristics of Polyaniline-Polysulfone Ultrafiltration Membranes

1.1 Introduction

Freshwater scarcity, widespread pollution, and stricter regulations have created an increased need for the development of water treatment technology.\textsuperscript{1,3} One such technology, filtration, is used to remove particulates (viruses, bacteria, colloidal matter, etc.) from water streams.\textsuperscript{2} Two basic filter types exist: media (depth) filters and membrane (sieving) filters.\textsuperscript{2} Media filters are a well established technology dating back to at least 2,000 B.C. in India for use in water purification.\textsuperscript{2} Depth filters rely on cheap, natural media such as sand, anthracite, crushed magnetite, garnet, etc. to treat wastewater.\textsuperscript{2,4} Membrane filtration also has been used to purify drinking water as early as World War II;\textsuperscript{2} however, the vast majority of modern water and wastewater treatment plants to this day still use granular media filters.\textsuperscript{2} Modern membrane filtration (comprising microfiltration, ultrafiltration, and nanofiltration processes) are widely used for industrial, biological, and analytical separations in addition to water and wastewater purification.\textsuperscript{2}

In general, the particle concentration in the product stream of granular media filters is proportional to the particle concentration in the feed; moreover, particle removal in depth filters is limited by the effectiveness of coagulation.\textsuperscript{2} Since the media is not fixed within the filter bed, preferential flow paths and bypassing of some particles also can occur. Relatively recent incidents such as Cryptosporidium outbreaks of 1993 (Milwaukee) and 2000 (Ontario, Canada) has led to large epidemics of waterborne disease and exposed the Achilles heel of media filtration – that is, intrinsically poor removal of particles in the micrometer size range especially when coagulation is sub-optimal.\textsuperscript{5} The Milwaukee Cryptosporidium outbreak forced public health officials and the water industry to consider replacing granular media filters with membrane filtration, which (relative to
media filtration) offers an absolute barrier to pathogens – protozoa, bacteria, and viruses – depending on the pore size of the membrane.² In other separations, membranes offer a much greater ability to tailor filtration selectivity by modifying the surface pore structure and chemistry.

Particle separation by filtration membranes primarily depends on the ratio of the particle size to the membrane pore size, and to a lesser extent the filtration rate, feed water chemistry, particle physical-chemical properties, and membrane chemistry. To cope with rising energy costs, stricter environmental regulations and industrial demand, the next generation of filtration membranes must be more selective and robust, while demanding lower chemical and energy inputs. New membrane materials must be explored to help meet these goals in applications such as water and wastewater treatment, in addition to other important industrial, biomedical, and analytical separations.

The conducting polymer, polyaniline (PANi) has been studied for use in numerous applications including battery electrodes,⁶ electromagnetic shielding devices,⁷,⁸ and anticorrosion coatings.⁹⁻¹¹ Interest in polyaniline has continued to grow due to its flexibility, electrical conductivity (when doped), relatively simple synthesis, and the low cost of aniline.¹² More recently, polyaniline has been studied as a membrane material.¹³⁻¹⁹ Fan et al. showed that blending polyaniline into polysulfone ultrafiltration membranes can improve performance, specifically higher permeability and lower fouling potential probably due to increased hydrophilicity.²⁰, ²¹ In this study, we synthesized a highly processible form of polyaniline and blended it with commercial polysulfone to produce mixed-matrix filtration membranes. Mixed-matrix membrane pore-structure, morphology, hydrophilicity, and separation performance were compared to identically formed pure polysulfone membranes.
3.2 Materials

Ammonium peroxydisulfate (APS) (Prod. No. A682, ACS grade, ≥98.0%), acetone (Prod. No. 268310010, HPLC grade, ≥99.8%), and sodium hydroxide (Prod. No. S612) were purchased from Fisher. Aniline (Prod. No. 10400, ACS grade, ≥99.5%), sulfuric acid (Prod. No. 320501, ACS grade, 95.0-98.0%), methanol (Prod. No. 179957, laboratory grade, ≥99.6%), potassium bromide (Prod. No. 221864, FT-IR grade, ≥99%), polysulfone beads (Prod. No. 182443, $M_n \sim 22$ kDa), bovine serum albumin (BSA) (Prod. No. A9647, ≥96%), and 1-methyl-2-pyrrolidinone (NMP) (Prod. No. 442778, ACS grade, ≥99.0%) were purchased from Aldrich. Silica nanoparticles (SNOWTEX-20L) were purchased from Nissan Chemical Corp. All materials were used as received.

3.3 Polyaniline Synthesis and Characterization

Polyaniline was formed from aniline via chemical oxidative polymerization.$^{22-25}$ An oxidant solution composed of APS dissolved in aqueous $\text{H}_2\text{SO}_4$ was mixed with a monomer solution composed of aniline dissolved in aqueous $\text{H}_2\text{SO}_4$. The mixture was rapidly stirred to evenly distribute oxidant and monomer prior to polymerization. Stirring was ceased after 1 h, and the mixture was left standing overnight. Polyaniline was recovered by filtration (0.45 µm Durapore® membrane, Millipore) and washed with sodium hydroxide followed by deionized water and methanol. A flow chart of the synthesis procedure is given in Figure 3.1.
Synthesized polyaniline was prepared for SEM analysis by adding 1000 mg/l PANi into 1 M sulfuric acid. The mixture was then sonicated for 10 s. A drop was placed on a clean (water, methanol, acetone, methanol, water rinse) silicon wafer attached by carbon tape to an SEM stub. The droplet was placed in a desiccator under vacuum overnight to evaporate. Residual liquid was removed by placing the stub in an oven at 50 °C for 2 h. The sample was not coated with gold because it was made electrically conductive by acid doping. Polymer molecular weight was determined by gel permeation chromatography.

3.4 Membrane formation and characterization

Polymer solutions were prepared with polyaniline:polysulfone weight ratios of 1:0 (pure polyaniline), 3:1, 1:1, 1:3, and 0:1 (pure polysulfone). The total polymer concentration was 18 wt.% in all cases. Films were cast on a commercial nonwoven polyester support fabric (NanoH₂O Inc.,...
Los Angeles, California) and immersed in deionized water at room temperature to induce precipitation. Polysulfone (PSf) was chosen as a copolymer because it has been well-studied as a filtration membrane material.\textsuperscript{26}

Permeability and rejection tests were conducted in a dead-end flow cell (HP4750 Stirred Cell, Sterlitech Corp.) using 4 cm diameter membrane samples. Membrane water permeability was determined for each composite membrane by measuring water volumetric flux at pressures ranging from 5 – 20 psi. The following expression relates water flux ($J_w$) to pressure drop ($\Delta p$) via a permeability coefficient ($L_p$):

\[
J_w = \frac{L_p \varepsilon}{d_p \mu l} \Delta p,
\]

where $\varepsilon$ is the membrane porosity, $d_p$ is the membrane pore diameter, $\mu$ is the liquid dynamic viscosity, and $l$ is the membrane thickness.\textsuperscript{27} If the membrane is asymmetric (integrally skinned), then $\varepsilon$ is surface porosity, $l$ is the membrane skin thickness, and $\Delta p$ is the pressure drop across the skin layer. Silica nanoparticles and BSA were used to evaluate the membrane separation performance. The nanoparticle concentration was measured using a turbidimeter (Z100AN, Hach Company). A UV-vis spectrophotometer (Lambda 20, Perkin Elmer) was used to determine the BSA concentration. Solute particle rejection ($r$) was calculated by the following equation:

\[
r = 1 - \frac{c_p}{c_f},
\]

where $c_p$ and $c_f$ are solute particle concentrations in the permeate and feed streams, respectively. Dynamic light scattering (ZetaPALS, Brookhaven) confirmed that BSA and silica nanoparticles had diameters of 6 nm and 48 nm, respectively. Membrane pore size can be approximated from solute particle rejection by using the following relationship\textsuperscript{2}:

\[
r = 1 - 2(1 - \lambda)^2 + (1 - \lambda)^4,
\]
where $\lambda = d_s / d_p$; $d_s$ and $d_p$ are solute particle diameter and membrane pore diameter, respectively.

Membrane samples were prepared for SEM (Nova 600 NanoLab DualBeam™-SEM/FIB, FEI Company) analysis by soaking in pH 1 $\text{H}_2\text{SO}_4$ solutions for 1 h and drying overnight in a desiccator. Membranes containing some polyaniline were made electrically conductive by doping, so surface coating (by gold, palladium, platinum, etc.) prior to imaging was unnecessary. Pure polysulfone membranes were sputter-coated with gold to prevent charging. Membrane cross-sections were prepared by freeze fracturing using liquid nitrogen. Membrane surface milling was achieved by a focused ion beam (FIB) operated using a gallium source at a current of 10 nA, accelerating voltage of 30 kV, and a magnification of 5,000X.

Membrane pore size and surface porosity were determined by image analyses of scanning electron micrographs using NIH ImageJ software. High magnification grey-scale surface images were converted to black and white images (Figure 3.2) following a previously described procedure.\textsuperscript{28} Surface porosity was calculated by dividing the sum of the black pixels ($A_{\text{black}}$) by the total pixels in an image. Average pore diameter ($d_{p,\text{avg}}$) was calculated by the following:

$$d_{p,\text{avg}} = \sqrt{\frac{4A_{\text{black}}}{n\pi}},$$

(3.4)

where $n$ is the number of continuous dark areas (pores) counted by the software. Maximum pore diameter ($d_{p,\text{max}}$) was measured by hand using ImageJ.

Figure 3.2: Grey-scale SEM surface image of PANi membrane (left) converted to black and white image (right) to determine membrane pore size and porosity.
Membrane surface roughness was measured using atomic force microscopy (AFM) (Synergy ESPM 3-D, Novascan). Air-dried membranes were scanned in tapping mode in 500 nm x 500 nm sections. Water contact angles were measured using a goniometer (DSA10, Krüss). The captive bubble technique was employed here rather than the sessile drop technique due to the porous and hydrophilic nature of pure polyaniline films. Ten drops were measured for each membrane with the highest and lowest values being discarded. Surface roughness-corrected free energy of cohesion ($\Delta G_{131}$) was calculated as previously described using a water surface tension value of 72.8 mJ m$^{-2}$.

Fourier transform infrared (FTIR) (FT/IR-420, JASCO) spectra were measured for each polymer composite. Films were cast without a polyester support fabric and dried. Dry films and KBr were then ground into fine powders using a mortar and pestle and pressed into pellets for FTIR analysis.

### 3.5 Results

A scanning electron micrograph (Figure 3.3) reveals that polyaniline synthesized following the method described above produces an agglomerated polymer structure. Polymer dispersions with agglomerated polyaniline weight fractions as high as 18% in NMP have been created and found to be stable for over a week.
Membranes of varying polyaniline and polysulfone content were formed using the immersion precipitation technique. Images of each membrane are shown below.

**Figure 3.3:** SEM image of synthesized PANi.

**Figure 3.4:** PANi:PSf composite membranes.

Water permeability and nanoparticle and protein rejection were measured for polyaniline-polysulfone composite membranes. Membrane performance results are shown in Figure 3.5. Pure polyaniline membranes are an order of magnitude more permeable than pure polysulfone and composite membranes, i.e., there is a sharp decrease in permeability when polysulfone is introduced. Membranes have comparable rejection for 48 nm silica particles. Membranes containing large
fractions of polyaniline showed little or no BSA rejection, while the pure polysulfone membrane showed greater than 45% BSA rejection.

Figure 3.5: Pure water permeability plus silica nanoparticle and BSA rejection for PANi-PSf composite membranes.

Fourier transform infrared analyses were performed for each polymer composite. Spectra are shown in Figure 3.6. Sulfones and secondary aromatic amines both have strong absorption bands at 1350 – 1300 cm$^{-1}$. Sulfones also have an absorption band at 1160 – 1120 cm$^{-1}$. This peak (highlighted in Fig. 3.6) diminishes as the polysulfone content decreases in each composite membrane.
Figure 3.6: FTIR spectra for polyaniline-polysulfone blend membranes.

Atomic force microscopy was used to measure surface roughness for each composite membrane. Roughness data are presented in Table 3.1. Average roughness (Ra) and root mean squared roughness (RMS) values are similar for all composite membranes. The surface area difference (SAD), which is the difference in actual membrane surface area and planar area, is lowest for the pure polysulfone membrane. The surface area difference increases with increasing polyaniline content until a maximum SAD is reached for the 1:1 PANi:PSf composite membrane, beyond which SAD decreases with increasing polyaniline content.
Table 3.1: Surface Roughness Values of Polyaniline-Polysulfone Blend Membranes

<table>
<thead>
<tr>
<th>PANi:PSf</th>
<th>Ra/nm</th>
<th>RMS/nm</th>
<th>Rmax/nm</th>
<th>SAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>4.1</td>
<td>5.6</td>
<td>47.2</td>
<td>16.4</td>
</tr>
<tr>
<td>3:1</td>
<td>3.0</td>
<td>3.8</td>
<td>30.7</td>
<td>37.8</td>
</tr>
<tr>
<td>1:1</td>
<td>3.7</td>
<td>4.6</td>
<td>35.9</td>
<td>85.3</td>
</tr>
<tr>
<td>1:3</td>
<td>2.1</td>
<td>2.8</td>
<td>27.4</td>
<td>24.9</td>
</tr>
<tr>
<td>0:1</td>
<td>4.1</td>
<td>5.4</td>
<td>40.6</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Captive bubble contact angles were measured using deionized water on all composite membranes. Contact angle values and surface energies for each membrane composition are given in Table 3.2. As expected, the pure polysulfone membrane is the most hydrophobic, and membrane hydrophilicity generally increases with increasing polyaniline content. When surface roughness is considered, the free energy of cohesion for the 1:1 PANi:PSf membrane approaches that of the hydrophobic pure polysulfone membrane.

Table 3.2: Water contact angles and surface roughness-corrected free energies of cohesion for polyaniline-polysulfone blend membranes.

<table>
<thead>
<tr>
<th>PANi:PSf</th>
<th>Contact Angle</th>
<th>$-\Delta G_{133}/\text{mJ m}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>24.2° ± 2.1°</td>
<td>129.8</td>
</tr>
<tr>
<td>3:1</td>
<td>25.3° ± 2.1°</td>
<td>120.6</td>
</tr>
<tr>
<td>1:1</td>
<td>32.0° ± 3.3°</td>
<td>106.1</td>
</tr>
<tr>
<td>1:3</td>
<td>43.0° ± 4.7°</td>
<td>115.5</td>
</tr>
<tr>
<td>0:1</td>
<td>64.7° ± 3.8°</td>
<td>102.0</td>
</tr>
</tbody>
</table>

Scanning electron micrographs (SEM) were taken for each composite membrane (Figure 3.7). Images show varied membrane morphology based on polymer composition. Cross-sectional SEM images of the composite membranes reveal that surface skin layers are thinnest for the pure polymer membranes (1:0 and 0:1), thickest for the equal polymer blend membrane (1:1), and of intermediate thickness for the other blend membranes (3:1 and 1:3). Pure polyaniline (PANi) and
polysulfone (PSf) membranes have a more open structure with many large, finger-like macrovoids. The 3:1 and 1:3 PANi:PSf composite membranes have fewer finger-like macrovoids. The 1:1 PANi:PSf membrane has a sponge-like substructure with few macrovoids.

Figure 3.7: Plan view (left), full cross-section (middle), and skin layer (right) SEM images of H₂SO₄ doped PANi-PSf blend membranes. Membranes are composed of PANi:PSf ratios of a) 1:0, b) 3:1, c) 1:1, d) 1:3, and e) 0:1 (gold-coated).

Scanning electron micrographs were taken while simultaneously exposing composite membrane surfaces to a focused ion beam (FIB). The FIB removes surface material by bombarding
the surface with gallium ions. Time step images in Figure 3.8 show varied membrane surface resistance to the FIB due to some combination of membrane chemical composition and skin layer thickness.

Figure 3.8: Plan view time sequence SEM images of PANi-PSf blend membranes exposed to a focused ion beam.
Membrane pore size can be calculated using silica nanoparticle and BSA rejection data and Eq. 3.3. Approximate pore diameters for each membrane are shown in Table 3.3.

Table 3.3: Membrane Pore Diameter, Surface Porosity, and Effective Pore Length Approximated from Membrane Water Permeability, Silica Nanoparticle Rejection, BSA Rejection, and SEM Image Analyses

<table>
<thead>
<tr>
<th>PANi:PSf</th>
<th>Water Permeability (Lp/m² h⁻¹ kPa⁻¹)</th>
<th>Nanoparticle Rejection (rNP)</th>
<th>BSA Rejection (rBSA)</th>
<th>Average Membrane Pore Diameter (dp)_avg/μm</th>
<th>Maximum Pore Diameter (dp_max)/μm</th>
<th>SEM Image Analysis (st²/μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>37.8</td>
<td>92%</td>
<td>0%</td>
<td>60 ≥ 6</td>
<td>11.1</td>
<td>2.1%</td>
</tr>
<tr>
<td>3:1</td>
<td>11.2</td>
<td>97%</td>
<td>1%</td>
<td>54 ≥ 6</td>
<td>7.0</td>
<td>4.6%</td>
</tr>
<tr>
<td>1:1</td>
<td>6.2</td>
<td>&gt; 99%</td>
<td>28%</td>
<td>&lt; 48</td>
<td>4.8</td>
<td>1.7%</td>
</tr>
<tr>
<td>1:3</td>
<td>6.2</td>
<td>&gt; 99%</td>
<td>36%</td>
<td>&lt; 48</td>
<td>5.8</td>
<td>1.8%</td>
</tr>
<tr>
<td>0:1</td>
<td>4.0</td>
<td>&gt; 99%</td>
<td>47%</td>
<td>&lt; 48</td>
<td>4.7</td>
<td>4.8%</td>
</tr>
</tbody>
</table>

Partial silica nanoparticle rejection (rNP) by the pure polyaniline membrane translates into an average pore diameter of 60 nm, classifying this membrane as a “loose” ultrafiltration membrane. Complete nanoparticle rejection, however, gives an incomplete picture of membrane pore diameter; pore diameter is less than the particle diameter. Partial BSA rejection indicates that the pure polysulfone membrane is a mid-range ultrafiltration membrane with an average pore diameter of 14 nm.

Membrane average pore diameter, maximum pore diameter, and surface porosity were approximated by analyzing surface SEM images of composite membranes (Table 3.3). Average membrane pore diameters ranging from 5 – 11 nm were found for composite polyaniline-polysulfone membranes. Pore diameter was found to decrease with increasing polysulfone content. Maximum observed pore diameters were typically 3-5 times greater than average pore diameters for each membrane, which may have affected solute rejection and permeability. Surface porosity ranged from 2 – 5%, and did not follow a noticeable trend with relative polymer content. Effective pore length was calculated using Eq. 3.1 and was found to generally increase with increasing polysulfone content.
3.6 Polyaniline processability

Concentrated solutions are needed if polyaniline is to be used in fiber spinning and conventional film casting techniques. Yang et al. added secondary amines to NMP to disperse high molecular weight polyaniline in NMP up to concentrations of 15 wt%, which is about the minimum concentration required to form an ultrafiltration membrane by nonsolvent induced phase inversion.\textsuperscript{33} We report a synthesis of polyaniline that produces a material that is stable in NMP solution up to 18 wt% without the use of any co-solvent additives. Although we have not experimentally determined the molecular weight of our as synthesized polyaniline, the similarity in synthetic conditions between our synthesis and those reported by Adams et al.\textsuperscript{34} and those reported by Tran et al.\textsuperscript{35} leads us to anticipate the molecular weight to be around M\textsubscript{n} of 10 (8-12) kDa and M\textsubscript{w} of 25 (20-40) kDa.

The room temperature synthesis of polyaniline using APS has been shown to produce nanofibers of controlled diameters when the acid and conditions for nucleation are controlled.\textsuperscript{36} Li et al. have shown that nanofibers are formed early during the chemical polymerization of aniline and that minor modifications of these conditions has a drastic impact on the morphology and dispersability of the resultant material.\textsuperscript{37} Adams et al. have shown that controlling the rate of oxidant addition and the reaction temperature has a profound influence on the structural regularity and molecular weight of the resultant polymer.\textsuperscript{34} They used \textsuperscript{13}C NMR to reveal irregularities, termed “defects,” in the molecular structure of polyaniline synthesized at room temperature by a rapid addition of the oxidant solution. Their finding, that performing the synthesis at reduced temperature with a drop-wise addition of the oxidant solution leads to a more regular structure, has led the polyaniline community to accept the low-temperature synthesis method as the standard method for producing “high-quality” polyaniline. However, for applications where conductivity is not a figure of merit other synthetic methods should be considered.
Here, we have created a high defect density polyaniline that is resistant to gel formation in NMP solution by rapid addition of the oxidant at room temperature followed by intentional disruption of the nucleation process by stirring for 1 hour. This is significant, as previous reports and our own experience with polyaniline has shown that polyaniline solutions in NMP gel at concentrations as low as 5-10 wt%. Yang and Mattes attribute gel formation in polyaniline to strong hydrogen bonding interactions between the amine and imine nitrogens on neighboring polymer chains as polymer chains are more closely in contact with one another in concentrated solutions. We hypothesize that our high defect density polyaniline chains are unable to pack as closely to one another, preventing the inter-chain hydrogen bonding interactions from reaching a critical stage where the fluidity of the system is lost and the gel formation process is irreversible. One can imagine drawing a parallel between a “high defect density” polyaniline and a cis-fatty acid in biochemistry. As opposed to a linear polyaniline (which can be thought of as a straight-chain hydrocarbon), the increased kinks and bends in the chain prohibit strong inter-chain interactions and lead to improved processability.

3.7 Membrane Morphology and Structure

According to the Hagen-Poiseuille model for flow through a porous membrane (Eq. 3.1), membrane permeability is proportional to the square of the membrane pore diameter. Pore diameters calculated from silica and BSA rejection over-predict the difference in water permeability between the pure polyaniline and polysulfone membranes \(^{[I_{p,1.0}]/I_{p,0.1} = 9.5; (d_{p,1.0}/d_{p,0.1})^2 = 19]}\). The pure polyaniline membrane \(\varepsilon^t_1\) factor is half that of the pure polysulfone membrane. Using solute particle rejection data to describe membrane pore size has a few limitations, however. Fouling of the membrane due to solute-membrane interactions may cause higher solute rejection, which can result in the calculation of a smaller pore diameter. Solutes such as BSA may deform when under
stress and can squeeze through pores smaller than their hydrodynamic radii, which can result in the calculation of a larger pore diameter. Membrane porosity and pore length cannot be independently determined from such an analysis. Several other factors may also play a role in membrane performance and morphology. Membrane hydrophilicity is known to affect membrane performance. An increase in polyaniline content leads to an increase in membrane hydrophilicity and may be partially responsible for the increased water permeability. These effects cannot be quantified from the simple size based permeability model.

Average membrane pore diameters determined from analysis of SEM surface images were smaller than those determined from solute particle rejection. However, maximum observed membrane pore diameters were similar in value to those calculated from solute particle rejection. A few larger pores may have had a large influence on solute particle retention by the membranes. An advantage of SEM image analysis is the ability to quantify membrane surface porosity. Pure polysulfone average membrane pore diameter is less than half that of the pure polyaniline membrane, but the surface porosity is more than twice that of the pure polyaniline membrane. Pure polyaniline membrane permeability, however, is 9.5 times greater than pure polysulfone membrane permeability. Differences in pore diameter, porosity, and effective pore area ($\varepsilon d_p^2$) do not explain the difference in membrane permeability between pure polyaniline and pure polysulfone membranes

$$\frac{L_{\text{polysulfone}}}{L_{\text{PANi}}} = 9.5; \frac{d_{\text{PANi,1:0}}}{d_{\text{PANi,0:1}}}^2 = 5.5; \frac{\varepsilon_{1:0}}{\varepsilon_{0:1}} = 0.44; \frac{\varepsilon_{1:0}}{\varepsilon_{0:1}} \cdot \left(\frac{d_{\text{PANi,1:0}}}{d_{\text{PANi,0:1}}}\right)^2 = 2.4.$$  Using the effective pore length ($l$) as a fitting parameter for membrane permeabilities produces the values of $l$ given in Table 3. The characteristic polysulfone membrane effective pore length was nearly 4 times longer than that of the pure PANi membranes; thus, providing a mechanistic, membrane structure-based explanation for the much higher flux of PANi membranes.

Surface SEM images (Fig. 3.7) show dark regions in the pure polyaniline membrane, which appear to be macrovoids under a thin, semi-transparent skin layer. These features are easily visible
as dark regions in the pure polyaniline membrane surface image and are visible, but less pronounced, in pure polysulfone and 3:1 PANi:PSf membranes. Macrovoids are not visible in the surface SEM images of 1:1 and 1:3 PANi:PSf composite membranes. The macrovoids visible in the pure polyaniline membranes appear in clusters and display some spatial ordering. Full SEM cross-sections reveal that each membrane has finger-like macrovoids. The 1:1 composite membrane is an exception as it appears to have a mixture of sponge-like and finger-like morphology.

Membrane skin layer thickness was analyzed from the time-step FIB-SEM images. An obvious limitation to this analysis lies in the assumption that each polymer has similar physical/thermal resistance to the FIB, whereby skin layer thickness is proportional to erosion time. The pure polyaniline membrane had the shortest erosion time (thinnest skin layer) of the composite membranes. The majority of the skin layer was removed after only 5 min. The pure polysulfone and 3:1 PANi:PSf membrane showed marked erosion near the 10 min mark indicating that their skin layers are thinner than those of the 1:1 and 1:3 PANi:PSf membranes. These results mirror the results of the skin layer SEM images. The FIB-SEM images allow for positive identification of macrovoids under the thin, transparent skin layers of the pure polyaniline, pure polysulfone, and 3:1 PANi:PSf membranes. The darker regions visible at $t = 0$ in these membranes become macrovoids after several minutes under the FIB. The 1:1 PANi:PSf membrane shows slight pitting after 10 min, which may be the exposed sponge-like sublayer. The 1:3 PANi:PSf membrane shows very slight pitting only after 15 min of FIB irradiation.

3.8 Conclusions

By modifying an existing method for synthesizing the conducting polymer polyaniline, a more processable polymer has been formed. Mixing polyaniline with polysulfone produced UF membranes with moderately increased water permeability and slightly decreased particle rejection.
Membrane macrovoid morphology was different for each composition of polyaniline-polymer composites. Pure polyaniline ultrafiltration membranes exhibited an order of magnitude higher water permeability and similar particle rejection compared to both pure polysulfone and PANi-PSf blended membranes. The high permeability and good selectivity of pure PANi membranes is attributed to their increased hydrophilicity and relatively thinner skin layer. Polyaniline and its blends represent a class of promising new materials for use as water filtration membranes.
3.9 References


Chapter 4. Tuning the Properties of Polyaniline-Based Ultrafiltration Membranes with Chemical Post-Treatments

4.1 Introduction

The conducting polymer, polyaniline, has historically been used to make sensors [1-3], battery electrodes [4], electromagnetic shielding devices [5, 6], and anticorrosion coatings [7-9]. Polyaniline has recently attracted attention as a membrane material [10-12]. However, polyaniline’s processability has been a concern with the choice of solvent generally limited to NMP and N,N’-dimethylpropyleneurea (DMPU) [13, 14]. Interchain and intrachain hydrogen bonding between the imine and amine nitrogens in the emeraldine base form of PANi causes aggregation and the eventual formation of a gel. As many as 3 to 4 hydrogen bonds may form between the tetrameric repeat unit in PANi emeraldine base in an NMP solution [15]. Gelation can occur at PANi concentrations of less than 1 wt% [16-18] and often takes place in a very short time interval [19-21]; hence, the high concentrations desirable for membrane formation (ca. 15-25%) are with few exceptions generally not possible [12].

Gel-inhibiting agents, typically secondary and tertiary amine additives, help alleviate some of these PANi processability problems [22, 23]. Gel-inhibiting agents hydrogen bond to the imine nitrogens and thereby prevent gelation by inter-chain hydrogen bonding [24-28]. Fig. 1 illustrates the interaction and hydrogen bonding expected to occur between the emeraldine base form of PANi and the gel inhibitor 4MP in NMP. While these additives provide a means to produce concentrated PANi solutions from which robust membranes can be formed, gel-inhibiting agents may alter the polymer structure and chemistry. This can negatively alter film mechanical strength, conductivity, hydrophilicity, etc. [14, 27-31]. More hydrophobic membranes are more prone to fouling and, ultimately, need to be cleaned more frequently and require higher operating pressures (= energy +
cost) over time to maintain productivity [32-44]. Herein, we demonstrate a method to recover the inherent hydrophilicity of PANi by post-treating PANi-NMP-4MP ultrafiltration (UF) membranes with camphorsulfonic acid.

4.2 Materials

Ultra-pure 18 MΩ deionized (DI) water was produced by a reverse osmosis system (RODI-C-12BL, Aqua Solutions, Inc.). Sulfuric acid (Sigma-Aldrich, No. 320501), ammonium peroxysulfate (Fisher, No. A682), sodium hydroxide (Fisher, No. S612), methanol (Sigma-Aldrich, No. 322415), NMP (Sigma-Aldrich, No. 443778), 4MP (Sigma-Aldrich, No. M73206), hydrochloric acid (Sigma-Aldrich, No. 258148), p-toluenesulfonic acid monohydrate (PTSA) (Fisher, No. AC17178), (+/−) camphor-10-sulfonic acid (CSA) (AlfaAesar, No. A12620), 4-dodecybenzenesulfonic acid (DBSA) (Sigma-Aldrich, No. 44198), ammonium hydroxide (Sigma-Aldrich, No. 320145), bovine serum albumin (BSA) (Sigma-Aldrich, No. A9647), sodium chloride (Fisher, No. S271), dimethyl sulfoxide-d$_6$ (Cambridge Isotope Laboratories, No. DLM-10), and potassium chloride (Fisher, No. P217) were all used as received.

4.3 Casting Solution Preparation and Membrane Formation

Polaniline was synthesized in our laboratory as previously reported in detail [12]. Polyaniline was dried in a vacuum oven (~25 in. Hg) at 50 °C overnight prior to addition to the solvents. Polymer solutions were prepared by adding 18 wt% crushed PANi powder to 82 wt% NMP (PANi-NMP) or a mixture of 72 wt% NMP and 10 wt% 4MP (PANi-NMP-4MP), i.e., 2 moles 4MP:mole PANi emeraldine base tetramer; 0.547 g 4MP/g PANi emeraldine base [15, 22, 26-28]. PANi was added to the solvent(s) over the course of 1 h while vigorously stirring. Polymer solutions were allowed to stir for 3 d in a tightly sealed glass vial.
PANi ultrafiltration membranes were formed by immersion precipitation [45]. Polymer solutions were allowed to stand sealed for 1 h before film casting. Films were spread using a casting knife (Gardco Adjustable Micrometer Film Applicator, Microm II, AP-99500701) with a blade height of 152 µm set using a feeler gauge. Films were hand-cast on a nonwoven polyester fabric (NanoH₂O, Inc., Los Angeles, CA) and immediately placed in a coagulation bath containing 3 liters of DI water at 20 °C. The relative humidity during film casting was 50-55%. Membranes remained in the coagulation bath for 30 min before being transferred to plastic storage bags where they were soaked in DI water. Water in the storage bags was replaced with fresh DI water every 30 min for 2 h. Membranes were then stored at 4 °C in DI water prior to post-treatment and further characterization.

4.4 Membrane Post-Treatment

PANi UF membranes were post-treated by placing membrane coupons in beakers containing 150 ml aqueous solutions of 100 mM HCl, H₂SO₄, PTSA, CSA, DBSA, or NH₄OH. A similar post-treatment was carried out using DI water at 50 °C. Gentle stirring was maintained at 125 rpm. A special post-treatment intended to remove CSA from the membrane was carried out in 100 mM NH₄OH at 50 °C for 3 h with gentle stirring. CSA post-treatment was conducted using 100 mM CSA at 50 °C for 1 h unless otherwise noted.

4.5 Membrane Characterization

Membrane samples were cut for performance testing using a 25 mm punch (Osborne arch punch, OS-149-m25, Campbell Bosworth Machinery Co.). Samples were kept wet and placed in a dead-end stirred cell (UHP-25, Advantec MFS, Inc.) with a membrane area ($A_m$) of 3.5 cm². Permeate volumetric flow rates were measured using a digital HPLC liquid flow meter (FlowCal
5000, Tovatech, LLC). Membranes were compacted with DI water under 20 psi transmembrane pressure at 20 °C until a decrease in permeability of < 5% over 30 min was achieved. Permeate volumetric flowrate ($Q_p$) was then recorded at transmembrane pressures ($\Delta \phi$) of 20, 10, and 5 psi. Membrane pure water permeabilities ($L_p$) were calculated from [46]:

$$L_p = \frac{Q_p}{A_m \cdot \Delta \phi}$$  \tag{4.1}

Membrane protein rejection was measured immediately after the pure water permeability test. Residual water from the permeability test was removed from the stirred cell and replaced with a 10 ml solution of 1000 mg l$^{-1}$ BSA in 50 mM NaCl. BSA has a hydrodynamic diameter of 6 nm in this solution [12]. The stir rate was maintained at 350 rpm ($Re_{SC} = 2963$). The stirred cell Reynolds number was calculated from

$$Re_{SC} = \frac{\rho \cdot \omega \cdot r_{SC}^2}{\mu}$$  \tag{4.2}

where $\rho$ is the fluid density (kg m$^{-3}$), $\omega$ is the angular velocity (rad s$^{-1}$), $r_{SC}$ is the stirred cell radius (9x10$^{-3}$ m), and $\mu$ is the fluid dynamic viscosity (kg m$^{-1}$ s$^{-1}$) [47]. The stirred cell mass transfer coefficient ($k_{SC}$) of 4.1x10$^{-6}$ m s$^{-1}$ was calculated using the results described in [47]

$$\frac{k_{SC} \cdot r_{SC}}{D} = Sh_{SC} = 0.27 Re_{SC}^{0.567} Sc^{0.33}$$

where $D$ is the diffusion coefficient of BSA (5.9x10$^{-11}$ m$^2$ s$^{-1}$), $Sh_{SC}$ is the stirred cell Sherwood number, and Sc is the Schmidt number ($Sc = \mu \cdot r_{SC}^{-1} \cdot D^{-1}$). A constant transmembrane pressure was set to give an initial permeate flux ($J_v = Q_v/A_m$) of 40 gallons ft$^{-2}$ d$^{-1}$ (19 µm s$^{-1}$), and 5 ml of permeate was collected (50% recovery). Protein concentrations in the feed ($c_f$) and permeate ($c_p$) were determined by UV-vis absorption at $\lambda = 278$ nm (DU® 730 Life Science UV/Vis Spectrophotometer, Beckman Coulter). Solute rejection ($R_s$) was calculated based on
Deionized water contact angles were measured using a goniometer (DSA10, KRÜSS GmbH). The captive bubble measurement technique was employed here due to the hydrophilicity of the PANi films. Ten drops were measured and the highest and lowest values were discarded. Fourier transform infrared (FTIR) (JASCO FT/IR-6300 with ATR PRO450-S ZnSe crystal) spectra were measured for each membrane. Films were dried in a desiccator overnight at 20 °C prior to measurement.

$^1$H-Nuclear Magnetic Resonance ($^1$H-NMR) studies were carried out in a Bruker Avance AV300 (300.1 MHz) instrument at room temperature. The membranes were not dried in vacuo or thermally to prevent NMP and/or 4MP from evaporating from the membranes. Saturated membrane solutions were prepared in DMSO-d$_6$ and the NMP/4MP standards were measured as neat solutions. The $^1$H-NMR chemical shifts were reported relative to the deuterated DMSO solvent signal.

Streaming current was measured using an adjustable gap electrokinetic analyzer (SurPASS Electrokinetic Analyzer, Anton-Paar GmbH). The flow channel gap was set at 100 µm, and a 1 mM KCl solution at 20 °C was used as the background electrolyte. Streaming current was determined in a pH range of 2-10, adjusted using HCl and NaOH. Membrane zeta potential ($\zeta$) was calculated using the Helmholtz-Smoluchowski equation,

$$\zeta = \frac{dI}{d\phi} \cdot \frac{\mu}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A},$$

(4.5)
where \( \frac{dI}{dp} \) is the slope of the streaming current versus pressure, \( \mu \) is the solution dynamic viscosity, \( \varepsilon \) is the dielectric constant of the solution, \( \varepsilon_0 \) is the vacuum permittivity, \( L \) is the streaming channel length and \( A \) is the cross-section of the streaming channel.

Membrane samples were prepared for SEM (Nova 600 NanoLab DualBeam\textsuperscript{TM}-SEM/FIB, FEI Company) by soaking in \( \text{H}_2\text{SO}_4 \) at pH 1 for 1 h to make PANi fully doped and electrically conducting. Samples were dried in a desiccator overnight at 20 °C. Cross-sections were prepared from unsupported films by freeze fracturing using liquid nitrogen. Membrane surface SEM images were analyzed for porosity and pore size by a previously described procedure [12, 48].

Membrane tensile strength analyses were conducted on 5 mm x 100 mm membrane samples. The thickness of the samples was measured using a micrometer before the analysis, and the average value of the thickness was used to calculate the result. All samples were placed in a United Testing Systems tensile test apparatus at 25 °C, with a gauge length of 80 mm, and pulled at a rate of 2 mm min\(^{-1}\). Two sets of sample conditions were used. One set of samples was measured under wet conditions, in which the samples were directly tested after removal from the water storage bags and dabbed dry using napkins. Another set of samples was tested under dried conditions, in which the samples were dried first in air for 1 h and then placed in a desiccator for 24 h.

Thermal gravimetric analyses (TGA) were conducted on a Seiko ExStar TG/DTA 6200 from Haake Instruments. The samples were measure under protection of \( \text{N}_2 \) flow (90 ml min\(^{-1}\)), with the heating rate at 2 °C min\(^{-1}\), and temperature tested from 20 – 550 °C. Samples were dried in a desiccator for 24 h prior to TGA measurements.

4.6 Results

*Effect of 4MP on PANi processability*
Adding 4MP in a 2:1 molar 4MP:PANi emeraldine base tetramer ratio improves the polymer solution quality. An 18 wt% PANi mixture containing 72 wt% NMP and 10 wt% 4MP produces a viable polymer solution within 1 d. A viable polymer solution is defined here as a mixture of polymer and solvent from which a membrane can be cast; non-viable polymer solutions form a gel within seconds that cannot be cast into a membrane. Polymer solutions containing our synthesized PANi with a 2:1 molar ratio of 4MP:PANi emeraldine base do not gel for several months. However, a PANi-NMP mixture without 4MP takes 2 d to form a viable polymer solution, and this polymer solution remains viable for 2 – 5 d before a gel forms. The addition of 4MP allows for the complete dissolution of PANi and greatly expands the window of polymer solution viability.

![Potential hydrogen bonding interactions](image)

*Fig. 4.1. Potential hydrogen bonding interactions between the emeraldine base form of PANi, the solvent NMP, and the gel inhibitor 4-methylpiperidine.*

*Effect of Chemical Post-Treatments on PANi Membrane Hydrophilicity*

Captive bubble water contact angles for PANi-NMP membranes and untreated and post-treated PANi-NMP-4MP membranes are summarized in Table 4.1 along with molecular weight, anion
dimensions, and $pK_a$ of the acids and bases used for post-treatment. Anion dimensions were approximated using Chem3D software (CambridgeSoft) via the protocol outlined by Yang et al. [28].

Table 4.1. Molecular Weight, Anion Dimensions, $pK_a$ of Post-Treatment Molecules, and Water Contact Angles for PANi-NMP-4MP Membranes After 1 h Post-Treatments at 50 °C [56].

<table>
<thead>
<tr>
<th>Membrane/Post-treatment</th>
<th>MW (Da)</th>
<th>Anion Dimensions (Å)</th>
<th>$pK_a$</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANi-NMP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24.2 ± 2.1</td>
</tr>
<tr>
<td>PANi-NMP-4MP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>41.9 ± 1.6</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18.0</td>
<td>-</td>
<td>15.7</td>
<td>40.5 ± 2.9</td>
</tr>
<tr>
<td>HCl</td>
<td>36.5</td>
<td>3.3</td>
<td>-6.1</td>
<td>53.0 ± 4.1</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>98.1</td>
<td>3.4, 2.5, 2.4</td>
<td>-3.0, 2.0</td>
<td>43.7 ± 3.2</td>
</tr>
<tr>
<td>PTSA</td>
<td>190.2</td>
<td>7.0, 4.3, 2.5</td>
<td>0.7</td>
<td>44.5 ± 3.6</td>
</tr>
<tr>
<td>CSA</td>
<td>232.3</td>
<td>7.0, 5.4, 5.6</td>
<td>2.0</td>
<td>18.4 ± 1.0</td>
</tr>
<tr>
<td>DBSA</td>
<td>326.5</td>
<td>22.2, 5.0, 2.4</td>
<td>2.6</td>
<td>43.9 ± 2.9</td>
</tr>
<tr>
<td>NH$_4$OH</td>
<td>35.0</td>
<td>-</td>
<td>9.2</td>
<td>47.1 ± 1.9</td>
</tr>
<tr>
<td>CSA-NH$_4$OH</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.2 ± 1.1</td>
</tr>
<tr>
<td>CSA-filter-acid-base-filter</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.1 ± 0.5</td>
</tr>
</tbody>
</table>

The dimension for the chloride ion is an ionic diameter [49]. The addition of 4MP to the polymer solution increases the membrane water contact angle from 22° to 42° (untreated) [12]. Post-treatment of this PANi-NMP-4MP membrane in H$_2$O at 50 °C for 1 h does not alter the membrane water contact angle. Post-treatments for 1 h with 100 mM H$_2$SO$_4$, PTSA, and DBSA at 50 °C have little effect on membrane hydrophilicity. Post-treatments for 1 h with 100 mM HCl and NH$_4$OH at 50 °C appear to increase membrane hydrophobicity. Post-treatment of the PANi-NMP-4MP membrane in 100 mM CSA for 1 h at 50 °C, however, reduces membrane water contact angle to 18.4°. In an attempt to remove excess CSA from the membrane surface, CSA-post-treated PANi-NMP-4MP membranes were further treated for 3 h in 100 mM NH$_4$OH at 50 °C (CSA-NH$_4$OH). This treatment does not further affect membrane hydrophilicity (contact angle = 17.2°). A PANi-NMP-4MP membrane was extensively post-treated by the following process: 1 h treatment in 100 mM CSA at 50 °C → 60 min filtration of DI H$_2$O under 20 psi at 20 °C → 10 min with 0.5 M
$\text{H}_2\text{SO}_4$ treatment at $45 \, ^\circ\text{C} \rightarrow 10 \, \text{min with} \, 1 \, \text{M NaOH treatment at} \, 45 \, ^\circ\text{C} \rightarrow 30 \, \text{min filtration with DI H}_2\text{O under} \, 20 \, \text{psi at} \, 20 \, ^\circ\text{C}. \, \text{This treatment is labeled “CSA-filter-acid-base-filter” in Table 1. CSA-treated membrane hydrophilicity was unaffected by the additional water filtration and acid and base treatments (contact angle = 17.1$^\circ$).}

Fig. 4.2. Water contact angle for PANi-NMP-4MP membranes after 100 mM CSA post-treatments at 50 $^\circ$C using differing time intervals.

The effect of CSA treatment time on membrane hydrophilicity is shown in Fig. 4.2. PANi-NMP-4MP membranes were treated with 100 mM CSA at 50 $^\circ$C. Membrane hydrophilicity began to increase after treatment for 10 min. There was a transitional time between 10 and 60 min where areas of the treated membrane remained relatively hydrophobic (contact angle = 42$^\circ$) while areas a
few millimeters away had recovered hydrophilicity (contact angle < 20°). This is the reason for the larger error bars for contact angle values at 15 and 30 min CSA treatment times. The maximum membrane hydrophilicity was achieved after 1 h of CSA treatment. The effect of CSA treatment temperature on membrane hydrophilicity is shown in Table 2. PANi-NMP-4MP membranes were treated with 100 mM CSA for 1 h. The membrane hydrophilicity was recovered at all temperatures tested.

Effect of CSA Post-Treatment on PANi Membrane Performance

Pure water permeability was measured for untreated and CSA-treated PANi-NMP-4MP membranes and is summarized in Table 4.2. We previously reported a membrane pure water permeability of 1050 µm s⁻¹ bar⁻¹ with 0% BSA rejection for an 18 wt% PANi-82 wt% NMP membrane containing no 4MP [12]. Membrane permeability decreases by 98% upon addition of 10 wt% 4MP to the polymer solution. BSA protein rejection of the PANi-NMP-4MP membrane increases from 0% to 91%. Post-treatment of the PANi-NMP-4MP membrane with 100 mM CSA for 1 h at 50 °C decreases BSA rejection by ~15% with a slight decrease in permeability.

Table 4.2. Pure water permeability and BSA rejection for untreated and CSA-post-treated polyaniline membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeability (µm s⁻¹ bar⁻¹)</th>
<th>BSA rejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANi-NMP-4MP</td>
<td>24.5 ± 3.0</td>
<td>0.91 ± 0.01</td>
</tr>
<tr>
<td>PANi-NMP-4MP CSA-treated</td>
<td>20.3 ± 4.4</td>
<td>0.74 ± 0.03</td>
</tr>
</tbody>
</table>

PANi Membrane Mechanical and Thermal Properties
Nonwoven support fabric and membrane thicknesses and tensile moduli are given in Table 4.3. The dried support fabric is about 13% thinner than the wet sample. Of the PANi membranes, only the untreated PANi-NMP membrane showed a minor decrease in thickness (7%). Post-treatment using 100 mM CSA at 50 °C had no effect on membrane thickness. Both CSA-treated and untreated PANi-NMP-4MP membranes showed no difference in wet/dry thickness. Tensile strength increases by adding a PANi layer to the support fabric. The PANi-NMP membrane has about double the breaking strength of the nonwoven fabric support. Tensile modulus decreases in the PANi-NMP-4MP membrane but is still greater than the support fabric. The PANi-NMP-4MP CSA-treated membrane has the greatest tensile modulus. This trend is the same for wet and dry membranes, with the dried membranes having a greater breaking strength.

Table 4.3. Nonwoven Support and Membrane Thickness and Tensile Moduli for Wet and Dry Testing Conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wet Thickness (μm)</th>
<th>Wet Modulus (MPa)</th>
<th>Dry Thickness (μm)</th>
<th>Dry Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonwoven support</td>
<td>170 ± 1</td>
<td>243 ± 26</td>
<td>148 ± 5</td>
<td>294 ± 21</td>
</tr>
<tr>
<td>PANi-NMP</td>
<td>230 ± 9</td>
<td>434 ± 66</td>
<td>214 ± 17</td>
<td>723 ± 61</td>
</tr>
<tr>
<td>PANi-NMP-4MP</td>
<td>224 ± 9</td>
<td>360 ± 65</td>
<td>223 ± 1</td>
<td>561 ± 90</td>
</tr>
<tr>
<td>PANi-NMP-4MP CSA-treated</td>
<td>222 ± 13</td>
<td>453 ± 98</td>
<td>220 ± 1</td>
<td>796 ± 28</td>
</tr>
</tbody>
</table>

**PANI Membrane Chemical Properties**

Fourier transform infrared (FTIR) spectroscopic analysis was carried out on an 18 wt% PANi-82 wt% NMP membrane (PANI-NMP), an 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane (PANI-NMP-4MP), an 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane treated for 1 h in 100 mM CSA at 50 °C (PANI-NMP-4MP CSA-treated), a CSA-treated 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane that was further treated with 100 mM NH₄OH for 3 h at 50 °C (PANI-NMP-4MP CSA+NH₄OH-treated), and neat CSA. These spectra are shown in Fig. 4.4. The locations of carbonyls (C=O), quinoid rings (Q), and benzenoid rings (B) peaks are outlined. This spectrum
matches very closely to those reported in previous studies [27, 50-53]. The spectrum for the CSA-treated PANi-NMP-4MP membrane exhibits a peak around 1740 cm$^{-1}$, which may correspond to the presence of the C=O bond of CSA. This peak is prominent in the neat CSA spectrum and is greatly diminished after NH$_4$OH treatment. The locations and ratios of quinoid to benzenoid peaks for each membrane are shown in Table 4.4. The ratio of quinoid (1587 cm$^{-1}$) to benzenoid (1495 cm$^{-1}$) peaks (Q/B) for the PANi-NMP membrane is 0.87, which matches values of the Q/B ratio found by others [27, 28]. The Q/B ratio of the PANi-NMP-4-MP membrane decreases to 0.52. There is no shift in Q peak between PANi-NMP and PANi-NMP-4-MP membranes.

Fig. 4.4. FTIR spectra for PANi membranes and CSA.
Table 4.4. Location of Quinoid and Benzenoid FTIR Absorptions and Q/B Ratios for Polyaniline Membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Wave No. (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q</td>
</tr>
<tr>
<td>PANi-NMP</td>
<td>1587</td>
</tr>
<tr>
<td>PANi-NMP-4MP</td>
<td>1588</td>
</tr>
<tr>
<td>PANi-NMP-4MP CSA-treated</td>
<td>1576</td>
</tr>
<tr>
<td>PANi-NMP-4MP CSA+NH&lt;sub&gt;4&lt;/sub&gt;OH-treated</td>
<td>1591</td>
</tr>
</tbody>
</table>

<sup>1</sup>H NMR experiments were performed to further investigate the composition of the PANi membranes before and after 1 h of 100 mM CSA at 50 °C treatment. <sup>1</sup>H NMR spectra are shown in Fig. 4.5. Spectra of NMP (a) and 4-MP (b) have been included for reference. The NMR spectrum of the PANi-NMP membrane made without 4MP (c) indicates that NMP is completely removed from the membrane during the phase inversion process. When 4MP is used as a gel-inhibitor in the polymer solution, some 4MP and NMP remain in the membrane after the phase inversion process (d). This is shown by the singlet at δ = 2.66 ppm, which is indicative of the N-CH<sub>3</sub> protons in NMP and the multiplet at δ = 0.91-0.81 ppm that can be attributed to the proton attached to the methyl group and the proton attached to the ring at the 4-position of the 6-membered ring in 4MP. Upon
treatment with 100 mM CSA, a fraction of the NMP and 4MP is removed from the membrane (c).

![NMR spectra](image)

Fig. 4.5. $^1$H NMR spectra for a) NMP, b) 4MP, c) a PANi-NMP membrane, d) a PANi-NMP-4MP membrane, e) a CSA-treated PANi-NMP-4MP membrane, and f) a NH$_4$OH-CSA-treated PANi-NMP-4MP membrane.

We cannot quantitatively interpret the amount of NMP and 4MP removed by CSA treatment due to the increased number of signals in the aromatic region when PANi is doped with a strong acid. We do, however, observe that more NMP than 4MP is removed by CSA post-treatment. Additionally, CSA remains in the membrane after treatment and washing with DI water, as shown by two peaks at $\delta = 1.01$ and 0.70 ppm that can be attributed to the two primary methyl groups on CSA. Treatment with 100 mM NH$_4$OH (f) reduces the peaks at $\delta = 1.01$ and 0.70 ppm, but they are still observed. Since the samples could not be dried using heat or vacuum, there is still some residual water in each membrane.
**PANi Membrane Surface Charge Characteristics**

The membrane surface charge for PANi-NMP, PANi-NMP-4MP, and PANi-NMP-4MP CSA-treated membranes are shown in Fig. 4.6. Streaming current measurements show that the addition of 4MP produces a more positively charged membrane as indicated by a shift in the isoelectric point from 4.5 to 5.8. The PANi-NMP membrane has a zeta potential of -50 mV at pH 7, while both untreated and CSA-treated PANi-NMP-4MP membranes have zeta potentials of -20 to -25 mV at pH 7. CSA post-treatment decreases the magnitude of the membrane zeta potential.

![Graph showing zeta potentials of PANi membranes](image)

Fig. 4.6. Zeta potentials of PANi membranes determined by streaming current measurements.
**PANi Membrane Surface and Cross-Sectional Morphology**

Surface and cross-sectional SEM images for PANi-NMP, PANi-NMP-4MP, and CSA-treated PANi-NMP-4MP membranes are shown in Fig. 4.7. SEM cross-sections show that these membranes have an asymmetric structure with finger-like macrovoids. The addition of 4MP produces a membrane with less void space when compared to the PANi-NMP membrane. CSA post-treatment does not appear to affect the membrane void structure. The membrane surface porosity and average pore diameter are reduced upon addition of 4MP. CSA post-treatment increases both surface porosity and average pore diameter.

![SEM images of PANi membranes](image)

*Fig. 4.7. PANi membrane cross-sections and surface SEM images.*

**4.7 Discussion**
The addition of 4MP to a PANi-NMP polymer solution affects PANi beyond disrupting interchain and intrachain PANi hydrogen bonding. The strong basicity (pKᵢ = 11.3) and size (7.29 Å) of 4MP are very similar to heptamethyleneimine (HPMI), which has a pKᵢ = 11.2 and size of 7.16 Å, respectively [28]. HPMI is a PANi gel-inhibitor that has been shown to reduce the quinoid structure in PANi EB to the benzenoid via ring substitution [27]. The decrease in the FTIR Q/B ratio from 0.87 to 0.52 for membranes cast using 4MP indicates that there may be some ring substitution, however, the lack of Q peak shift may show there is no covalent bonding.

PANi-4MP hydrogen bonding and ring substitution reduce the interaction between water and the relatively hydrophilic PANi imine nitrogens. The presence of the relatively hydrophobic ring and methyl group on 4MP, as shown in Fig. 4.8, leads to an increase in PANi UF membrane hydrophobicity.

The membrane hydrophilicity is recovered by 1 h post-treatment using 100 mM CSA and maintained after an additional 3 h 100 mM NH₄OH treatment at 50 °C. The reduction in the FTIR peak at 1740 cm⁻¹ after NH₄OH treatment (Fig. 4.4) along with the reduction in ¹H NMR peaks at δ = 1.01 and 0.70 ppm in Fig. 4.5f) show that the excess CSA has been removed. There may be some residual CSA dissolved in the water remaining in the NH₄OH-treated membrane. Membrane hydrophilicity is not recovered after a 1 h post-treatment using 100 mM NH₄OH at 50 °C, so this NH₄OH treatment does not contribute to membrane hydrophilicity when used to remove excess CSA. Although the mechanism for hydrophilicity is uncertain, we believe there may be some strong interaction between the hydrogen-bonded 4MP and CSA that produces a more hydrophilic membrane. CSA treatment may remove the hydrogen-bonded 4MP, but only at the membrane surface. If CSA were to remove 4MP only at the exposed surfaces of a PANi-NMP-4MP membrane due to physical and/or mass transfer limitations, then ¹H NMR would not detect a noticeable decrease in 4MP because treated films are dissolved in a solvent for analysis and the bulk of the
membrane may still contain 4MP. FTIR is a surface technique and is more sensitive to chemical changes at the membrane surface. We are unable to detect the presence or removal of 4MP from a PANi membrane perhaps due to the similar chemical structure of 4MP and PANi. Treating PANi with an acid protonates the PANi backbone and saturates the imine nitrogens with which 4MP forms hydrogen bonds. Likewise, the acid protonates 4MP and eliminates its ability to hydrogen bond with PANi. One might expect that any acid would liberate hydrogen bonded 4MP. Acids other than CSA are unable to restore membrane hydrophilicity. It is known that CSA induces an expanded coil conformation in PANi, increasing the separation between neighboring chains [54, 55]. However, PANi is normally in a tightly coiled conformation and we suspect that HCl and H_2SO_4 are too small to expand PANi chains sufficiently to create the free volume necessary for the outward diffusion of 4MP. The relatively 2-dimensional geometry of p-toluenesulfonic acid does not promote chain expansion and dodecylbenzenesulfonic acid is likely too large to fit between PANi chains.

Fig. 4.8. Schematic diagram illustrating the reduction and ring substitution of 4MP onto PANi emeraldine base.
Introduction of 4MP produces a less porous membrane with smaller pores. The resulting membrane is much less permeable, but has much higher protein rejection. The higher porosity and larger pores observed in CSA-post-treated membranes potentially arise due to structural re-arrangement of PANi caused by the post-treatment process such as polymer disentanglement or the like. The resulting membrane has a lower BSA rejection. These defects can be minimized by designing a more gentle post-treatment process. Although PANi membrane hydrophilicity is recovered, membrane surface charge is still shifted after CSA post-treatment. This again indicates that there may be strongly associated 4MP remaining on the membrane surface even after CSA post-treatment.

4.8 Conclusions

Pure polyaniline ultrafiltration membranes with improved protein rejection have been formed with the aid of a gel-inhibiting agent, 4-methylpiperidine. These membranes, however, show decreased water permeability and increased hydrophobicity when compared to PANi membranes made from NMP only. 4MP was found to reduce the quinoid ring structure of PANi emeraldine base to the benzenoid form by ring substitution. Hydrogen-bonded and ring-substituted 4MP increased PANi membrane hydrophobicity by occupying a relatively hydrophilic imine nitrogen site and replacing it with a relatively hydrophobic ring and methyl group. Post-treatments using acid solutions indicate that the camphorsulfonate ion causes PANi to take on a more expanded coil conformation, which allows the hydrogen-bonded 4MP to diffuse out of the membrane. Removal of this fraction of 4MP enabled polyaniline ultrafiltration membranes to recover their hydrophilicity. Tailoring membrane properties by a simple post-treatment step has implications for extending the range of separation performance for PANi based membranes.
4.9 References


Chapter 5. Highly Dispersible Polypyrrole Nanospheres for Advanced Nanocomposite Ultrafiltration Membranes

5.1 Introduction

In recent years, ultrafiltration (UF) membranes for bio-separations have been demonstrated as a simple, energy efficient, and readily scalable alternative to traditional purification processes.\(^1\)\(^-\)\(^3\) Fundamental advances in membrane technology that improve the efficiency of separations can lower costs, save time, and may someday lead to new devices such as wearable blood dialysis systems.\(^4\) In evaluating a membrane for use in a particular separation there are criteria/figures of merit that determine the utility of a particular membrane: water permeability, target solute retention, fouling resistance, and chemical and mechanical stability.\(^5\)\(^,\)\(^6\) Typical high-performance synthetic polymers commonly used in the formation of UF membranes include polysulfone, polyethersulfone, and polyacrylonitrile.\(^7\)\(^,\)\(^8\) These polymers are known to be relatively inexpensive, chemically inert, soluble in common organic solvents, insoluble in water, and mechanically tough. However, UF membranes formed from these polymers by nonsolvent induced phase separation (NIPS) generally show an inverse relationship between permeability and retention. An important goal is to improve the permeability (and thereby reduce the energy input) of a membrane without sacrificing selectivity. Another major obstacle in membrane separations is fouling by organic and inorganic species that decrease permeability and overall process efficiency.

The concept of incorporating nanomaterials into polymer matrices is not new, and these composite materials have permeated throughout many aspects of everyday life. Previous work on the incorporation of nanomaterials into membranes has focused on gas separation membranes. There are surprisingly few reports of nanocomposite UF membranes in the literature despite the frequently encountered synergy afforded by blending materials together at the nanoscale. Progress in this field seems limited by the types of nanomaterials that can be incorporated and screened for
performance enhancement. Recent findings have encouraged further exploration of polypyrrole as a membrane material due to its anticipated biocompatibility. Research in our own lab has produced polypyrrole nanomaterials that are sufficiently processable for incorporation into UF membranes. Furthermore, incorporation of conductive nanomaterials into membranes is an attractive target as it opens the door to active transport processes where an electrostimuli can be used to migrate ionic species near the membrane surface.

In this work, PPy nanospheres were synthesized and used in the formation of solution blended polysulfone (PSf) nanocomposite UF membranes by nonsolvent induced phase separation (NIPS). The influence of nanoparticle loading on the morphology, surface energy, charge characteristics, thermal stability, water permeability and protein retention of PPy/PSf nanocomposite membranes is examined.

5.2 Chemical Structure and Morphology of PPy/PSf Nanocomposite Membranes

The structure, morphology, and dimensions of PPy nanospheres have been described in great detail elsewhere. Membranes of varying PPy and PSf content were formed using the NIPS precipitation technique. As the nanosphere loading increases, the membrane color changes from white to brown to gray and then to black. When dried, the membranes display a very smooth and shiny surface, implying that smooth, thin-skinned ultrafiltration membranes have been formed.
The attenuated total reflection/Fourier transform infrared (ATR/FT-IR) spectra of the pure PSf and PPy/PSf nanocomposite membranes are shown in Figure 5.1. The characteristic vibrational bands of PSf occur at 690, 834, 1160, 1240, and 1324 cm\(^{-1}\) due to the C–S–C linkage, the aromatic rings, the symmetric sulfone, the aromatic ether, and an asymmetric sulfone, respectively.\textsuperscript{20–22} With addition of varying concentrations of PPy nanospheres, the characteristic bands attributed to PSf exhibit no chemical shifts, indicating an interaction typical of physical blending.

Figure 5.2 shows the cross-sectional and surface morphologies of membranes with different concentrations of PPy nanospheres with diameter of 85 nm, as observed by scanning electron microscopy (SEM). The cross-sectional morphologies of the pure PSf and nanocomposite membranes exhibit typical finger-like structures consisting of a dense or nanoporous top layer with a
thickness of 1–2 μm and a porous sublayer with large macrovoids. However, the finger-like structures in the nanocomposite membranes, especially in the membranes containing 10% PPy nanospheres, appear more interconnected than those of the pure PSf membrane, perhaps due to more cavities left by the migration of PPy nanospheres during solvent-exchange. Additionally, it appears that macrovoid formation is reduced in the nanocomposite membranes, as a more sponge-like morphology is observed (Figure 5.2, insets). The pure PSf membrane without the support has a thickness of 140 μm, whereas the values decreased to 130 and down to 85 μm after addition of 2–20% PPy nanospheres, respectively, as shown in Figures 5.2a–e.
With increased PPy nanosphere loading, the membrane surface pore diameters increase and the surface becomes rougher (Table 5.1). The nanocomposite membranes with 10% PPy nanospheres show the highest surface roughness and porosity (5.6%) as determined by analyzing the SEM micrographs using NIH ImageJ software. Atomic force microscopy (AFM) was also used for morphological characterization of the membrane surface to complement SEM. According to the 3D AFM images and histogram analyses of the membranes, the morphological characterization
results are presented in Table 5.1, elucidating a few trends corresponding to concentrations of PPy nanospheres. Generally, with the addition of PPy nanospheres, the surface roughness of the nanocomposite membranes appears to be greater than that of the pure PSf membrane. In the range of the scan areas 1 µm × 1 µm, the nanocomposite membranes exhibit the highest root-mean-square (RMS) roughness, average roughness (Rₐ), and maximum roughness (Rₘₐₓ) with values of 8.5, 6.5 and 60.9 nm, respectively, at 10 wt% concentration of PPy nanospheres, compared to 2.6, 3.3 and 24.5 nm of pure PSf membranes. With further increase in concentration of PPy nanospheres up to 20%, however, the surface structure starts to become smooth again. The huge change in Rₐ, RMS, and Rₘₐₓ, but small change in surface area difference (SAD), is evidence that homogeneous and smooth PPy/PSf nanocomposite membranes have been created. These surface roughness data were also used in conjunction with contact angle data to produce free energy of interaction values. PPy nanospheres were observed existing in both the top and bottom surfaces of the nanocomposite membranes, indicating that the increased roughness may be caused by the accumulation of hydrophilic PPy nanospheres on the membrane surface. Even the finger-like and sponge-like structures of the nanocomposite membranes show some individual or aggregated nanospheres, as

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Rₐ (nm)</th>
<th>RMS (nm)</th>
<th>Rₘₐₓ (nm)</th>
<th>SAD (%)</th>
<th>Contact angle (°)</th>
<th>-ΔG_f (mJ/m²)</th>
<th>d_p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>2.6</td>
<td>3.3</td>
<td>24.5</td>
<td>1.8</td>
<td>64.7±3.8</td>
<td>103.4</td>
<td>7.7</td>
</tr>
<tr>
<td>2% PPy</td>
<td>2.5</td>
<td>3.6</td>
<td>45.2</td>
<td>2.0</td>
<td>54.0±5.8</td>
<td>114.8</td>
<td>7.0</td>
</tr>
<tr>
<td>4% PPy</td>
<td>5.1</td>
<td>7.0</td>
<td>64.6</td>
<td>1.6</td>
<td>42.1±0.7</td>
<td>126.0</td>
<td>7.2</td>
</tr>
<tr>
<td>10% PPy</td>
<td>6.5</td>
<td>8.5</td>
<td>60.9</td>
<td>2.9</td>
<td>45.6±4.1</td>
<td>122.3</td>
<td>7.5</td>
</tr>
<tr>
<td>20% PPy</td>
<td>3.0</td>
<td>3.7</td>
<td>26.8</td>
<td>3.9</td>
<td>42.9±2.0</td>
<td>124.1</td>
<td>8.2</td>
</tr>
</tbody>
</table>
indicated in Figure 5.2 (insets). This implies that the PPy nanospheres have good miscibility with the PSf matrix, leading to improved surface porosity and more interconnected cross-sectional morphologies.

### 5.3 Hydrophilicity, Charged Surface, and Thermal Stability

The influence of nanoparticle loading on the hydrophilicity and surface energy of these composite membranes is presented in Table 5.1. Note that upon addition of only 2% PPy nanospheres, the contact angles of the resulting nanocomposite membranes become lower than that of pure PSf membranes (65 vs. 54°). The contact angles further decreased to ~42° when the concentration of PPy nanospheres is increased to 4%. Then, the contact angles remain relatively constant with values of 42−46° when 10−20% PPy nanospheres were added. When surface roughness is considered, the surface Gibbs free energies (ΔG_{13}) of the pure PSf and nanocomposite membranes can be calculated from the contact angles, and these values are shown in Table 5.1. As expected, the pure PSf membrane is the most hydrophobic, and the membrane surface energies generally increase with increasing PPy concentration (103 vs. 122 mJ/m²).

Zeta potential measurements for the pure PSf and nanocomposite membranes were determined as a function of streaming pH. The decrease in zeta potential as pH increases is a typical characteristic of filtration membranes. The PPy/PSf nanocomposite membranes have amine, amino, and sulfone groups which will be protonated at low pH leading to a positive charge (i.e., a positive zeta potential); the groups will be deprotonated as the pH increases, causing the membrane charge to become more negative (i.e., a negative zeta potential). At the isoelectric point (IEP) of pH = ~3.4, the pure PSf membrane has a net charge of zero (i.e., zeta potential = 0 mV). The IEP values increased to pH = 4.2−4.8 with the addition of PPy nanospheres. More importantly, either positively charged at low pH due to the protonation or negatively charged at higher pH due to
deprotonation, the nanocomposite membranes demonstrate much higher zeta potentials compared to the pure PSf membranes. Additionally, as the PPy nanosphere loading was increased, the nanocomposite membranes became more highly charged. Clearly, the addition of PPy nanospheres has promise for improving separation efficiency of PSf membranes because hydrophilicity and anti-fouling capability generally increase as membrane surfaces become more hydrophilic, energetic, and charged.\textsuperscript{9,27,28}

Thermal stabilities of the membranes are measured by thermogravimetric analysis (TGA) and differential TGA (DTGA) scans. When the membranes are heated to 500 °C, parent PSf has negligible weight-loss as compared to the nanocomposite which experiences ~7% weight-loss. The acidic dopants of PPy nanospheres would be volatilized upon heating, and may explain why the nanocomposite membranes show a slightly lower thermal stability than parent PSf membrane before 500 °C. When the membranes are heated to 600 °C, however, the nanocomposite membranes show a slower weight-loss rate than the pure PSf membrane (11.2 vs. 17.1 %/min). Moreover, when the membranes are heated from 600 to 1000 °C, both parent PSf and the nanocomposite exhibit only ~5% weight-loss. The nanocomposite membrane exhibits a relatively more-massive residue at 1000 °C as compared to parent PSf membrane (47 vs. 30%). When the weight-loss is calculated by subtraction of the PPy mass, negligible differences between membranes are indicated. This implies that PPy has an insignificant influence on the thermal stability of the parent PSf, likely due to the adequate miscibility between the two polymers which is consistent with the ATR/FT-IR analyses.

5.4 Separation Performance

While microscopy and surface energy characterization indicates that PPy nanospheres produce hydrophilic films resembling UF membranes, meaningful performance data were obtained by ultrafiltration experiments. The testing procedures employed in this study are described in
greater detail in the supporting information available online. Figure 5.3 shows a simple fouling experiment, in which compacted membranes are fouled with BSA while flux decline and BSA retention arise are recorded. After collecting 5 mL of permeate, the membranes were rinsed using deionized water at room temperature in an attempt to clean the membrane surface and recover some of the lost permeability. Performance data from these tests are presented in Table 5.2.

We found that the introduction of as little as 2% PPy nanospheres produces UF membranes with markedly improved performance over the parent PSf membrane. All nanocomposite membranes showed improvements in initial, compacted, fouled, and recovered permeability with the most notable improvements in the higher PPy content membranes (46 vs. 4.3, 22 vs. 4.0, 7.8 vs. 1.8, and 12 vs. 2.9 μm/s/psi). All membranes rejected BSA proteins above 85%, indicating average pore diameters of around 8 nm (See supporting information), consistent with expectations from

Table 5.2: Impact of PPy Nanosphere Loading Percentage on Membrane Performance.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial Permeability (μm/s/psi)</th>
<th>Compact Permeability (μm/s/psi)</th>
<th>Fouled Permeability (μm/s/psi)</th>
<th>Recovered Permeability (μm/s/psi)</th>
<th>Recovered Permeability (%)</th>
<th>Flux Decline (%)</th>
<th>BSA Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>4.35</td>
<td>4.03</td>
<td>1.85</td>
<td>2.92</td>
<td>72.4</td>
<td>54.1</td>
<td>94.3</td>
</tr>
<tr>
<td>2% PPy</td>
<td>19.5</td>
<td>7.63</td>
<td>4.03</td>
<td>5.81</td>
<td>76.1</td>
<td>47.2</td>
<td>86.5</td>
</tr>
<tr>
<td>4% PPy</td>
<td>19.7</td>
<td>5.83</td>
<td>2.92</td>
<td>4.74</td>
<td>81.2</td>
<td>49.9</td>
<td>88.3</td>
</tr>
<tr>
<td>10% PPy</td>
<td>34.0</td>
<td>20.2</td>
<td>7.39</td>
<td>10.9</td>
<td>53.7</td>
<td>63.4</td>
<td>82.5</td>
</tr>
<tr>
<td>20% PPy</td>
<td>46.2</td>
<td>22.5</td>
<td>7.85</td>
<td>12.3</td>
<td>54.6</td>
<td>65.1</td>
<td>83.2</td>
</tr>
</tbody>
</table>
The parent PSf membrane showed higher BSA retention of >94%, approaching absolute retention when concentration polarization arguments are taken into consideration. We observed a lower relative flux decline upon BSA fouling in membranes containing 2 and 4% PPy nanospheres. While it is tempting to attribute this observation to the hydrophilicity and surface charge improvements associated with the introduction of nanoparticles, this observation can also be explained by the greater average pore diameters present in the 2 and 4% PPy nanosphere containing membranes. Additionally, while the 10 and 20% PPy membranes showed the largest relative flux decline of 63-65% upon fouling, their fouled permeability was still considerably higher than that of the pure PSf membranes (7.8 vs. 1.8 µm/s/psi).

Figure 5.3: Fouling experiments displaying the pure water flux measured as a function of time for membranes with varying PPy nanosphere content. After a stable flux of 20 µm/s was obtained, the membranes were challenged with 1 g/L BSA solution and the flux decline recorded. After 10 mL of permeate was collected, the membranes were washed with water and the flux recovery was recorded. BSA retention data, acquired during the course of the experiment, is plotted against the right axis for each membrane.

microscopy. The parent PSf membrane showed higher BSA retention of >94%, approaching absolute retention when concentration polarization arguments are taken into consideration.

We observed a lower relative flux decline upon BSA fouling in membranes containing 2 and 4% PPy nanospheres. While it is tempting to attribute this observation to the hydrophilicity and surface charge improvements associated with the introduction of nanoparticles, this observation can also be explained by the greater average pore diameters present in the 2 and 4% PPy nanosphere containing membranes. Additionally, while the 10 and 20% PPy membranes showed the largest relative flux decline of 63-65% upon fouling, their fouled permeability was still considerably higher than that of the pure PSf membranes (7.8 vs. 1.8 µm/s/psi).
Another way to analyze the data obtained from the fouling experiments is to discuss the total hydraulic resistance present at different stages in the experiment. Initially, prior to introduction of the BSA, the total resistance to water flow through the membrane ($R_t$) is wholly attributed to the resistance of the membrane ($R_m$) itself. Upon introduction of BSA, the flux immediately declines due to fouling of the membranes. This fouling adds resistance to the system and we can describe this contribution as $R_f$. At any point in the experiment the total resistance is a sum of the contributions from the membrane and the fouling layer, simply $R_t = R_m + R_f$. Figure 5.4 shows membrane performance in terms of the hydraulic resistance due to the fouling layer as a function of the volume of water that has passed during the experiment. It is clear from the figure that the pure polysulfone membrane experiences the largest increase in resistance due to fouling from BSA proteins. The cleaning step, although decidedly unsophisticated, is effective enough to restore nearly two-thirds of the permeability that was lost upon fouling with BSA. The PPy nanosphere-
containing membranes also lose permeability upon fouling with BSA, but the effect is not as severe as for the pure PSf membrane. The total irreversible fouling for the nanocomposite membranes is less than half of the corresponding value for PSf, indicating that these membranes are both resistant to fouling and also efficiently cleaned using only water.

It is difficult to speculate on the mechanism for separation performance enhancement upon nanoparticle introduction as many factors are in play. In general changes in membrane pore structure are the main contributors to membrane performance. It has been reported that high roughness leads to two changes in the modified membrane: an increase in efficient filtration area and a decrease in the anti-fouling property, potentially aiding in performance enhancements.\textsuperscript{22} Additionally, we anticipate that the PPy nanospheres behave as porogenic agents. Because the PPy nanospheres used were \textit{in a} protonated and oxidized form, a unique porosity is induced \textit{via} dedoping during the NMP/water exchange, leading to void spaces where small molecules such as water can pass through, while larger molecules such as BSA are rejected.

\textbf{5.4 Experimental}

\textit{Materials.}

All the chemicals such as pyrrole, 2,4-diaminodiphenylamine, ferric chloride (FeCl\textsubscript{3}), hydrochloric acid (HCl), 1-methyl-2-pyrrolidinone (NMP), polysulfone (PSf, \textasciitilde 22,000 by MO), bovine serum albumin (BSA, \textasciitilde 66 kDa) were purchased from Sigma-Aldrich and used as received. Potassium chloride (KCl), sodium hydroxide (NaOH), and sodium chloride (NaCl) were purchased from Fisher Scientific. All the materials were chemical grade and used as received.

\textit{Synthesis of Polypyrrole (PPy) Nanospheres.}
A scaled-up synthesis of PPy nanospheres was carried out as follows: 0.5 g of pyrrole and 0.15 g of 2,4-diaminodiphenylamine (10 mol % relative to pyrrole) as an initiator were dissolved in 0.3 L of methanol, while 1.2 g of FeCl₃ as an oxidant was dissolved in 0.3 L of 1.0 mol/L of HCl. The two solutions were cooled to 0 °C and rapidly mixed. The reaction was vigorously shaken for 10–15 s by hand and then left undisturbed overnight. The as-synthesized products were purified by centrifugation at a speed of 4500 rpm/min using DI water/methanol (90/10) at 15 °C until the supernatant became colorless. A black powder was obtained by drying the above solution at 50 °C for one week to remove all the water. The structure, morphology, and size measurements of the PPy nanospheres are presented elsewhere.

Membrane Formation via Nonsolvent Induced Phase Separation (NIPS).

A procedure well-known as NIPS in the field of membrane science was used to prepare the ultrafiltration (UF) membranes. In this process, five compositions, i.e. 0, 30, 60, 150 and 300 mg of polypyrrole nanospheres dispersed in 6.83 g of N-methyl-2-pyrrolidone (NMP) and then 1.5, 1.47, 1.35 and 1.2 g of polysulfone beads were added, respectively. The mixtures consisting of 1.5 g polymers and 6.83 g of NMP were stirred at 50 °C overnight to produce casting solutions at a fixed concentration of 18 wt% with five PPy concentrations (0, 2, 4, 10 and 20 wt%) used for all the polymers. The solutions were cast on a commercial nonwoven polyester support fabric and then immersed in 18 MΩ laboratory deionized water at room temperature to induce precipitation by a solvent/non-solvent (NMP/water) exchange forming homogeneous UF membranes.

Measurements and Characterization.

The morphologies of the pure PSf and PPy/PSf nanocomposite membranes were observed by a JEOL JSM-6700 field emission SEM. FT-IR spectra of the membranes were record on a
JASCO ATR/FT-IR-620 spectrometer. TGA/DTGA scans of the membranes without the support fabric were carried out on a Perkin Elmer TGA Pyris 1 by heating the samples from room temperature to 1000 °C at a rate of 10 °C/min. The hydrophilicity of all the UF membranes was determined by the captive bubble technique using a DSA10 Krüss goniometer, at least seven contact angle measurements were performed across each membrane coupon at equally spaced intervals. Streaming current was measured using an adjustable gap electrokinetic analyzer (SurPASS Electrokinetic Analyzer, Anton-Paar GmbH). The flow channel gap was set at 100 µm, and a 1 mM KCl solution at 20 °C was used as the background electrolyte. Streaming current was determined in a pH range of 2-10, adjusted using HCl and NaOH. Membrane zeta potential (ζ) was calculated using the Helmholtz-Smoluchowski equation,

\[
\zeta = \frac{dI}{dp} \cdot \frac{\mu}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A},
\]

where \(dI/dp\) is the slope of the streaming current versus pressure, \(\mu\) is the solution dynamic viscosity, \(\varepsilon\) is the dielectric constant of the solution, \(\varepsilon_0\) is the vacuum permittivity, \(L\) is the streaming channel length and \(A\) is the cross-section of the streaming channel. MQ water initial permeability and BSA retention tests were conducted in a Batch-type UHP-25 K ultrafiltration apparatus under a transmembrane pressure of ~10 psi at 25 °C. The permeability was determined for each membrane by slowly increasing pressure to maintain a pure water flux of 0.421 mL min\(^{-1}\) until a flux decline of less than 5% was observed over an hour. BSA with a diameter of ~6 nm was used to evaluate the membrane bio-separation performance. BSA concentrations in the permeate streams (\(C_p\)) and feed streams (\(C_f\)) were determined by an HP 8453 UV-vis spectrophotometer. Solute particle retention (\(r\)) was calculated by the equation, \(r = (1 - C_p/C_f) \times 100\%\). Permeability and retention for each membrane were measured five times and then averaged. The surface average pore diameters (\(d_p\) of
the membranes were approximated from BSA retention by using the equation,\(^{23,29}\)

\[
r = 1 - 2(1 - \lambda)^2 + (1 - \lambda)^d,
\]
where \(\lambda = d_s/d_p\), \(d_s\) is BSA diameter of \(~6 \text{ nm}\).

### 5.5 Conclusions

Adjusting the concentration of highly dispersible PPy nanospheres can be used to tailor the hydrophilicity, surface charge, morphology, permeability, and solute retention of PSf nanocomposite ultrafiltration membranes. High loadings of PPy nanospheres produce significant improvements in membrane permeability, translating into >10.6 times initial water permeability, >5.5 times water permeability, >4.2 times BSA fouled permeability, >4.2 times recovered permeability than that of a pure PSf ultrafiltration membrane (46 \(\mu\text{m/s/psi}\) vs. 4.3, 58 \(\mu\text{m/s/psi}\) vs. 1.8, and 12 \(\mu\text{m/s/psi}\) vs. 2.9 \(\mu\text{m/s/psi}\)), while retaining relatively high BSA retention (85–94\%). With nanoscale pores, high porosity, improved hydrophilicity, and tunable surface charge properties, the PPy/PSf nanocomposites hold great promise for advanced bio-separation membranes. Further research will focus on electro-ultrafiltration using PPy/PSf nanocomposite membranes, where studying the water permeability, separation factors, and anti-fouling properties under an applied electric field may lend meaningful insight into the development of new bioseparation technologies.
5.6 References


Chapter 6. Poly(aniline-co-ethylaniline) Copolymer Nanofibers via Rapidly-Initiated Chemical Oxidative Polymerization

1.1 Introduction

One-dimensional polymer nanostructures such as nanofibers, nanowires, nanotubes, and nanobelts have become extensively studied in recent years due to the promise of dimensionally-confined electron transport and the ability to form percolative networks at low concentrations. These properties hint at the production of all organic electronic devices that will be cheap, lightweight, and flexible. Additionally, the high surface area associated with nanostructure leads to a high charge to mass ratio, producing charge-stabilized colloids in aqueous systems. Polyaniline is one of the most studied conducting polymers due in large part to its propensity to form 1-dimensional nanostructures. Control over nanostructure formation requires consideration during synthesis as well as during post-processing. A novel method of producing nanofibers by controlling nucleation conditions during chemical oxidative polymerization was developed that produces homogeneous dispersions of polyaniline nanofibers.\(^1\) The technique has recently been applied to derivatives of polyaniline as well as other families of conducting polymers such as polythiophene and polypyrrole.\(^2\) Even more recently the technique was applied to the synthesis of copolymers of aniline, and an aniline derivative, N-ethylaniline, to produce copolymer nanofibers.\(^3\) Here we show that a similar approach can be used to synthesize copolymer nanofibers of poly(aniline-co-2-ethylaniline). The optical and electronic properties of these materials can be tuned by altering the feed ratio during polymerization as well as by the choice of initiator molecule used during polymerization.
Experimental

All chemicals were obtained from Sigma-Aldrich and used as received without additional purification. In a typical synthesis, aniline and ethyl aniline derivative were dissolved in 1M HCl to achieve a total monomer concentration of 0.32 M. To this solution was added an initiator such as p-phenylenediamine dissolved in a minimal amount of ethanol. The resultant initiator concentration is 0.0064 M, corresponding to 2% relative to the monomer concentration. Next, an equal volume solution of 0.08 M ammonium peroxydisulfate in 1 M HCl is rapidly added to the monomer solution, the container is capped, shaken for 5-10 seconds, and allowed to sit undisturbed overnight. The darkly colored mixture is then loaded into 12,000-14,000 dalton molecular weight cut-off (Fisher Scientific) dialysis tubing and is dialyzed against deionized water for several days.

The purified copolymer nanofibers were dialyzed against 0.1 M NH₄OH and then against water to produce nanofibers in the dedoped form. These samples were centrifuged at 4000 RPM for 20 minutes to remove the majority of the solvent and then dried under vacuum at 60°C. Samples for NMR were prepared by dissolution in deuterated dimethyl sulfoxide (DMSO-d₆) and filtered through glass wool. NMR spectra were collected on a Bruker ARX400 spectrometer.

Aqueous nanofiber dispersions were diluted with either 0.1 M HCl or 0.1 M NH₄OH for UV-Vis absorption measurements obtained on an HP 8452 spectrometer.
Samples for scanning electron microscopy imaging and sheet resistance measurements were prepared by dropcasting copolymer nanofiber dispersions from 0.1 M HCl to ensure that samples are conducting. Films for sheet resistance measurements were dropcast onto cleaned glass slides and air dried. Resistance measurements were obtained using a modified two-probe method and a Hewlet Packard 3478A multimeter.

**Results and Discussion**

*Synthesis of Copolymer Nanofibers*

A wide range of substituted anilines have been polymerized into nanofibers using the rapidly mixed method in the presence of an initiator previously. Here, 2-ethyl aniline is combined in varying stoichiometries with aniline and is then polymerized by chemical oxidation in the presence of p-phenylenediamine and N-phenyl-1,4-phenylenediamine and also in the absence of an initiator. Initiation of the reaction in the absence of these small molecule initiators occurs slowly, with the onset of color occurring most rapidly in pure polyaniline and pure poly(ethylaniline) syntheses. In the presence of an initiator, all reactions proceed quickly with a dark blue/black color developing almost instantly upon oxidant addition. This is consistent with previous reports where the combination of low oxidation potential and low solubility of the initiator in 1 M HCl are thought to be responsible for essentially eliminating the induction period in polyaniline polymerization.
Electron microscopy analysis of synthesized copolymer samples reveal that in the absence of an initiator, poly(2-ethylaniline) synthesized by rapidly mixed polymerization forms a granular or agglomerated polymer morphology as seen in Figure 6.2. When an initiator is used during synthesis, the resultant morphology resembles the polyaniline nanofibers produced by rapidly mixed reactions. In addition to producing a nanostructured morphology for 2-ethylaniline homopolymers, the full range of copolymer compositions with aniline form nanofibers when an initiator is used as is shown in Figure 6.3. It appears that there are noticeable morphological differences between copolymer samples synthesized with the two different initiator molecules. Although both initiators produce a nanofibrillar morphology, samples synthesized with p-phenylene diamine samples appear to have a less rigid nanofiber structure where softer edges and more curves are present.
Figure 6.3: Scanning electron micrograph of poly(2-ethylaniline) synthesized by rapid mixing in the presence of N-phenyl-1,4-phenylenediamine (left), p-phenylenediamine (center), and no initiator (right).
Composition of Copolymers

It has previously been reported that 2-ethylaniline has a higher reactivity ratio than aniline and thus copolymer materials are enriched in ethylaniline with respect to the monomer feed ratio between aniline and ethylaniline. Here however, we are introducing a second “aniline source” when we include p-phenylenediamine or N-phenyl-1,4-phenylenediamine as an initiator. The composition of the copolymers can be determined by integration of aliphatic (δ = 1.04 ppm) and aromatic (δ = 6.5-7 ppm) proton regions in a 1H NMR spectrum. The actual copolymer composition (vertical axis) is plotted against the feed composition of ethylaniline used in the synthesis in Figure 6.4.

Interestingly, although 2-ethylaniline is reported to have a higher reactivity ratio than aniline, we see less enrichment in ethylaniline content in comparison to reported values by Conklin et al. In syntheses with a low ethylaniline content we observe a higher reactivity ratio for ethylaniline to aniline signified by a 1:1 feed ratio producing copolymers with 60%, 72%, and 76% ethylaniline for NPPD, PPD, and no initiator, respectively. These compositions consist of less ethyl derivative incorporated in comparison to the conventionally-synthesized copolymers reported by Conklin. As we are now incorporating a second “aniline source” in the form of these aniline-resembling initiator molecules, this is not infeasible. More interesting is what occurs for pure poly(2-ethylaniline) synthesized in the presence of initiator molecules. Here, where the only “aniline source” is the initiator molecule, we observe a maximum ethylaniline content of 75% ethyl derivative. This can only be explained by a low yield of the poly ethylaniline synthesis where all of the “aniline-like” initiator is incorporated into the copolymer structure so that around 1 in 4 monomer units is aniline and the other 3 are ethylaniline. If we assume a polymerization yield of 16 percent, not uncommon for polyaniline, and an initiator loading of 4 percent, this result is then rationalized.
Absorption Spectra

UV-Vis spectra were collected for doped and dedoped samples of all copolymer compositions. The spectra of pure polyaniline and poly(2-ethylaniline) are shown in Figure 6.4 below. The spectra show the characteristic peaks of polyaniline with absorptions for dedoped polymers occurring at 300 and 600 nm and absorptions for doped polymers occurring at 400 and 800 nm. There is a slight blue shift in absorption for the poly(2-ethylaniline) nanofibers relative to the parent polyaniline material, indicating a slightly lower degree of delocalization or conjugation along the polymer backbone. This phenomenon is expected, as the ethyl substituent is expected to disrupt the planarity of the conjugated pi system. The intensity of the polaron transition that occurs at long wavelengths is also diminished in the poly(2-ethylaniline) nanofibers.

Figure 6.4: Copolymer composition versus feed composition of poly(aniline-co-ethylaniline) materials synthesized by rapid mixing and comparison to values reported in Conklin et al.
Electrical Properties of Copolymers

The conductivity of polyaniline derivatives is always lower than that of the parent polymer. Here we measured a sheet resistance of 1 kΩ/sq for pure polyaniline nanofibers synthesized in the absence of an initiator. Pure polyaniline nanofiber samples synthesized in the presence of initiators PPD and NPPD had sheet resistance values of 2 kΩ/sq and 4 kΩ/sq respectively. These represent the high end of conductivity for the samples in this study, as the alkylated aniline units are known to disrupt planarity and effect electron transport. The results of compositional characterization by NMR indicate that there is only one pure polyethylaniline material whose conductivity can be characterized as all of the nanofiber samples contain a considerable amount of “aniline-like” monomer units due to the inclusion of initiator molecules in the polymer backbone. The sheet resistance for pure poly(2-ethylaniline) is 5 MΩ/sq, over 3 orders of magnitude more resistive than

Figure 6.5: UV-Vis-NIR spectrum of homopolymer nanofibers synthesized in the presence of aniline dimer (NPPD). Dedoped polymers show absorption bands around 300 and 570 nm while doped polymers absorb more strongly around 400 and 800 nm.
pure polyaniline samples. The sheet resistance of copolymer nanofiber samples falls within these extremes for each respective initiator. A plot of sheet resistance versus copolymer composition is shown in Figure 6.6 below. All compositions aside from pure polyaniline syntheses are greater than 50% ethylaniline in the resulting copolymer nanofibers. A straightforward comparison lies in copolymer samples that are determined to be 70% ethylaniline by NMR. These materials, highlighted in the box, have greatly differing conductivities despite having a similar chemical composition. We observe that for copolymer samples with 70% ethylaniline sheet resistance decreases in the trend: NPPD > no initiator > PPD. This contrasts the pure polyaniline scenario where the sheet resistance decreases in the trend: NPPD > PPD > no initiator. It is clear that using the aniline dimer (NPPD) as an initiator harms the conductivity of the resulting polymer, but that for copolymers with 2-ethylaniline, PPD can be used to increase the conductivity of the resulting copolymer.
Conclusions

The rapidly-initiated method for the polymerization of aniline to produce nanofibers has been used to produce copolymer nanofibers of poly(aniline-co-ethylaniline). Electron microscopy reveals that nanofibers are produced in all cases where an initiator molecule such as p-phenylenediamine or N-phenyl-1,4-phenylenediamine is employed. The resultant copolymer composition can be tuned using different feed ratios of aniline and aniline derivative and are enriched in ethylaniline content due to a higher reactivity ratio. It is also apparent that the initiator molecules used in the synthesis of these nanofibers are readily incorporated into the polymer backbone, decreasing the effective amount of ethylaniline within the copolymers. Absorption experiments show that ethyl substituents cause a blue shift in characteristic absorption peaks. Electrical measurements show that increasing ethylaniline content increases the sheet resistance of nanofiber samples from 1 kΩ/sq for pure polyaniline up to 5 MΩ/sq for pure poly(2-ethylaniline).
Also noteworthy is that the initiator p-phenylenediamine lowers the sheet resistance of copolymer samples with 70% ethylaniline content. These materials show promise for use in a variety of semiconducting applications.
References


Chapter 7. Carbon Nanotube/Polyurethane Composite Coatings Through Polyaniline/DBSA: Fabrication and Electrical Properties

7.1 Introduction

Polymeric materials are used in many different situations. The electronic, chemical and mechanical properties of each particular resin determine the limits of its useful application. Structural materials such as carbon fiber/polymer composites are increasingly being incorporated as replacements for more dense metallic materials in applications where a high strength to weight ratio is advantageous. An unfortunate consequence of this replacement is the build up of electric charge when these insulating materials are in contact with metals or other materials with differing dielectric constants.¹ This electrical potential builds until a means of dissipation is found, either by contact, an electrical short, or dielectric breakdown. The high voltages produced by this process can compromise the electronic properties of materials comprising sensitive electronic devices.² To address this problem, semiconducting coating materials have been actively explored over the last several decades. These materials bridge a gap between the dense and conductive metallic materials and the lightweight, but insulating polymeric materials used in aerospace applications.

Nanotechnology has changed the face of composite and aerospace engineering. The high strength to weight ratio of carbon nanotubes and graphene have triggered a large influx of investment in basic research. Unfortunately, there have been few significant innovations in this field with respect to incorporating these strong and highly conducting materials into polymer composites. A major limitation to the incorporation of carbon nanotubes into polymer composites is the insolubility of these “inorganic carbon” materials.³ Surface modification through oxidative acid treatment produces hydrophilic functional groups along a carbon nanotube and at its ends, but the produced dispersions are only stable on a timescale of hours and suffer a loss in conductivity due to
disruptions in conjugation. Other strategies using surfactants are problematic due to the requirement to remove the surfactant or suffer the increased resistance due to poor contacts. Here we provide an approach to achieve stable dispersions of non-functionalized single-walled carbon nanotubes (AP-SWCNTs) within a polyaniline nanofiber matrix, where dodecylbenzene sulfonic acid (DBSA) is used as both a surfactant, and an acidic dopant. These composites are conducting through carbon nanotube pathways, as even the dedoped composites are conducting and also show improved film-forming characteristics when compared to the pure polyaniline/DBSA material. Additionally, we are able to incorporate these organic solvent-based materials into solvent systems that are relevant to the polyurethane systems approved by Boeing engineers, producing coatings within the static dissipative regime. We believe this innovation will form the basis for a new class of polymer-based static dissipative coatings for a range of aerospace and land-based applications.

7.2 Materials/Methods

All materials were used as received without further purification. Aniline, hydrochloric acid, ammonium peroxydisulfate, ammonium hydroxide, dodecylbenzene sulfonic acid (70 wt% in 2-propanol) were obtained from Sigma Aldrich. AP-SWCNTs were obtained from Carbon Solutions Inc. Akzo Nobel solvent-based 3-component polyurethane clearcoat system (TR-109, PC-233, ECL-G-7) was obtained from our collaborators at The Boeing Company.
**Polyaniline Nanofiber Synthesis**

A large-scale synthesis of polyaniline nanofibers was carried out by a method developed in our research group and outlined in Figure 7.1.\(^4\) Briefly, a solution of 0.08 M ammonium peroxydisulfate (APS) in 1 M hydrochloric acid (HCl) was combined with a solution of 0.32 M aniline in 1 M HCl and rapidly shaken for 15 seconds. After shaking, the mixture was allowed to sit undisturbed for 24 hours. The mixture was then filtered and washed with water until the filtrate was colorless. The material was then collected and dried in a furnace at 60°C. The dry material was ground to a fine powder and then redispersed in 0.1 M ammonium hydroxide (NH\(_4\)OH) and stirred overnight. Next the mixture was filtered and washed with deionized water. The purified material was dried in an oven at 60°C. The dry powder was ground using a mortar and pestle and then dried under vacuum at 60°C.

![Figure 7.1: The chemical (or electrochemical) oxidation of aniline at low pH produces the doped, conductive form of polyaniline, depicted in the green emeraldine salt form.](image)

**Dispersal of Carbon Nanotubes**

The dry polyaniline base nanofibers were combined with DBSA in a 1:1 ratio of dimer to acid. This mixture was diluted to 10 wt% with solvent and then sonicated in a bath sonicator for 1 hour. Next, as-produced single-walled carbon nanotubes (APSWCNTs) were added in a proportion of 20% loading relative to polyaniline/acid. The mixture was sonicated overnight and then allowed
to cool prior to filtration. A typical glass wool pipette filtration system was used to remove insoluble particulates.

*Polyurethane Composite Formation*

A filtered polyaniline/DBSA/carbon nanotube dispersion in chloroform was evaporated to dryness in order to determine the solids content. An appropriate volume of this nanotube dispersion was combined with polyurethane pre-polymer solution to achieve the desired loading of conductive material within the polyurethane matrix. A schematic for the preparation of these composites is shown in Figure 7.2 below. Polyurethane/conducting material composites were then spin-coated onto cleaned glass substrates at 5,000 RPM for 10 seconds.

Figure 7.2: Schematic illustration of the process for dispersing carbon nanotubes within a polyaniline and polyurethane matrix.
7.3 Results and Discussion

Nanostructured polyaniline is known to produce charge-stabilized colloids at low pH in aqueous systems in what is known as the emeraldine salt form. The polyaniline backbone becomes protonated and the positive surface charge on the polymeric material repels itself from neighboring chains/particles so that the colloid is stable. The salt form of the material is very insoluble in organic solvents that are needed to produce polyurethane composite material when the acid used to dope polyaniline is one of the conventional strong acids that are used to dope polyaniline such as hydrochloric, sulfuric, nitric, and perchloric acid. The counteranions (or conjugate bases) of these acids behave as relatively hard anions and allow polyaniline chains to pack tightly together and make it difficult for solvent molecules to interact with the functional groups along the polymer backbone. The use of bulky organic sulfonic acids such as camphorsulfonic acid and dodecylbenzene sulfonic acid prevents this tight packing between polymer chains and simultaneously allows the organic anions to interact with solvent molecules. In this light, we are able to produce stable dispersions/solutions of polyaniline in chloroform and toluene when camphorsulfonic acid and dodecylbenzene sulfonic acid are used as acidic dopants for polyaniline.

Perhaps more interesting is the ability of this polyaniline/DBSA material to disperse unfunctionalized carbon nanotubes in the same solvent system. We used relatively inexpensive ($50/g) “as-produced” single-walled carbon nanotubes that do not undergo acidic treatment intended to remove metal catalyst particles and oxidize the surface and edges of the nanotubes. Acidic treatment is often used to make the single-walled nanotubes dispersible in aqueous systems, a feature that would likely hinder our attempts at producing stable dispersions in nonpolar organic systems. We observe that after producing a stable dispersion of polyaniline/DBSA, addition of (20% loading) APSWCNTs followed by overnight sonication results in a well-dispersed carbon nanotube network within the polyaniline/DBSA matrix.
Transmission electron microscopy images shown in Figure 7.3 reveal that the nanotubes are in the form of bundles within the polymer matrix, as the observed diameter is seldom less than 20 nm, indicating that the bundles are composed of a minimum of 10 nanotubes. Metal catalyst particles can be clearly seen in the TEM images, where the dense metallic materials appear as black particles due to a large Z-contrast. Also apparent is the network formed by nanotubes within the matrix where very long bundles of tubes connect seemingly empty regions of space.

Figure 7.3: Transmission electron micrograph of polyaniline/DBSA/CNT composite materials shows carbon nanotube bundles connecting regions of conducting polymer (left). The image on the right shows polyaniline/DBSA/CNT composite materials forming a connected network within the bulk material. Bottom right corner shows Formvar™/carbon support.
Scanning electron microscopy also reveals a well-connected network of carbon nanotubes as seen in Figure 7.4. Here the nanotubes and the catalyst particles appear lighter in tone in comparison to the polyaniline/DBSA matrix due to a greater amount of available secondary electrons. Figure 7.5 reveals an interesting phenomenon that occurs under extended irradiation with the electron beam. The figure shows six consecutive SEM images taken of the same region of the carbon nanotube/polyaniline composite sample. Initially (Panel 1) it is impossible to confirm the presence of the carbon nanotube network as it is hidden within the polymer matrix. Metal catalyst particles are visible in the first image, implying the presence of carbon nanotubes within the matrix. However, with extended exposure to incident electrons, the polymer matrix seems to erode, revealing the presence of a well-connected network of nanotube bundles.
Figure 7.5: Consecutive scanning electron micrographs of polyaniline/DBSA/CNT composite material reveals that under electron beam irradiation the polymer matrix is degraded.
For applications as a static dissipative material, engineers would ideally like a coating material that is relatively transparent when deposited as a thin film. Transmittance measurements of a polyaniline/DBSA/CNT/polyurethane thin film reveals a transmittance over the visible region of around 80 percent as shown in Figure 7.6. The highest region of transparency for these films occurs between around 480 to 620 nm, indicating that the material should take on the green color associated with doped polyaniline. This sample is composed of 30% PANi/DBSA/CNT material within a polyurethane matrix.

![Figure 7.6: Spin-coated films of polyaniline/DBSA/CNT material loaded into polyurethane matrix. Percentage indicated the amount of polyaniline/DBSA/CNT material loading versus total solids. Visible transmittance spectrum of 30% loaded film is shown on the right.](image)

Microscopy and spectroscopy indicate that we have formed a well-connected carbon nanotube network within a doped polyaniline matrix and can therefore expect our composite material to be reasonably conductive. Sheet resistance measurements of 10%, 20%, and 30% loaded polyurethane films are shown below in Figure 7.7 in comparison to a pure polyaniline/DBSA/CNT film (labeled 100%). While the 10% loaded film is not conducting, 20% and 30% loaded films have sheet resistance values of $2 \times 10^6$ and $5 \times 10^5 \, \Omega/\text{sq}$, placing them within the static dissipative regime. The pure PANi/DBSA/CNT film is more conductive, showing a sheet resistance of $10^5 \, \Omega/\text{sq}$. The polyurethane composite films are mechanically tough at least to a simple test, i.e. they withstand peeling with Scotch Tape™.
7.5 Conclusions

Here we have shown a simple method for using polyaniline nanofibers doped with dodecylbenzenesulfonic acid to disperse non-functionalized carbon nanotubes in chloroform. A standard glass wool filtration is sufficient to remove insoluble particulates for spray-coating or spin-coating. The carbon nanotubes form a connected, percolative network within the polyaniline/polyurethane matrix and produce films with sheet resistances within the static dissipative regime. The high conductivity and neutral absorption spectrum of the carbon nanotubes allows for more conductive and transparent films when compared to polyurethane films consisting solely of a conducting polymer as the conducting filler.
7.6 References

1. R.P. Kusy, Metal Filled Polymers (Ed.: S.K. Bhattacharya), Dekker, New York, 1986,

