

**SYNTHESIS AND CHARACTERIZATION OF
CHEMICALLY POLYMERIZED SELF-DOPED
POLYANILINE: POLY(ANILINEBORONIC ACID)**

BY

INSUN YU

A Thesis submitted to
the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements for the Degree of

MASTERS OF SCIENCE

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University of Manitoba
Winnipeg, Manitoba

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**Synthesis and Characterization of Chemically Polymerized Self-Doped Polyaniline:
Poly(Anilineboronic Acid)**

BY

Insun Yu

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree
Of
Master of Science**

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ABSTRACT

The majority of recent research in the field of conducting polymers, which includes polyaniline, has been focused on finding new ways of synthesizing and manipulating substituted conducting polymers with certain desired properties. For example polyaniline suffers from low solubility as well as loss of redox activity and electrochemical redox processes at pH values above 3 or 4. These limitations have been largely overcome by self-doping in which the dopant is covalently attached to the polymer backbone. Nevertheless, polyaniline still has drawbacks due to its low molecular weight and as a result its marginal mechanical properties.

This thesis describes the synthesis of a substituted conducting polymer, poly(aniline boronic acid), in the presence of excess D-fructose and fluoride. Under these polymerization conditions, an anionic tetrahedral boronate species along the polyaniline backbone leads to the self-doped state of the polymer. The properties of this polymer have been investigated including its optical properties, redox activity, molecular weight, conductivity and thermal stability. Due to the boronic acid-saccharide equilibrium reaction, the self-doped state of poly(anilineboronic acid) can be switched to a non self-doped state in a phosphate buffered saline (pH 7.4) and exhibits

redox activity in a wide pH range (pH 1-13). The polymer also has a number average molecular weight of 1,100,000 g-mol⁻¹ and a weight-average molecular weight of 1,807,000 g-mol⁻¹ with a polydispersity of approximately 1.7. The high molecular weight is maintained following removal of boronic acid groups *via* an *ipso*-substitution reaction, suggesting that the boronic ester crosslinks do not contribute significantly to the high molecular weight observed. According to thermogravimetric analysis results, the thermal stability of the polymer is greater than that of HCl-doped polyaniline and other self-doped forms of polyaniline. Unlike polyaniline, which experiences complete decomposition of the backbone near 400 °C, self-doped poly(anilineboronic acid) remains largely intact, possessing a conductivity near 0.01 S-cm⁻¹.

The role of boronic acid chemistry on the thermal stability of the polymer is discussed in this work as well. To date, attempts to address a low molecular weight of conventional polyaniline and the volatility of its dopants through crosslinking have not been successful in yielding enhanced mechanical properties while maintaining the conductivity. This is likely due to the incompatibility of the volume reduction accompanying crosslinking and the presence of counter ions. A new strategy is demonstrated to form anionic crosslink sites by utilizing a chemically modified conducting polymer (poly(anilineboronic acid)). The structure of this crosslinked

polymer has been investigated using ATR-FTIR and magic-angle spinning (MAS) ^{11}B NMR spectroscopy. Due to the crosslinked structure, the conducting polymer possesses unprecedented macro and micro hardness.

CHAPTER 1

INTRODUCTION

1.1 History of Polyaniline

In the past, all carbon-based polymers were considered to be insulators and were utilized as inactive packaging and insulating materials in the electronics industry. In 1958, Natta and his co-workers first synthesized polyacetylene as a black powder. Its conductivity, between 7×10^{-11} to 7×10^{-3} S-cm⁻¹, depending on how it was processed and manipulated, was in the semiconductor range.¹ In the early 1970's, Shirakawa synthesized a shiny metallic film, trans-polyacetylene, rather than the expected black powder. This was accidentally done when too much catalyst was added to the reaction vessel while synthesizing polyacetylene from acetylene gas. In the 1980's, Shirakawa, MacDiarmid and Heeger further investigated trans-polyacetylene oxidized with iodine or bromine vapour and discovered that conductivity of iodine-doped trans-polyacetylene was as high as 10^5 S-cm⁻¹, which is in the metallic range.² Due to this important discovery, the three were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers.

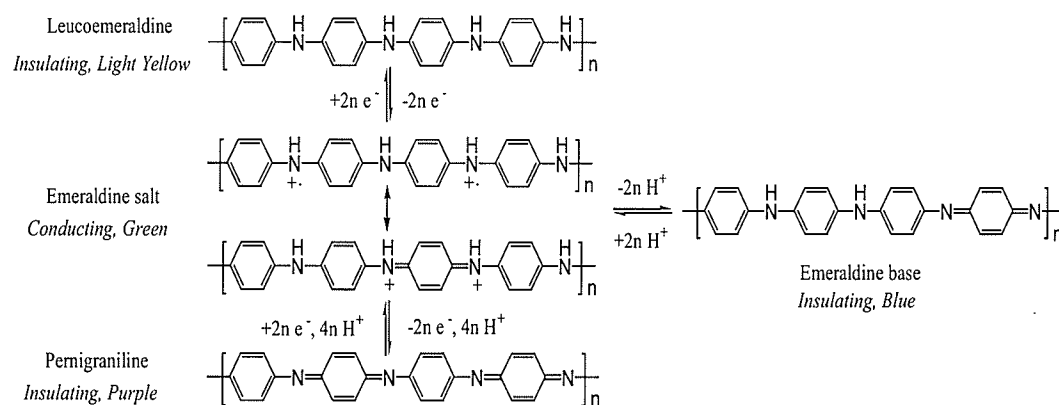
Since the discovery of intrinsically conductive polymers, they have been intensively investigated due to their electrical conductivity, electrochromism and electroactivity.³ Among conducting polymers, polyaniline (PANi) is one of the most promising due to its straightforward polymerization, environmental stability, relatively high conductivity and potential applications in rechargeable batteries,^{4, 5} sensors,⁶⁻⁹ electrochromic display devices,^{10, 11} corrosion protection agents^{12, 13} and organic light-emitting diodes.¹⁴⁻¹⁸ PANi has been known since 1840, and was originally synthesized as a powder whose color changed depending on pH. In the 1950's and 60's, its polymerization mechanism was studied by chemical and electrochemical means.¹⁹⁻²¹ Nevertheless, it was practically ignored because of its lack of solubility in common organic solvents, which leads to difficulty in solution processing techniques for industrial applications.

In the mid-1980s, MacDiarmid and co-workers rediscovered that PANi could be transformed to a conducting form by either electrochemical or chemical oxidation of the leucoemeraldine base or protonation of the emeraldine base through acid-base chemistry giving it a high conductivity approaching that of conventional metals (for example copper metal).²² Since then, it became the focus of intensive study.

1.2 Structure and Properties of Polyaniline

In the early 1910's, Green and Woodhead proposed that PANi was an octamer structure and can exist in four interchangeable oxidation states.^{23, 24} The optical and electrical properties depend on which of the states PANi is in. PANi consists of benzenoid rings between quinoid imine and benzenoid amine structures; thus, a nitrogen heteroatom is incorporated between two conjugated phenyl (C_6H_4) rings in the backbone. It exists in three oxidation states which are leucoemeraldine, emeraldine and pernigraniline, and a doped form, emeraldine salt, by protonation with a protonic acid or by charge transfer with an oxidization agent, as shown in Scheme 1.1. In addition, each state absorbs UV-Vis light and exhibits different colors as shown in Figure 1.1. The optical spectra changes are interpreted as rotations of the constituent molecular units out of a coplanar geometry where phenyl rings and nitrogen atoms are energetically favored. The distorted conformation reduces electron transfer integrals in a ring-nitrogen unit and thus increases the energy band gap between the π valence band (VB) and the π^* conducting band (CB).²⁵⁻²⁷ Leucoemeraldine (a fully-reduced form) consisting of benzenoid rings shows a light yellow color and is insulating due to the high-energy band gap of the π - π^* transition (~ 3.7 eV) which assigned to the first absorption at 311-330 nm.²⁸⁻³⁰ The band gap is associated with the angular orientation

of each phenyl ring and the angle of each nitrogen-phenyl-nitrogen unit due to inter-ring steric repulsion between P_z -orbital electrons of nitrogen and phenyl rings, which forces the phenyl rings out of the plane. Therefore, the ring distortion lowers electron mobility over the backbone resulting in electron delocalization and increases the energy gap.



Scheme 1. 1 Interconversion between different oxidation states of polyaniline.

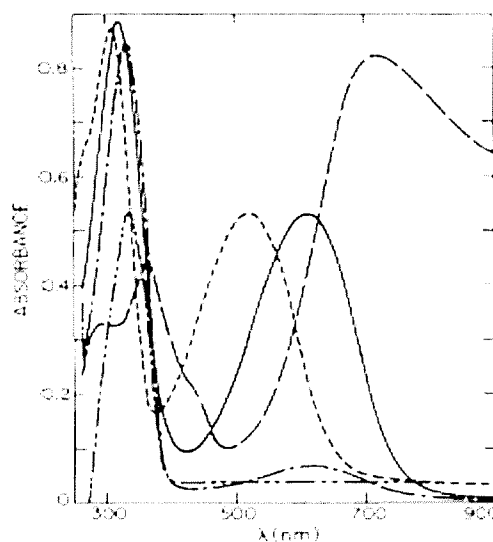


Figure 1. 1. UV-vis spectra for four different oxidation states and a doped state of polyaniline in DMF. Emeraldine base (—), Pernigraniline (- - -), nigraniline (- —) and Leucoemeraldine (- - —) and Emeraldine salt (— —). Reproduced with permission from *J. Am. Chem. Soc.* 1986, 108, 8811. Copyright 1998 Am. Chem. Soc.³⁰

When this form is oxidized, it is converted to emeraldine salt (half-oxidized form) in which half the nitrogen atoms are positively charged and double-bonded to quinoid rings. The resonance form of this structure leads to strong visible absorptions (green color) and is a good conductor. Its electrical conductivity, known for the past thirty years, is due to conjugated systems, which are formed by π -bonds in the carbon rings and between the ring and a nitrogen atom. The π -bond conjugation leads the

positive charges to be delocalized and spread over the PANi polymer. Thus, their good mobility through the chain makes the polymer electrically conducting. The emeraldine salt form can be easily deprotonated to form the emeraldine base form in a base solution by acid-base chemistry resulting in a blue insulating material. When the emeraldine form is further oxidized, pernigraniline (a fully oxidized form) is obtained. All nitrogen atoms in this form exist in a conjugated structure (as a quinone-diimine form), which has a strong purple color. In spite of its highly conjugated structure, the pernigraniline form is non-conducting due to the half-filled π valence band, which has a bandwidth of 2.9 eV and is split by a energy gap of 1.4 eV. The band gap and bandwidth of pernigraniline have been explained by a Peierls distortion in both bond length³¹ and ring-torsion^{31,32} dimerization.

The cyclic voltammogram in Figure 1.2 shows the electrochemical behavior of PANi, which consists of two major redox transitions. These two redox processes are associated with interconversions between different oxidized states of PANi. Below 0.1 V vs. Ag/AgCl, PANi exists in a leucoemeraldine form. While the potential is scanned from 0.1 to 0.3 V vs. Ag/AgCl, the form is changed to green-colored emeraldine salt form. The emeraldine salt is maintained in the potential window of 0.3 to 0.6 V vs. Ag/AgCl in an acid condition while it turns into the blue-colored base form in a neutral

solution. Above 0.6 V vs. Ag/AgCl, PANi is in a pernigraniline form.

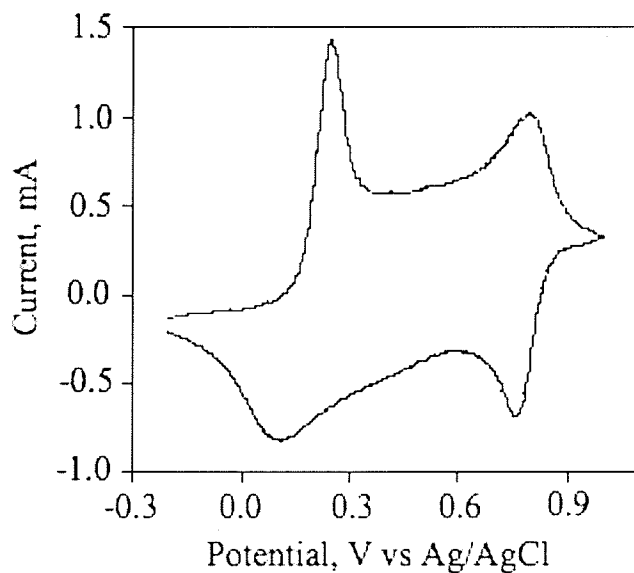


Figure 1. 2. Cyclic voltammogram of polyaniline on a glassy carbon electrode with a scanning potential range of -0.2 to 1.0 V vs. Ag/AgCl in an aqueous 0.5 M HCl solution. Scan rate = 100 mV-s⁻¹.

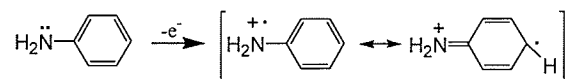
1.3 Synthesis and Molecular Weight of Polyaniline

The synthesis of PANi is either achieved chemically^{22,33-35} or electrochemically³⁶⁻⁴⁰ by oxidation of aniline (C₆H₅NH₂) in an aqueous solution of a protonic acid (e.g., HCl). The mechanism for the growth of the PANi chain involves an

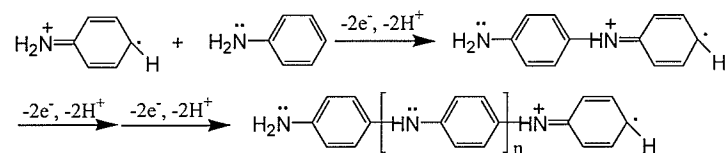
incorporation of a neutral aniline monomer into the chain as shown in Scheme 1.2.^{20,41,}

⁴² The mechanism is commonly referred to as a cation-radical polymerization and includes three steps: initiation, propagation and termination. In the initial step, one electron is removed from the nitrogen atom of aniline, and the radical-cation intermediate (anilinium cation-radical) is generated. The radical-cation intermediate exists in the resonance forms of the species. In the propagation process, two cation-radicals are covalently bonded to produce a cation-radical dimer, which has a much lower oxidation potential than aniline and is rapidly oxidized. The cation-radical dimer combines with an anilinium cation-radical to produce a trimer, which is readily oxidized to a new cation-radical. Thus, the formation of a cation-radical dimer accelerates the propagation of a polymer chain with another monomer unit in the *para* position by head-to-tail coupling. As the reaction continues, the chain is grown on until the molecular weight of the polymer is formed high enough to precipitate. This is done via an electrophilic substitution reaction, and is thought to occur in both chemical and electrochemical polymerization of aniline.

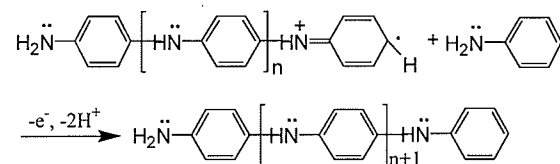
Initiation



Propagation



Termination



Scheme 1. 2. Cation-radical mechanism of aniline polymerization.

Electrochemically synthesized PANi results in a film deposited on a working electrode. The electrochemical method can easily control the rate of polymerization and provides the polymer with a more reproducible molecular weight distribution.⁴³ Nevertheless, it is not practical for producing bulk polymer for use in industrial applications because it is difficult to collect the polymer from the electrode. Due to this limitation, efforts are concentrated on the production of PANi through chemical synthesis. Unfortunately, this method has its own limitation.

The physical, chemical and mechanical properties of a polymeric material are known to depend strongly on its molecular weight and molecular weight distribution.⁴⁴

This is also the case for PANi, where there exists a positive correlation between increased molecular weight and performance properties in a variety of formats such as films, fibers and composites.⁴⁵ In addition, it is desired that polyaniline has relatively low polydispersity which leads to effects on properties such as melt viscosity, tensile strength (toughness), thermal stability and resistance to corrosion.⁴⁶ Chemical synthesis of polyaniline generally consists of aniline oxidation using an oxidizing reagent such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ^{21, 47-49} and potassium dichromate,^{50, 51} which simultaneously oxidizes the monomer and provides the dopant anion, in an aqueous protonic acid solution at a sub-zero temperature.²¹ Unfortunately, chemically synthesized polyaniline suffers from low molecular weight, which leads to weak mechanical strength.³³ Molecular weights of chemically polymerized polyaniline reported in the literature are in a wide range of 30,000 to 350,000 $\text{g}\cdot\text{mol}^{-1}$ with polydispersity between 1 and 6.^{33, 48, 52-55}

Recently, considerable attention has been devoted to the development of new approaches to synthesize polyaniline having high molecular weight while maintaining high conductivity. The common strategies have been to change oxidizing reagents, lower reaction temperature^{33, 48, 52-55} or introduce cross-links during polymerization.⁵⁶ These approaches may render the polymer less soluble in most known common organic solvents⁵⁷ and are time consuming. Various approaches have been reported to

overcome the poor solubility in organic and aqueous media. Polyaniline substituted with alkyl or alkoxy chains or polar substituents is the most effective approach to solve this problematic solubility. Alkyl substituted polyaniline, however, is of fairly low molecular weight and suffers from reduced conductivity due to steric effects related to the size of the alkyl substituents. The steric effects cause ring-distortion and decrease interunit electron transfer.⁵⁸

Among the properties not directly affected by high molecular weight, thermal stability is the most important. In general, thermal stability of a conducting form of PANi is affected by the characteristics of dopants and how the dopants are bonded with the polymer backbone as well as the structure of the backbone itself. Attempts to enhance its thermal stability have focused on stabilizing the dopant, which is typically volatile. Approaches include use of ring-substituted self-doped polyaniline, N-substituted self-doped polyaniline, high molecular weight dopants, as well as blend and crosslinking. To date, improvements have been limited due to the thermal reactivity of the dopants used.

1.4 Chemical modification of Polyaniline: Self-doped Polyaniline

Extensive efforts in the field of conducting polymers have been directed toward achieving the synthesis of water-soluble conducting polymers through chemical modification, mainly due to environmental concerns for industrial applications.⁵⁹⁻⁶³ Recent research has also been directed towards controlling physical, chemical and electronic properties in the bulk polymer and at the interface by chemical or electrochemical synthetic approaches. The chemical modification of polyaniline has also been directed towards improving its mechanical properties and processability as well as its electrical and chemical properties. In order to control these properties, a common approach is to functionalize the polyaniline backbone on either amine groups to form N-substitution⁶⁴ or ring-substitution.^{41, 65} New approaches to functionalize the backbone have been demonstrated by many researchers, using the copolymerization of aniline with substituted anilines or post-modification reaction of polyaniline based on electrophilic substitution, nucleophilic addition and coupling with diazonium salt.⁶⁶ Until recently, the most successful approach in obtaining a soluble and conductive polyaniline as well as one possessing high thermal stability has been through the formation of a self-doped polyaniline. Self-doped polyaniline has exhibited a variable range of conductivity depending on a self-doping level as well as a number of tradeoffs,

including low molecular weight. This is due to steric hindrance which inhibits electrophilic attack from propagating a polymer chain (see Scheme 1.2).⁶⁷

Self-doped PANi is significant due to its unique properties, including water solubility⁶⁸⁻⁷¹ as well as electroactive properties in a wider pH range, particularly in neutral aqueous solutions. In contrast, conventional PANi is generally insoluble in most common organic and aqueous solvents. Its emeraldine base form has been found to have limited solubility in NMP, DMF, THF, benzene and chloroform⁷² as well as in acetic acid^{73,74} and fluorinated solvents⁷⁵ where the emeraldine salt form is also soluble. In addition, it does not show either conductivity or electrochemical redox processes at pH > 4, which restricts the application of the polymer in fields such as biocatalysis and biosensors where neutral or physiological pH is required. In order to overcome this limitation, aromatic rings on the polyaniline backbone have been substituted with different acidic groups such as carboxylic,⁷⁶ phosphonic,⁷⁷ and sulfonic moieties.⁷⁸⁻⁸⁰

The first self-doped polyaniline⁷⁸ was sulfonic acid ring-substituted polyaniline, sulfonated polyaniline, whose conductivity is independent of the external dopant over a wide pH range due to the immobile, covalently bonded, acid species (-SO₃H). This structural feature has led to improvement in two main fields application: rechargeable batteries (e.g., secondary rechargeable lithium batteries) and sensors.^{81,82} The utility of

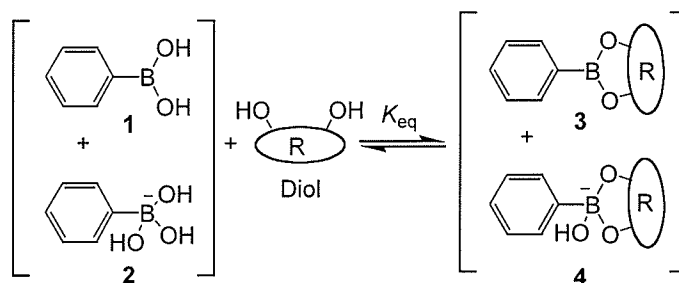
PANi as cathodic materials, which consumes the electrons flowing from the anode following an external electric circuit, for rechargeable batteries is associated with the ability of charge compensation via insertion and expulsion process of ionic species in order to maintain its electroneutrality. Self-doped PANi possesses an ionisable, negatively charged substituent (e.g. $-\text{SO}_3^-$) as an inner dopant bound to the polymer backbone. This can improve the efficiency of the charge compensation processes (relative to its redox behavior) because only cations (e.g., a proton or lithium cation) are used for the process. Thus, there is no anion exchange during the reversible reduction and oxidation process between polymer and electrolyte in the batteries.⁸³ Conventional PANi, which mainly relies on anions for its charge compensation, possesses a lower energy density and thus yields battery systems with a lower power capacity. Additionally, due to the wide range of acceptable pH values, self-doped polyaniline can be used to create sensors and biosensors under pH-neutral solutions. Furthermore, the appearance of a novel water-soluble self-acid-doped polyaniline allows a third major application: a free-standing film formed from its aqueous solution exhibiting a conductivity of $0.03 \text{ S}\cdot\text{cm}^{-1}$, which is sufficiently high so that it can be used as an electromagnetic interference shielding, electrostatic-discharge or antistatic material.⁶⁹

1.5 Boronic acid substituted Polyaniline

Boronic acid chemistry has been of particular interest in biological and medical applications such as saccharide sensors,^{84, 85} and drug delivery agents^{86, 87} as well as in synthetic applications as protective agents or catalysts⁸⁸ in organic reactions and a chemical precursor to give a wide range of functional groups with substitution reactions and coupling reactions.⁸⁹ A particularly important application involving boronic acid chemistry is the generation of selective boronic acid based sensors with a high affinity for saccharides, such as glucose. These have been developed due to the increasing number of diabetic patients⁹⁰ who have also suffered from acute renal failure.^{91, 92} In the cases, regularly monitoring and controlling blood glucose level are crucial.

The complexation of aromatic boronic acids with saccharides (as well as alkyl and aromatic diols) forms a stable and reversible boronate ester which exists in the relative concentration ratio of the neutral trigonal ester **3** and the tetrahedral boronate ester **4** as shown in Scheme 1.3.⁹³ The binding constants (K_{eq}) as well as the relative concentrations of **3** and **4** are dependent on the formation of the anionic boronic acid **2**, i.e., the pKa of aromatic boronic acid and the pH of the aqueous solution.⁹³ Typically, D-fructose has a higher affinity with aromatic boronic acids than D-glucose, and higher binding constants can be obtained above the pKa of the boronic acid (pKa of

phenylboronic acid is 8.8.), where the anionic tetrahedral boronate is formed to a significant degree.⁹³ Since pH is an essential factor for physiological applications, two common approaches for enhancing the affinity at lower, near neutral pHs have been pursued. These include the introduction of Lewis base groups (e.g., fluoride and ortho aminomethyl groups),⁹⁴ which donate electrons into the empty boron *p*-orbital and form a tetrahedral boron with *sp*³ hybridization, and the substitution of the aromatic ring with an electron withdrawing group to lower the pKa.⁹⁵



Scheme 1.3. Boronate ester formation.

Poly(anilineboronic acid), which was first produced by Fabre and co-workers, has been synthesized electrochemically both under slightly acidic and neutral conditions in the presence of fluoride.^{96, 97} The addition of fluoride can enhance the boronic acid-saccharide complexation under neutral conditions and facilitates the

formation of four-coordinate and anionic boronate species.⁹⁴ Thus, fluoride covalently bonds with the electron-deficient boron site and forms a stable and anionic tetrahedral boronic acid, which leads to increased solubility in aqueous solutions. The formation of a unique anionic boronic ester increases the binding constant with saccharides and extends redox activities of polyaniline in a wide range of pH.

Herein, a new approach is presented to produce a water-soluble, self-doped, substituted polyaniline, which contains the attachment of an anionic four-coordinate boronate species. The polymer has a much higher molecular weight as well as relatively high conductivity and thermal stability compared to other types of self-doped polyaniline. Furthermore, a new strategy utilizing self-doped poly(anilineboronic acid) to form anionic crosslink sites is demonstrated. In so doing, a self-doped, crosslinked conducting polymer is formed, possessing unprecedented hardness and high thermal stability while maintaining conductivity.

CHAPTER 2

EXPERIMENTAL

2.1 Materials and reagents

Aniline, 3-aminophenylboronic acid hydrochloride salt, polyaniline emeraldine base (average Mw 100,000), ammonium persulfate, D-fructose and 1-methyl-2-pyrrolidinone were purchased from Aldrich Chemical Inc. Sodium Fluoride, hydrogen peroxide 30 %, pH 7.4 phosphate buffer saline (PBS) stock solution (10X) and concentrated HCl were purchased from Fisher Scientific. Bulk distilled water was first filtered and ion exchanged to yield 18.3 M Ω quality water using an Milli-Q-Academic A10 (Millipore Corporation).

2.2 Chemical polymerization of PABA

PABA was chemically polymerized under ambient conditions as follows. An aqueous monomer mixture (19.5 ml) of 40 mM 3-aminophenylboronic acid as monomer, 40 mM sodium fluoride and 10 M D-fructose was prepared in a 100 mL reaction vessel. Aqueous 40 mM ammonium persulfate (0.5 ml, oxidizing agent) was

slowly added over a period of 10 min into the mixture, while stirring the reaction solution. The pH of the reaction mixture was approximately 7 before adding oxidizing agent. The mixture was stirred overnight at room temperature. In a similar manner PABA could also be prepared in phosphate buffer saline solution (pH 7.4).

2.3 Experimental Procedures and Instruments

2.3.1 UV-Vis Spectroscopy

UV-Vis spectra were obtained between 200 and 1000 nm on an Agilent 8453 spectrophotometer with ChemStation software for analysis. Polymer thin films deposited on indium tin oxide (ITO, $R_s=6 \pm 2 \Omega/\text{square}$, Delta Technologies) glass slides was exposed to pH 7.4 phosphate-buffered saline in a 1 cm path length quartz cuvette, and its spectra was recorded as a function of time over the course of an hour.

2.3.2 Fourier Transform Infrared Spectroscopy (PM-IRRAS & ATR Spectroscopy)

Infrared spectra were obtained using a NexusTM 870 spectrometer (Thermo

Nicolet Corporation) equipped with an attenuated total reflectance (ATR) accessory and polarization modulated infrared reflectance absorption (PEM-IRRAS) accessory. The instrument was setup at a resolution of 8 cm^{-1} in order to record PM-IRRA spectra of polymer thin films on ITO glass slides. A MCT(HgCdTe)/A detector, which was cooled with liquid nitrogen, was used to collect 300 interferograms for each spectrum at a gazing angle of 67° . ATR spectra of polymer pellets were collected using a hemispherical Germanium optic crystal and a deuterated triglycine sulfate and thermoelectrically cooled (DTGS TEC) detector. 100 interferograms were accumulated to obtain each ATR spectrum at a spectral resolution of 8 cm^{-1} .

2.3.3 Cyclic Voltammetry

Cyclic voltammetric measurements were carried out using a CH Instrument CHI-660 workstation controlled by a PC. A three-electrode cell was used, which consists of a glassy carbon (GC) disk (Bioanalytical Systems, 3.0 mm diameter) working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. Cyclic voltammograms of an electrochemically deposited polymer film and a film coated with a chemically prepared polymer on the working electrode were

conducted in a 0.5 M HCl aqueous solution with a scan rate of 100 mV·s⁻¹.

2.3.4 Four-point Probe Conductivity Measurements

Conductivity measurements were carried out using a four-point probe (Signatone Corporation, SP4-62.5-85-TC), which is the probe head with 62.5 mil spacing, 85 g spring pressure, tungsten carbide tips with 1.6 mil tip diameter, connected to a FLUKE 87 multimeter to obtain voltage and the CH Instrument used for a constant-current source. Applied current and measured voltage are in the range of 1 – 5 mA and 0.002 – 2 V, respectively. The conductivity value is calculated using the equation by $\sigma = \frac{1}{2\pi S} \cdot \frac{i}{V}$, where S is the spacing between probes, i is the applied current through two outer probes, and V is the voltage drop across the two inner probes. Polymer pellets were pressed at 10,000 psi for 5 minutes, resulting in a pellet thickness significantly larger than the separation between probes.

2.3.5 Gel Permeation Chromatography

The molecular weight of PABA was determined on a gel permeation chromatography (GPC) system. An isocratic pump with a degasser (Agilent 1100 Series) was installed with the GPC system in order to maintain a flow rate (0.5 ml·min⁻¹

¹) and pressure (~ 40 bar). An Agilent 1100 Series manual injector consisting of a Rheodyne 7-port sample injection valve and an external 20 μ l sample loop was used to introduce samples. A PLgel 5 μ m MIXED-C column (Polymer Laboratories Inc.) was used and calibrated with polystyrene standards in pure NMP, which was the mobile phase used in these studies. The column temperature was maintained at 70°C. A MiniDAWN Tristar detector (Wyatt Technology), operating at 690 nm, was used as an absorbance detector.

2.3.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Mettler TGA/SDTA851^o (Mettler Toledo) on samples on the order of 10 mg, with a heating rate of 20 °C·min⁻¹ under nitrogen gas from 100 to 800 °C.

2.3.7 Microhardness Measurements

Microhardness measurements were performed using a Leitz Wetzlar Miniload test machine (Ernst Leitz, Wetzlar, Germany), with a diamond indenter for the Vickers hardness test. As shown in Figure 2.1 a, the indenter is in the form of a square-based

pyramid, and the apical angle between opposed pyramid faces is 136° . To calibrate the tester, the diamond indenter is pressed into the surface of a polished calibration standard at a constant load, which can range up to approximately 120 kgf, and the impression size measured (no larger than 0.5 mm) using the optical microscope (see Figure 2.1 b). The Vickers hardness value (V_H) is given by $V_H = \frac{1.854F}{d^2}$, where F is applied mass in kgf, and d is the length of the indentation diagonal in mm. V_H is expressed in $\text{kgf}\cdot\text{mm}^{-2}$ and was converted to Pa ($\text{N}\cdot\text{m}^{-2}$).⁹⁸ For the conversion, the applied force converts kgf to newtons ($1\text{kgf} = 9.807\text{N}$), and the area converts mm^2 to m^2 to obtain results in Pa using the above formula. Three indentations were made at random sites on a pellet. The hardness of each pellet was the mean of these three measurements. A load of 25 g was used throughout.

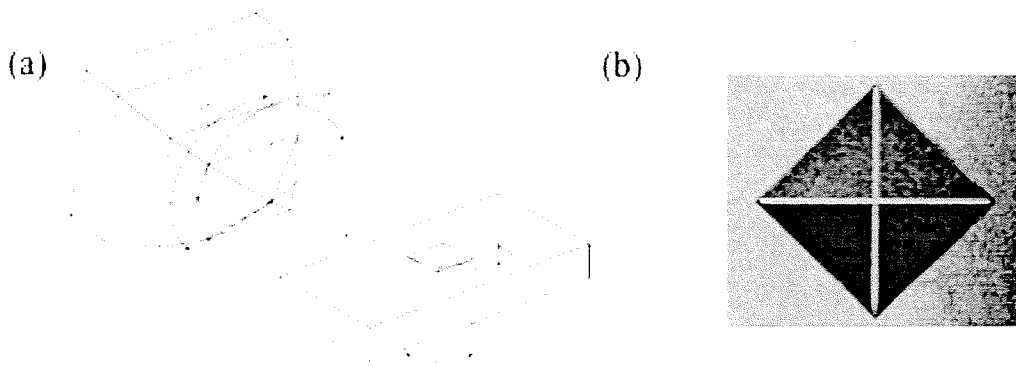


Figure 2. 1. Illustration of Vickers' hardness test.⁹⁹

2.3.8 ^{11}B Nuclear Magnetic Resonance Spectroscopy

^{11}B NMR studies were carried out using a Bruker AMX 500 NMR spectrometer to examine the structural interconversion between 3-aminophenylboronic acid (**1**) and a boronate ester (**2**) (see Scheme 3.1). The samples were prepared using 10% D_2O in $10\times$ PBS. Chemical shifts were determined relative to borontrifluoride etherate (^{11}B NMR reference).

^{11}B Nuclear Magnetic Resonance (NMR) spectrum of a coarse-ground pellet (14 mg) was obtained at the ^{11}B resonance frequency of 192.4 MHz ($B_0=14.1$ T) on a Varian Inova 600 spectrophotometer. For the one-dimensional Magic Angle Spinning (MAS) experiment spinning at 12 kHz, a pulse of 1.5 μs with a radio-frequency (RF) field of 25 kHz ($<15^\circ$ tip angle) was used to ensure homogeneous excitation of all boron sites. The spectrum is the result of 800 transients separated by a relaxation delay of 10 s. For the two-dimensional MQMAS spectrum multiple-quantum excitation and conversions were achieved using 7 μs and 3 μs pulses with an 83 kHz RF field, respectively, and a 15 μs z-filter at 8 kHz RF. These conditions result in preferential excitation of the four-coordinate borons (due to much smaller quadrupolar interaction) filtering the three-coordinate boron signal.

2.3.9 Scanning Probe Microscopy and Nanoindentation

Tapping mode scanning probe microscopic (TM-SPM) images and nanoindentation of polymer films cast from NMP on a Si substrates were obtained with a Veeco Nanoscope IV. The spring constant (k) of a force modulation etched silicon probe (FESP) cantilever (Veeco Metrology) is in the range of 1-5 N·m⁻¹.

Microhardness values of the polymer were estimated based on two assumptions: the spring constant of the probe was 1 N·m⁻¹, and the geometry of the indentation was in the form of a cone. The hardness function is given by $H(N \cdot m^{-2}) = \frac{F}{A}$, where F is the cantilever force, and A is the lateral surface area of cone. The area of the lateral surface is related to the circumference of the circle times the lateral height of the cone, l : $A = \pi \times r \times l$, where r and l were obtained from tapping mode images following indentation. To obtain the contact force (F) of the cantilever, the force curve, which is voltage applied versus the z position of the piezo, was plotted. Based on the plot, the z piezo sensitivity (125 nm·V⁻¹) was determined. The force is defined by the equation: $F = k(\Delta z)$, where Δz is the z distance from the setpoint to the point where the cantilever pulls off a surface and k is the spring constant of the cantilever ($k=1-5$ N·m⁻¹). To obtain the Δz distance, the sensitivity is multiplied by the setpoint voltage: $\Delta z = 1.5 \text{ V} \times 125 \text{ nm} \cdot \text{V}^{-1} = 187.5 \text{ nm}$. Therefore, the contact force is

calculated by $F = k(\Delta z) = 1\text{N} \cdot \text{m}^{-1} \times 187.5\text{nm} = 187.5\text{nN}$, where the spring constant is assumed to be $1\text{N} \cdot \text{m}^{-1}$. Within the limit of these assumptions, the force was estimated to be within 1 order of magnitude of this value.

CHAPTER 3

SELF-DOPED POLY(ANILINEBORONIC ACID)

In general, homopolymerization of an aniline derivative (e.g., aminobenzenesulfonic acid) as monomer is one ideal, direct way to obtain fully substituted polyaniline (PANi), which can enhance low conductivity of sulfonated PANi, the first water soluble self-doped polymer.⁷⁸ However, it has not been successfully achieved because the substituents often have a strongly electron withdrawing nature, which inhibits the oxidation process. In addition substituents can result in steric effects that may interfere with the radical-cation coupling reaction and in turn impede the propagation of a polymer chain, thereby reducing the yield and significantly lowering molecular weights. The limited molecular weight of the obtained polymer can be also expected to suffer from effective termination of polymerization resulting from precipitation.^{100, 101}

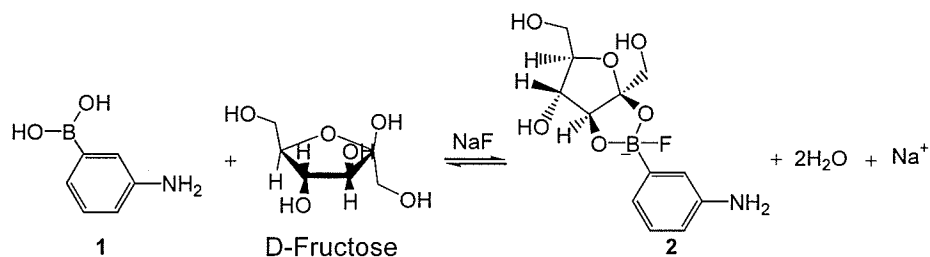
In this chapter, a new method using an aniline derivative, 3-aminophenylboronic acid (3-APBA), is described to create a chemically modified PANi derivative, PABA, which can be switched between self-doped and non-self doped states in a neutral medium such as pure water and phosphate-buffered saline (pH 7.4). The

self-doped state of PABA can be controlled *via* the complexation between boronic acid groups along the backbone with D-fructose in the presence of fluoride. This new approach allows the formation of a water-soluble, self-doped, conducting polymer under the polymerization conditions. In turn, this facilitates the synthesis of PANi over a wider pH range. The resulting polymer has redox activity in an extended pH range of a solution and good solubility in an aqueous solution containing the original conditions of the polymerization. In addition, its molecular weight is high (Mw 1,807,000) and it has relatively high conductivity and better thermal stability compared to that of other self-doped PANi derivatives. To obtain the electrochemical, chemical and physical properties on self-doped PABA, the polymer was examined using various techniques such as UV-Vis and infrared spectroscopy, four-probe conductivity techniques, cyclic voltammetry (CV), gel permeation chromatography (GPC) and thermogravimetric analysis (TGA).

3.1 Synthesis of Poly(anilineboronic acid)

Self-doped PABA using 3-APBA was synthesized under ambient conditions by adding an oxidant (ammonium persulfate). The detailed procedures are described in

Chapter 2.2. The polymerization mechanism has not been previously elucidated; however, it is believed to follow the cation-radical mechanism reported for aniline polymerization (shown in Scheme 1.2).¹⁰² Under neutral pH conditions in the presence of excess D-fructose (10 M) and 1 equivalent of fluoride, 3-APBA (**1**) is converted to a boronated ester (**2**)^{103, 104}, which can in turn form the basis of a self-doped polymer (see Scheme 3.1). As shown in Table 3.1, ¹¹B NMR of the monomer derivative (**2**) indicates that the tetrahedral boronate ¹¹B signal is approximately 20 ppm upfield from trigonal boronic acid, and the relative shift is a measure of the relative amounts of the two forms.⁹⁴ Oxidative polymerization of **2** was carried out under the given polymerization conditions, resulting in a self-doped polymer. Poly(**2**) was soluble and not precipitated out under the polymerization conditions. Poly(**2**) was precipitated by reducing the fluoride concentration via dilution, following rinsing with water and HCl.



Scheme 3. 1. Conversion of 3-aminophenylboronic acid (1) into boronate ester (2) in the presence of 1 equivalent of fluoride and excess D-fructose under neutral conditions.

Table 3.1. ¹¹B NMR chemical shifts of 3-aminophenylboronic acid (3-APBA) adducts.

Solution conditions	¹¹ B chemical shift (ppm)
40 mM 3-APBA (pH = 7.4)	29.2
40 mM 3-APBA + 40 mM NaF + 10 M Fructose (pH = 7.4)	6.4

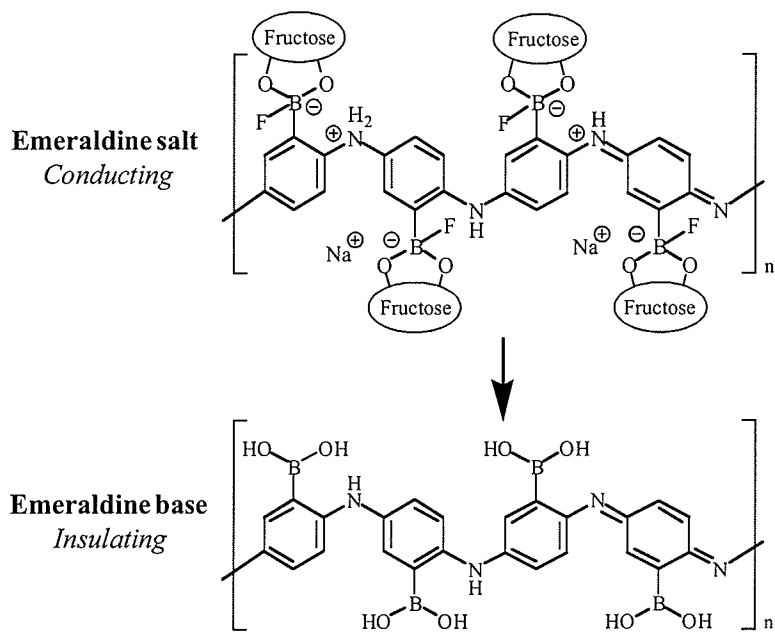
Shifts measured relative to reference borontrifluoride etherate

3.2 Structure and Properties of Poly(anilineboronic acid)

3.2.1 Optical properties

The UV-Vis spectra of soluble form of poly(2) (see Scheme 3.1) in the presence of D-fructose and fluoride as well as thin films of the precipitated form of poly(2) are similar to those of the emeraldine salt form of unsubstituted PANi. They

exhibit absorption bands near 350 and 820 nm due to the π - π^* and bipolaron band transitions, respectively. The existence of these bands in pure water suggests that poly(2) exists in a self-doped state. Poly(2) was converted to poly(1) by the removal of D-fructose from the polymer in phosphate-buffered saline solution shown in Scheme 3.2. The conversion to the non-self-doped state and subsequently to the emeraldine base form of the polymer is characterized by the appearance of an absorption band at 600 nm and the disappearance of the peak at 820 nm, as shown in Figure 3.1. The switching behavior is reversible by exposing the base form of poly(1) to the original concentrations of D-fructose and fluoride either in phosphate-buffered saline or pure water.



Scheme 3. 2. Conversion of proposed structures of the poly(2) conducting and poly(1) insulating forms of PABA in phosphate-buffered saline solution.

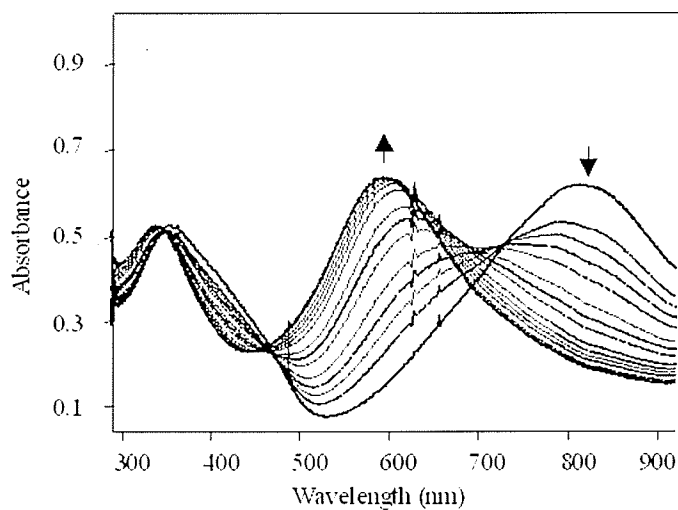


Figure 3. 1. UV-vis spectral changes of a poly(2) thin film as a function of time upon exposure to pH 7.4 phosphate-buffered saline over the course of an hour.

3.2.2 Redox Activity

Redox activity of electrochemically polymerized self-doped PABA thin films has been reported in a wide pH range of a solution (pH = 1 to 13) with the same electroactive behavior as other self-doped forms of PANi.¹⁰⁵ The cyclic voltammograms of self-doped PABA, shown in Figure 3.2, have two sets of redox peaks where the transition of oxidation states occur. The first redox couple at $E_{1/2} = \sim 0.2$ V vs. Ag/AgCl represents the interchange of the reduced insulating form (LB) into the conducting half-oxidized form (EB). The second redox couple at $E_{1/2} = \sim 0.65$ V vs. Ag/AgCl corresponds to interconversion of the EB form to the fully oxidized form (PB). Thin films of poly(2) that had been converted to poly(1) exhibit electrochemical behavior similar to that of films of poly(1) deposited electrochemically under acidic conditions in the presence of fluoride alone^{7, 106} showing the two sets of redox peaks at the approximately same peak potential (see Figure 3.2 (a) and (b)). In addition, the redox behavior is similar to that observed for unsubstituted PANi, which shows two sets of redox peaks at about 0.18 and 0.74 V³⁷, suggesting facile conversion between oxidation states. Consequently, this result demonstrates that chemical polymerization under the conditions has no detrimental influence on the electronic properties of the polymer.

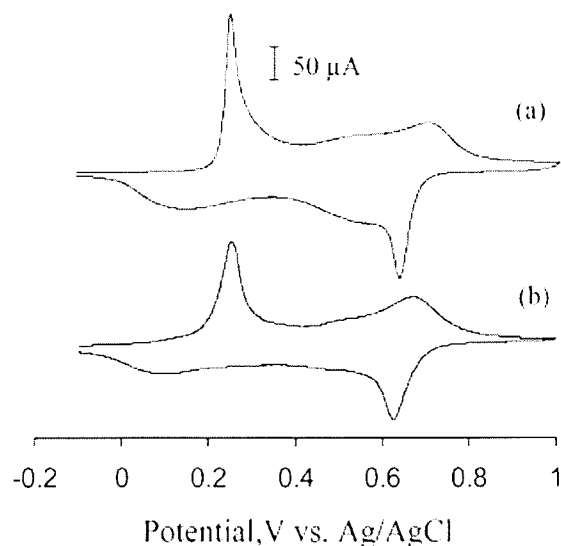


Figure 3. 2. Cyclic voltammograms of (a) an electrochemically deposited film and (b) a film cast from precipitate of poly(1) on glassy carbon in 0.5 M HCl at a scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$.

3.2.3 Conductivity

Typical conductivity of HCl-doped PANi is reported in the range of 1 to 10 $\text{S}\cdot\text{cm}^{-1}$ using four-probe conductivity measurements in air.¹⁰⁷ In our study, the main interest was the thermal stability of conductivity for doped PANi. In the literature, the results have shown HCl-doped PANi loses its conductivity above 100 °C because HCl used as dopant is readily evaporated. The polymer is insulating above 400 °C because the backbone is completely decomposed.¹⁰⁸⁻¹¹⁰ In case of self-doped PABA, the thermal

stability of conductivity can rely on temperature where an anionic tetrahedral boronic acid substitution is decomposed from the aromatic ring because those functional groups make PABA conductive. To determine the conductivity stability of PANi, all of the polymer samples (HCl doped PANi with a molecular weight of 30,000 and 100,000 g-mol⁻¹ and PABA with a molecular weight of 1,807,000 g-mol⁻¹) were heated at 100 and 500 °C under vacuum for 24 h. The conductivity of the heat-treated polymers is shown in Table 3.2. Under vacuum at 100 °C for 24 h, the conductivity of HCl doped PANi with Mw 30,000 and 100,000 g-mol⁻¹ pellets decreased from 7.95 to 0.19 and from 4.68 to 0.13 S-cm⁻¹, respectively. The decrease in conductivity is due to the loss of the volatile dopant (HCl) at 100 °C. These results are consistent with the previous literature.¹⁰⁹ Furthermore, the conductivity of lower molecular weight PANi decreased slightly more than that of the higher molecular weight PANi.

The conductivity of self-doped PABA as a compressed pellet of air-dried powder was 0.96 S-cm⁻¹, which is similar to other self-doped PANi as shown in the literature¹¹¹, but it is lower compared to values reported for HCl-doped PANi. The reason is that the boronic acid substituted groups on the polymer backbone cause the distortion of the π -conjugated polymer chain so that the delocalization of electrons on the polymer backbone is decreased.^{58, 69, 112} A decrease in conductivity from 0.96 to

0.094 S-cm⁻¹ is observed when PABA was treated at 100 °C. However, the decrease in the magnitude of conductivity of heat-treated PABA is lower than that of HCl doped PANi treated under the identical condition. This is likely due to the covalently linked tetrahedral boronic acid substitution on PANi backbone, which is not easily decomposed from the polymer backbone. Similar decomposition is observed in mercaptopropylsulfonic acid-substituted PANi.¹⁰⁸

After being heated to 500 °C under vacuum, the conductivity of the doped PANi decreases significantly compared to that of the self-doped PABA. The conductivity of PANi and PABA is about 3.9×10^{-4} and 0.9×10^{-2} S-cm⁻¹, respectively. This is because the PANi backbone decomposes above 420 °C, as shown in the TGA data. However, the process of cross-linking on the PABA polymer above 100 °C may make a more thermally stable backbone when heated to high temperature. Furthermore, the conductivity of heated PABA is relatively high compared to that of HCl doped PANi.

Table 3.2. Conductivities of PABA and PANi pellets heat-treated at different temperatures.

Dry condition	Conductivity (S-cm ⁻¹)		
	PANi (Mw 30,000)	PANi (Mw 100,000)	PABA (Mw 1,807,000)
Air	7.95	4.68	0.96
Vacuum 100 °C	0.19	0.13	0.094
Vacuum 500 °C	3.9×10 ⁻⁴	3.3×10 ⁻⁴	0.9×10 ⁻²

3.2.4 Molecular Weight of Poly(anilineboronic acid)

Chemically polymerized PABA under the given conditions (described in Chapter 2) where the polymer was soluble resulted in a high molecular weight polymer. However, it was not clear whether interchain anhydride formation (i.e., crosslinking) between boronic acid groups on the polymer backbone contributed to the observed high molecular weight. In order to investigate this possibility, the boronic acid groups on the polymer were removed via an ipso-substitution reaction involving hydrogen peroxide (Scheme 3.3).^{7,113} The reaction occurs rapidly in aqueous hydrogen peroxide solution and was monitored with cyclic voltammetry, *ex situ*, as a function of reaction time. A reaction time of 10 minutes was sufficient to completely convert the polymer

as indicated by the evolution of the two sets of redox peaks characteristic of PANi to a single set (shown in Figure 3.3).⁷

Additional confirmation that the ipso-substitution reaction had reached completion was obtained with PM-IRRA spectra of a reacted thin film. The results are shown in Figure 3.4 before and after the reaction. IR bands characteristic of PANi are observed at 1603, 1510, and 1180 cm^{-1} corresponding to quinoid, benzenoid and the aromatic C-N stretching ring modes.¹¹⁴ The data obtained for the unreacted PABA film also exhibited bands characteristic of the boronic acid functional group at 1115 as well as 985 and 888 cm^{-1} assigned to aromatic B-OH bending and the B-F stretching modes, respectively.¹¹⁵ The asymmetric B-O stretching mode is observed at 1330 cm^{-1} . The ratio of the relative intensities of quinoid to benzenoid ring modes (I_{1603}/I_{1510}) is ~ 1.6 , which suggests that the percentage of imine units is higher than that of amine units. These results and the presence of B-F stretching vibration indicate that PABA is in its oxidized self-doped form. Following the reaction with hydrogen peroxide for 10 minutes, a change in the spectrum consistent with the replacement of boronic acid with hydroxyl groups is observed. All the characteristic bands of boronic acid at 888, 985, 1115 and 1330 cm^{-1} vanish and a new peak at 1287 cm^{-1} appears corresponding to O-H deformation and C-O stretching modes in phenol.¹¹⁵ These results indicate that the

boronic acid groups are replaced with hydroxyl groups during the 10 minute reaction time.

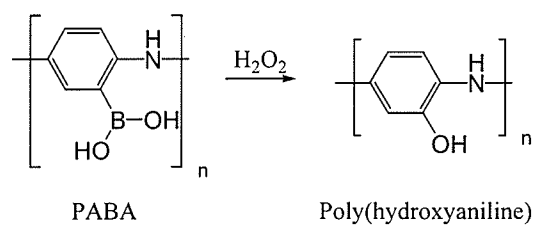
In the literature, the molecular weight determination studies of PANi using GPC used the reduced leucoemeraldine base form of polymer dissolved in 0.5% LiCl-NMP mobile phase.¹¹⁶⁻¹¹⁹ The reduced leucoemeraldine form was prepared by reduction of emeraldine base form of PANi, either by dissolving in NMP containing various amounts of LiCl^{116, 117} or by reduction with aqueous hydrazine.^{118, 119} The reduced form was investigated at relatively high concentrations (above 0.5 mg·ml⁻¹), and in turn the addition of lithium salt was reportedly required to prevent aggregation.^{117, 120} In the present study, the concentration of the PABA solution was significantly lower (0.033 mg·ml⁻¹) than the value where PANi is reported to aggregate (above 1 mg·ml⁻¹), therefore the lithium salt was not used in this study. Under these conditions, the weight average molecular weight determined for in-house chemically synthesized PANi⁴⁷ and a commercially obtained PANi sample (Mw 100,000) agreed with previous reports and showed no indication of aggregation.

The molecular weight and molecular weight distribution of PABA, determined using GPC, are shown in Figure 3. 5a and indicate a number- and weight-average molecular weight of 1,100,000 and 1,807,000 g·mol⁻¹, respectively and a polydispersity

of 1.7. In Figure 3.5b, the molecular weight of the hydroxyl substituted polymer was determined under identical conditions exhibiting a major peak corresponding to a weight-average molecular weight of 990,000 g-mol⁻¹. The fact that the majority of the polymer retains its high molecular weight suggests that the high molecular weight observed for PABA is not due to significant boronic acid anhydride cross-linking.

Additional peaks corresponding to molecular weights of approximately 190,000 and 2,800 g-mol⁻¹ are clearly observed as a result of the ipso-substitution reaction. It is not clear whether this is due to the fact that some cross-linking existed in the original polymer or if there is some decomposition of the polymer in the presence of peroxide with time. However, for PANi treated under the identical reaction conditions used for the ipso-substitution reaction with PABA, increase in the 50% fraction of polymer molecular weight was observed as compared with those of the pristine PANi. The increase in molecular weight is likely due to the cross-linking and branching by interchain reactions in the polymer particles.¹²¹ These results indicate that any decomposition process in the presence of peroxide is associated with hydroxyl substituted PANi. Indeed, if PABA is left in contact with the peroxide reaction mixture for prolonged periods of time, the polymer is completely dissolved. This suggests that decomposition is occurring rather than a simple cleaving of low molecular components

attached through boronic acid anhydride linkages. H_2O_2 treatment of aminophenol was reported to give as main intermediate 1,4-hydroquinone, and a series of dimeric species, which eventually decomposed to organic acids such as muconic, maleic, fumaric, D,L-malic, oxalic and formic acid.¹²²



Scheme 3. 3. *ipso*-substitution reaction of PABA with hydrogen peroxide.

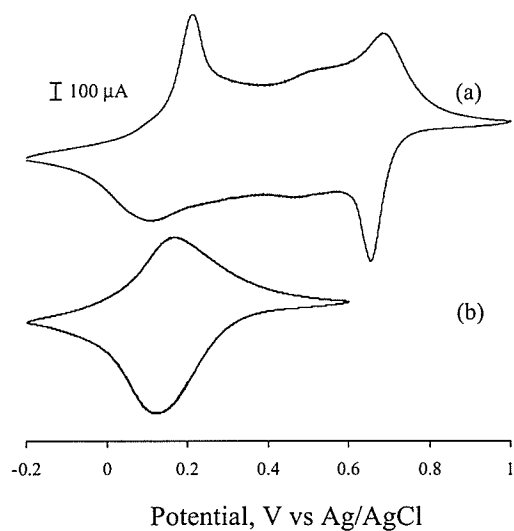


Figure 3. 3. Cyclic voltammograms of PABA (a) before and (b) after exposure to 30% H_2O_2 for 10 minutes in 0.5 M HCl. Scan rate = $100 \text{ mV}\cdot\text{s}^{-1}$.

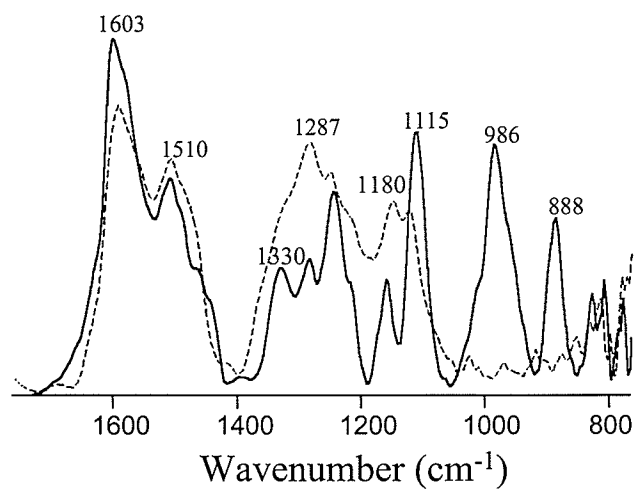


Figure 3. 4. PM-IRRAS spectra of PABA before (—) and after (---) exposure to 30% H_2O_2 for 10 minutes.

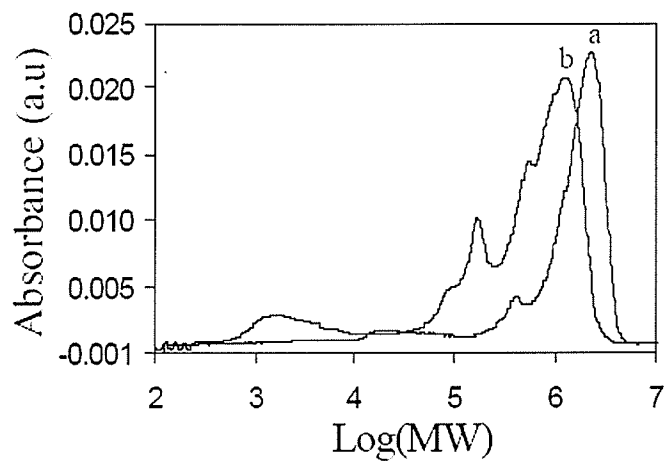


Figure 3. 5. GPC chromatograms of PABA dissolved in NMP ($0.033 \text{ mg}\cdot\text{ml}^{-1}$) (a) before and (b) after exposure to 30% H_2O_2 for 10 minutes.

3.2.5 Solubility

PANi is insoluble in common organic and aqueous solvents, which causes difficulties for processing. In contrast with PANi, self-doped PANi has shown solubility in neutral and basic aqueous media without losing its electroactive behavior due to the presence of functional groups (e.g., sulfonic acid) along the backbone.⁶¹ Poly(**2**) (see in Scheme 3.1) was redissolved in the polymerization solution described in the section 3.1.1. After D-fructose was removed by washing with 0.5 M HCl, the polymer precipitate was in a self-doped state and showed relatively high solubility in NMP while doped PANi is insoluble.

CHAPTER 4

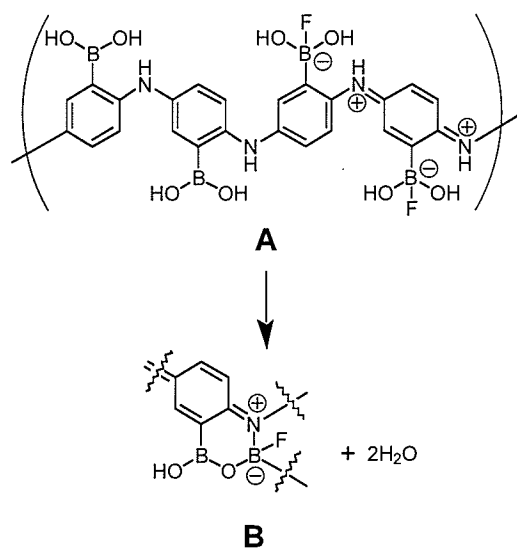
Self-crosslinked, Self-doped Poly(anilineboronic acid)

In this chapter, a new strategy is presented to utilize self-doped PABA that forms anionic crosslink sites by dehydration. In so doing, a self-doped, cross-linked conducting polymer is formed, possessing unprecedented hardness while maintaining conductivity. This strategy offers a completely new approach that may be used to enhance the physical properties of conducting polymers or other modification procedures that compromise the desirable electronic properties of the polymer.

4.1 Structure of Cross-linked, Self-doped Poly(aniline boronic acid)

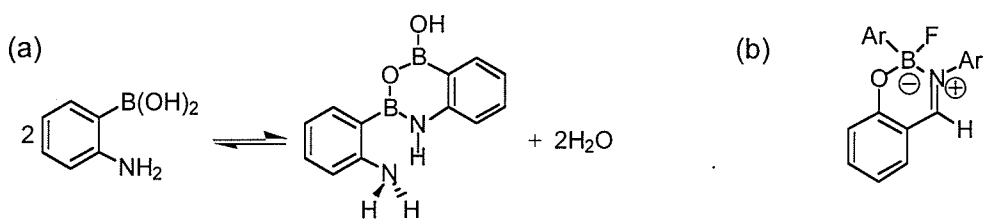
PABA exhibits unique self-doped properties through the formation of four-coordinate boronate species in the presence of fluoride.⁹⁷ The presence of boronic acid groups along the conjugated backbone of polyaniline (Scheme 4.1 A) also offers many possibilities for chemical modification and reactivity. The enhanced thermal stability (as described in Chapter 4.2.1) is likely imparted by anhydride formation as a result of crosslinking. Intermolecular reaction between boronic acid groups and imines in PABA

containing fluoride may produce crosslinks involving four-coordinate boron (Figure 4.1 B), which would lead to a crosslinked, self-doped polymer. There are reports in the literature on the formation of analogous six-member heterocyclic complexes (shown in Scheme 4.2.) containing a boron-imine dative bond such as fluorine containing salicaldimine-boron complexes¹⁰⁹ and the dimer of 2-amino phenylboronic acid formed in aprotic solvents and in the solid state.¹¹⁰ The key advantage of such a structure is that the crosslink site can also act as a dopant site. In turn, this structure can accommodate the volume shrinkage associated with crosslinking while maintaining the anionic dopant required for conductivity. This results in a crosslinked conducting polymer that should exhibit enhanced hardness and thermal stability.



Scheme 4. 1. Proposed crosslinking reaction of PABA. Emeraldine salt form of PABA

A, self-doped in the presence of fluoride. Proposed crosslink **B**, resulting from an interchain dehydration reaction between a boronic acid-imine and a boronic acid moiety.



Scheme 4. 2. (a) Reaction of a boron heterocyclic formation resulting from 2-amino phenylboronic acid¹¹⁰ and (b) salicaldimine-boron complex formation containing fluoride.¹⁰⁹

4.1.1 Investigation of Cross-linked structure using ATR spectroscopy

The formation of the proposed cross-linked structure of PABA was investigated using infrared attenuated total reflectance (IR-ATR) spectroscopy. In Figure 4.1, the ATR spectra of PABA pellets reveal changes consistent with increased crosslinking while maintaining the basic polyaniline structure. Vibrations characteristic of polyaniline are observed at 1597, 1462 and 1130 cm^{-1} and correspond to quinoid, benzenoid and C-N stretching ring modes, respectively.¹²³ The assigned characteristics of the polymer peaks obtained from PM-IRRAS and ATR spectroscopy do not exactly overlap. This is likely due to the different instrumental apparatus used and/or differently prepared samples: PABA-coated thin films for PM-IRRAS spectra and compressed pellets for ATR spectra. However, the differences are not significant with respect to assigning the IR peaks of the polymer. In aromatic boronic acids, B-OH bending modes are observed at 895 and 1024 cm^{-1} , while the vibration attributed to B-F stretching mode lies at 803 cm^{-1} .¹²⁴ The spectrum of the heat-treated pellet shows a decrease in B-OH bending modes and an additional peak at 1493 cm^{-1} assigned to a B-N stretching mode. Also, there is an increase in the intensity of 1281 and 803 cm^{-1} vibrations assigned to B-O and the B-N stretching mode of a dative bond. While B-F and B-N stretching modes overlap at 803 cm^{-1} , the increase in intensity can only be

associated with an increase in the formation of B-N dative bonds.¹²⁴ All of the spectral observations are consistent with increased crosslinking involving the formation of boronic acid anhydride and boron-nitrogen dative bonds shown in Scheme 4.1 B. Furthermore, the relatively unchanged ratio of vibrations at 1597 and 1462 cm^{-1} indicates that the ratio of quinoid to benzenoid structures in the film remains the same after heat treatment; hence, the polymer remains in an oxidized state.

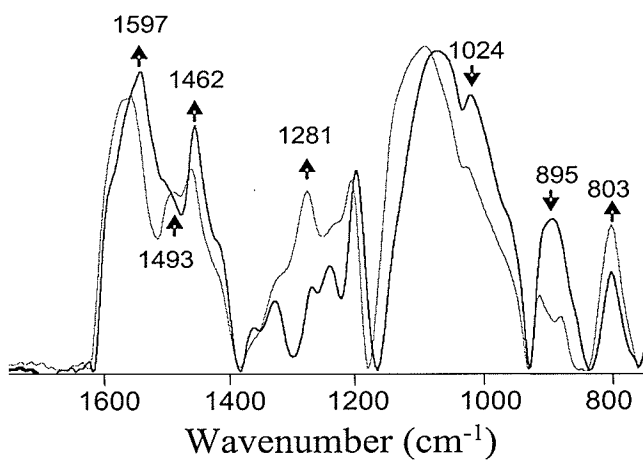


Figure 4. 1. Fourier-transform infrared attenuated total reflectance absorption spectra of PABA pellet (—) air-dried and (---) heat-treated.

4.1.2 Evidence of Cross-linked Structure from ^{11}B NMR Spectroscopy

Magic-angle spinning (MAS) ^{11}B spectrum is an ideal method for classifying a three- or four- coordination structure of boron.^{125, 126} At sufficiently high magnetic fields (i.e., ≥ 11.7 T) the signals corresponding to the boron coordination are generally resolved and yield relative populations by direct peak integration.

In Figure 4.2, the MAS ^{11}B spectrum obtained for heat-treated PABA, the three-coordinate boron gives rise to the broad signal centered at 16.5 ppm, and the four-coordinate boron produces a sharper peak at 1.5 ppm. A two-dimensional multiple-quantum magic-angle spinning (MQMAS)¹²⁷ experiment reveals that two four-coordinate boron sites are present in the sample in Figure 4.2 B, one of which – located at 6.6 ppm – is partly obscured by the quadrupole-broadened three-coordinate boron signal in the MAS spectrum. While the precise identity of the four-coordinate boron species is unclear, the chemical shifts are consistent with the local atomic connectivities indicated in Scheme 4.1. Fitting the one-dimensional MAS spectral intensities using the site information from the two-dimensional MQMAS experiment reveals that $21 \pm 2\%$ of the boron in the sample is four-coordinate. Since such sites can act as a dopant (as shown in Scheme 4.1 B) the NMR results suggest that the heat-treated polymer is doped to that level, which is sufficient to account for the measured conductivities based

on other forms of self-doped polyaniline. Han et al. reported self-doped conductivities of 0.42 and 0.77 S-cm⁻¹ for mercaptopropylsulfonic acid-substituted PANi with self-doped degrees of 20% and 26%, respectively.¹⁰⁸ For sulfonic acid-substituted PANi with a self-doping degree of 26%, the conductivity was 10⁻⁵ S-cm⁻¹.

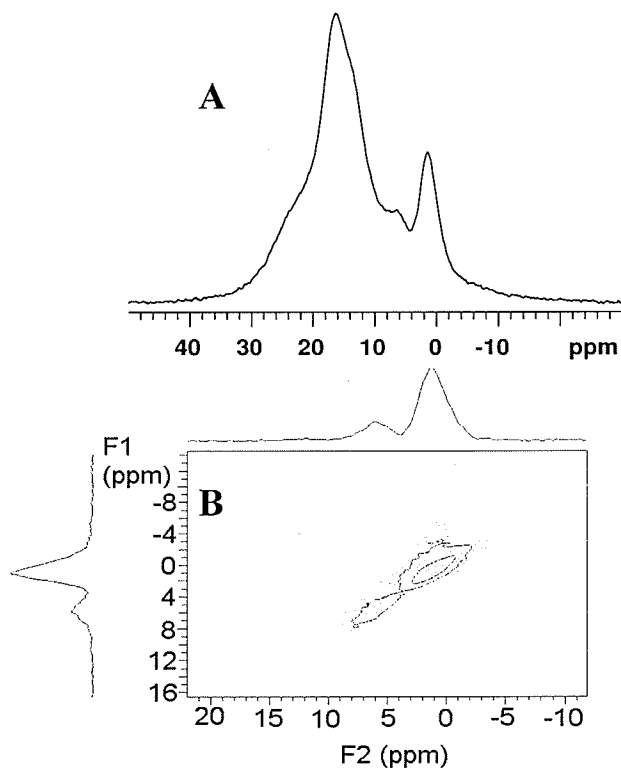


Figure 4. 2. ¹¹B NMR spectra of heat-treated PABA pellet obtained at 192.4 MHz (14.1 T) **A:** One-dimensional MAS experiment **B:** Two-dimensional sheared MQMAS experiment optimized to preferentially excite four-coordinate boron sites (displayed region).

4.2 Properties of Cross-linked, Self-doped Poly(anilineboronic acid)

4.2.1 Thermal Stability

The high molecular weight and the self-doping nature of PABA are expected to increase the thermal stability of the polymer. In general, the thermal stability of PANi emeraldine salt is dependent on the characteristics of dopants and how the dopants are bonded to the polymer backbone as well as the structure of the backbone itself. Self-doped PANi, such as sulfonated PANi, has been reported to be much more thermally stable than its parent unsubstituted PANi doped with HCl.¹²⁸ For example, Han et al. reported that the mercaptopropanesulfonic acid substituted self-doped PANi has better thermal stability than HCl-doped PANi and sulfonated PANi.¹⁰⁸ The covalently bonded electron donating mercaptopropanesulfonic acid substitutions at the polymer backbone stabilizes the aromatic benzenoid ring and thereby reduces the decomposition of the backbone.¹¹¹ Based on the previous literature, we hypothesized that PABA would have better thermal stability in comparison to HCl-doped PANi. Since the functional group of PABA, an anionic tetrahedral boronic acid, is covalently linked to the PANi backbone, and since it acts as an electron donating group, as in the case of mercaptopropanesulfonic acid substituted PANi it was expected to stabilize the

aromatic benzenoid ring and in turn enhance stability.

In order to explore the thermal stability of PABA, TGA was performed on both PANi and PABA. TGA of HCl-doped PANi shows three major mass loss steps under nitrogen.¹²⁸ The first transition is associated with the evaporation of water below 100 °C. The second transition occurs near 200 °C and is associated with the loss of HCl resulting in the concomitant loss of conductivity. The third transition occurs above 400 °C and is associated with the decomposition of the PANi backbone. HCl-doped PANi with a molecular weight of 30,000 g·mol⁻¹ produced by a standard method⁴⁷ and a molecular weight of 100,000 g·mol⁻¹ (commercially obtained) exhibit these transitions as shown in Figure 4.3. In contrast, while PABA exhibits a transition near 200 °C there is a marked decrease in the weight loss above 500 °C compared to PANi. Interestingly, a slow rate of weight loss is observed throughout the thermogram, likely due to the cross-linking process and the associated loss of water (see Scheme 4.1.). Above 500 °C, the decomposition of the polymer occurs slowly resulting in only 8% weight loss. The total weight loss for PABA was about 24% of the initial weight which is significantly less than the nearly 50% weight loss experienced by HCl-doped PANi. These results indicate that a self-doped PABA has thermal stability not only higher than that of HCl-doped PANi but also higher than that of the self-doped sulfonated and

mercaptopropanesulfonic acid substituted self-doped PANi (for which the total weight loss is around 40%).¹⁰⁸ The enhanced thermal stability is likely imparted by anhydride formation as a result of crosslinking.

The intermolecular reaction between boronic acid groups and imines in PABA in the presence of fluoride can produce a crosslinked polyaniline. For example, aryl boronic acid chemistry is rich with examples of the formation of boron chelates.

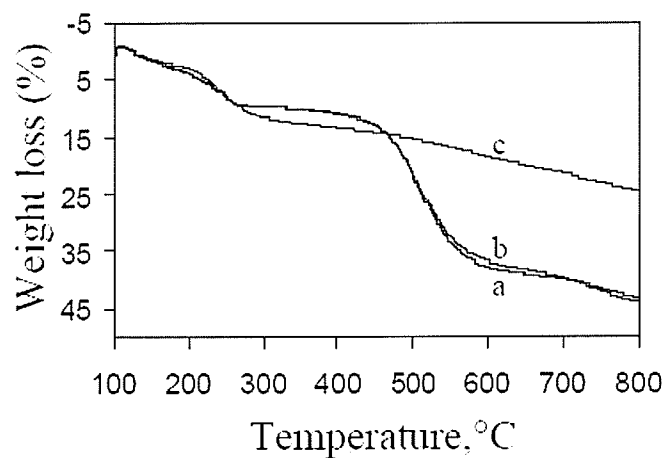


Figure 4. 3. Thermograms of (a) PANi (Mw 30,000), (b) PANi (Mw 100,000) and (c) PABA (Mw 1,807,000) dried in air.

4.2.2 Microhardness

Microhardness measurement (e.g., Vickers hardness) is a standard method of

evaluating the mechanical properties of materials ranging from “hard” polymers to “superhard” materials such as diamond and cubic boron nitride. This kind of measurement is especially useful for characterizing polymers since it is related to yield stress, modulus of elasticity, and some secondary amounts relaxation transitions. Common “hard” plastics typically exhibit hardness values ≤ 0.3 GPa. In order to achieve increased hardness, more complex materials such as functionally graded polymer composites containing significant amounts of much harder fillers have been explored. Rather than creating a composite material, heat-treating techniques were explored. In our approach we exploited hydrolysis chemistry resulting from the intermolecular reaction between boronic acid groups and imines in PABA containing fluoride to produce crosslinks with an analogous structure involving four-coordinate boron (Scheme 4.1 B), in order to produce a self-doped, crosslinked polyaniline possessing increased hardness. The heat treatment was performed by heating compressed polymer pellets overnight at 100 °C under the dynamic vacuum. This is the temperature where the anhydride formation of PABA takes place via crosslinking (see section 4.2.1).

The hardness values obtained for air-dried and heat-treated PABA pellets were 0.347 ± 0.009 and 0.491 ± 0.008 GPa (shown in Table 4.1), respectively. These values

are dramatically higher than PANi (< 0.03 GPa) and those reported for other bulk polymers and approach values achieved with composites. The increase in hardness of the heated PABA is a result of increased crosslinking facilitated by heating and removal of water (a product of the crosslinking reaction) under vacuum.

Table 4. 1. Hardness of PABA and PANi pellets heat-treated at different temperatures.

Heated Temperature	Hardness (GPa)	
	PANi (Mw 30,000)	PABA (Mw 1,807,000)
Air	< 0.03	0.347 ± 0.009
Vacuum 100 °C	< 0.03	0.491 ± 0.008

4.2.3 Atomic Force Microscopy and Nanoindentation

Nanoindentation with a TM-AFM system was used to estimate surface hardness of thin films cast onto rigid substrates (e.g., Si, ITO, etc.) from NMP. These measurements are important since many industrial applications involve the use of thin films. In these applications, the effect of the solvent on the polymer and the polymer hardness are very important characteristics.

Nanoindentation was achieved by performing deflection versus distance experiments, stopping the approach once a certain deflection, corresponding to a defined force, was achieved. The indentation left behind can then be imaged using the same tip, and corresponds to the surface area of the polymer required to support the applied force. Figures 4.4 a and b show the morphology and four identical indentations of a PANi and PABA film cast from an NMP solution. The cross-section images in Figure 4.4 c and d show the depth of the indentations in the PANi and PABA films to be approximately 2.4 and 1.4 nm, respectively. From this data, the hardness of the PANi and PABA films was estimated to be approximately 0.12 and 3.5 GPa, respectively. This estimate was performed with the formula $H(\text{N}\cdot\text{m}^{-2}) = F/A$ and with an applied force of 187.5 nN as discussed in Chapter 2. These results show that the PABA film has a hardness one order of magnitude greater than that of the PANi film. The flatness of the PANi film (apparent in the profile line of Figure 4.4 c) reinforces the notion that the film is soft. The morphology of soft films can easily be perturbed by the lateral and vertical forces of an AFM probe, resulting in unrealistically flat images. The PABA film has a more varied height profile due to its greater hardness which resists deformation by the AFM probe.

While there is a great deal of uncertainty in the absolute hardness values due to

the uncertainty in the spring constant of the tip, the measurements for the films appear to be an order of magnitude greater than the Vicker's hardness measurements of the pellets. This may be due to the influence of the NMP solvent which causes polyaniline plasticized by crosslinking and gives a smooth, dense film possessing greater hardness.¹²⁹ It should be noted that through ion-implantation the hardness of a conventional polymer can be increased as high as 20 GPa.¹³⁰ Given the difference in hardness between the PANi and PABA films, it may be worthwhile to explore the hardness of an ion-implanted PABA film in the future.

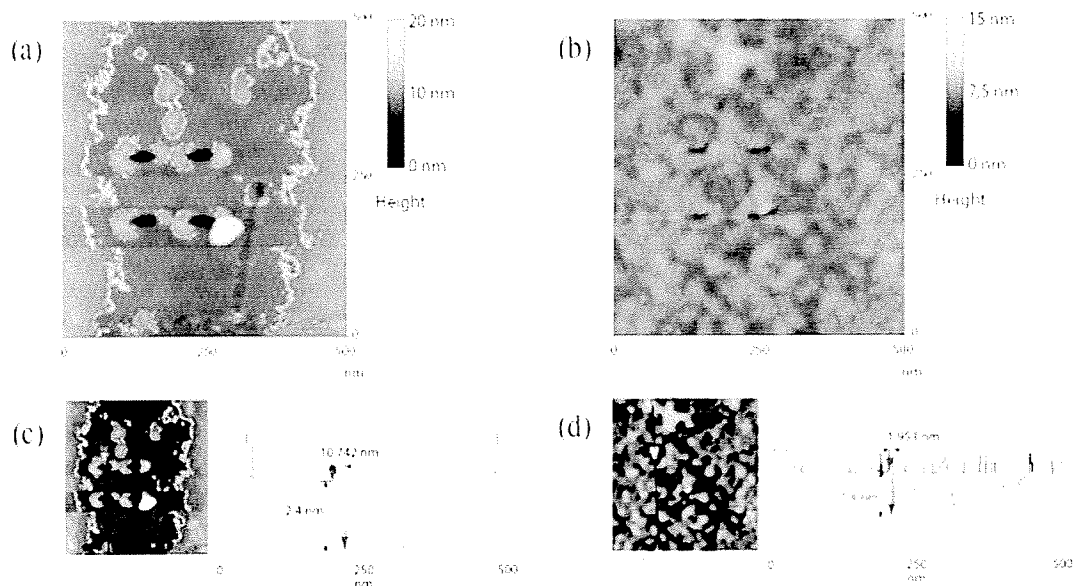


Figure 4. 4. AFM images and nanoindentations of a (a) PANi and (b) PABA film and cross-section images of the (c) PANi and (d) PABA film.

CHAPTER 5

CONCLUSIONS

In conclusion, a novel substituted conducting polymer, self-doped PABA, has been synthesized under the neutral solution (10 M D-fructose) in the presence of fluoride. The polymer produced under these conditions has the unique ability to switch between the self-doped and non-self-doped state. GPC results show that the self-doped PABA produced has the high molecular weight of $1,800,000 \text{ g}\cdot\text{mol}^{-1}$, and that it is not simply due to crosslink formation involving the boronic acid functional groups. The redox activity and conductivity are similar to other self-doped forms of PANi in the entire pH range. According to the TGA results, thermal stability of self-doped PABA is significantly higher than that of HCl-doped PANi produced by conventional methods due to anionic tetrahedral boronic acid groups covalently linked to the PANi backbone. The thermogram of PABA implies that crosslinking with anhydride formation probably occurs from around $100 \text{ }^{\circ}\text{C}$ up to $800 \text{ }^{\circ}\text{C}$. After heat-treatment at 100 and $500 \text{ }^{\circ}\text{C}$, PABA is still conducting with one and two orders less of magnitudes compared to the conductivity of as-synthesized PABA. Nevertheless, the conductivity of HCl doped PANi is decreased with two and four orders of magnitudes at 100 and $500 \text{ }^{\circ}\text{C}$, respectively. These results suggest that the thermal stability of the conductivity of

PABA is much better than that of HCl doped PANi due to the boronic acid substitution on the polymer as well as possible cross-linking between polymer chains by anhydration during thermal treatment.

In addition, a new strategy to generate a crosslinked, self-doped conducting polymer is presented as well as the characteristics of the polymer. By having a negatively charged crosslink site that can simultaneously act as a dopant, this approach circumvents major obstacles encountered using traditional methods of crosslinking. Furthermore, no fillers or other nonconducting crosslinking agents are required, that would ultimately reduce conductivity. We demonstrate this method by self-crosslinking PABA, which results in the creation of four-coordinate boron through the formation of a dative boron-imine bond. Under unoptimized conditions, the percentage of four-coordinate boron and in turn the level of doping is estimated to be 21%. In addition to retaining a high degree of conductivity, the crosslinked PABA exhibits significant hardness, surpassing more common "hard" polymer. Optimization of the synthesis and processing conditions in conjunction with the novel use of ^{11}B NMR is expected to provide further elucidation of the unique role of boron in the structure of the polymer. These results have the potential to significantly broaden the range of applications and environments in which conducting polymers are used.

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