A CHARACTERIZATION OF ORGANIC AND INORGANIC POLYMERIC
MATERIALS BY SOLID-STATE NMR

A Dissertation

Presented to

The Graduate Faculty of the University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Jennifer L. Rapp

August, 2007
A CHARACTERIZATION OF ORGANIC AND INORGANIC POLYMERIC MATERIALS BY SOLID-STATE NMR

Jennifer L. Rapp

Dissertation

Approved:

Advisor
Dr. Matthew P. Espe

Department Chair
Dr. Kim C. Calvo

Committee Member
Dr. Peter L. Rinaldi

Dean of the College
Dr. Ronald F. Levant

Committee Member
Dr. Michael J. Taschner

Dean of the Graduate School
Dr. George R. Newkome

Committee Member
Dr. Jun J. Hu

Date

Committee Member
Dr. Rex D. Ramsier
ABSTRACT

Alumina nanofibers, having average diameters of 500 nm, have been fabricated via the electrospinning process. Annealing the as-spun nanofibers at temperatures ranging from 525 °C-1200 °C was found to produce intermediate forms of alumina, transition aluminas before conversion into the thermodynamically stable phase, α-alumina. An in depth characterization of these alumina nanofibers via solid-state nuclear magnetic resonance (SSNMR) and other characterization techniques provide valuable information about the bulk and surface properties of these alumina nanofibers. As the surface of alumina materials have been known to have chemical and catalytic capabilities, the reactive nature of these alumina nanofibers were studied by the adsorption of phosphorus compounds on the surface of the nanofibers. Two phosphorus containing compounds were used; a chemical warfare agent simulant, dimethylmethyl phosphonate (DMMP) and methyl phosphate. The interaction of these materials with the surface of the alumina nanofibers were studied by SSNMR.

Protonation (doping) of polyaniline, with a protonic acid renders it conducting, altering its electronic and structural properties. One of the highest reported conductivities of doped polyaniline is when it is doped with camphorsulfonic acid (HCSA) and cast from a m-cresol solution. Several models of the crystal structure of this system have
been proposed, however they have not been proven experimentally. Solid-state NMR has been used to investigate the structure and specific interactions that occur between the dopant and/or solvent within the conducting polymer system. The structure of polyaniline synthesized in the presence of a polyacid, poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAAMPSA) was also investigated, by the use of solid-state NMR.
ACKNOWLEDGEMENTS

I would like to thank the following people, who have made my journey through graduate school and the completion of my dissertation possible:

- Dr. Matthew P. Espe, my advisor. Without his guidance, encouragement, dedication and sense of humor, I don’t think I would have made it this far. I sincerely thank him for all of the time he spent with me and his never-ending patience during early and late phone conversations, constant trips to his office and the roller-coaster ride of emotions that occurred during the transition of gaining self-confidence and becoming an independent researcher.

- The Molecular Spectroscopy Lab staff: Dr. Todd Wagler, Simon Stakleff, Dr. Venkat Dudipala and Dr. Joe Massey. Their help with spectroscopy training, software and computer advice and constant support will forever be remembered and appreciated.

- My committee members: Dr. Peter Rinaldi, Dr. Michael Taschner, Dr. Jun Hu and Dr. Rex Ramsier. I will always appreciate their support and guidance given to me during my time as a graduate student.
• My lab group: Wendy Lewis, Saida Ortiz, Somali Gosh and Anna Pischera. They not only made the Espe group the best lab to be associated with, but they are wonderful friends. I will never forget their advice, both personal and professional, support and all the wonderful memories we had together.

• My family: Robert, Sharon and Krystal Rapp. Their constant support, encouragement, love and understanding made me the person I am today. They always have been my “rock” and when things get tough, I know I just have to lean on them and they will support me.

• My collaborators: Ricky Tuttle and Ayesha Chowdry. Their hard work and dedication in the electrospinning and annealing of the nanofibers, as well as additional characterization of the materials is greatly appreciated.

• Jeremy Cross and his family: They watched me grow and gave me support and uplifting words of encouragement when I needed it. They have always been in my corner and I will never forget their love and friendship. Thank you for the years we spent together and I wish you all the best in the future.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>I.  ALUMINA</td>
<td>1</td>
</tr>
<tr>
<td>1.1 History and Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Modes of Production</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Transition Aluminas: Bulk Properties</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Transition Aluminas: Surface Properties</td>
<td>9</td>
</tr>
<tr>
<td>1.5 Alumina Nanofibers</td>
<td>16</td>
</tr>
<tr>
<td>1.6 Research Objectives</td>
<td>18</td>
</tr>
<tr>
<td>II. SOLID-STATE NUCLEAR MAGNETIC RESONANCE</td>
<td>20</td>
</tr>
<tr>
<td>2.1 Theory</td>
<td>20</td>
</tr>
<tr>
<td>2.2 Solid-State Internuclear Interactions</td>
<td>28</td>
</tr>
<tr>
<td>2.3 Solid-State NMR Methods</td>
<td>36</td>
</tr>
<tr>
<td>III. EXPERIMENTARY</td>
<td>44</td>
</tr>
<tr>
<td>3.1 Alumina Nanofiber Synthesis and Electrospinning Conditions</td>
<td>44</td>
</tr>
<tr>
<td>3.2 Alumina Nanofiber Formation and Annealing Conditions</td>
<td>45</td>
</tr>
<tr>
<td>3.3 Phosphorus Deposition</td>
<td>46</td>
</tr>
<tr>
<td>3.4 Characterization Methods</td>
<td>47</td>
</tr>
</tbody>
</table>
IV. RESULTS AND DISCUSSION..................................................................................................................49

4.1 Electrospun Nanofibers ......................................................................................................................49
4.2 Nanofibers Calcinated at 1200 °C........................................................................................................53
4.3 Transition Aluminas ............................................................................................................................57
4.4 The “Dry” Bake Method ......................................................................................................................63
4.5 Surface Characterization of the Alumina Nanofibers .........................................................................68
4.6 Water Vapor and Its Effect on the Formation of α-Alumina .................................................................71
4.7 Surface Reactivity of the Alumina Nanofibers Prepared Via the “Dry” Bake Method..........................73

V. POLYANILINE......................................................................................................................................86

5.1 Background of Polyaniline ..................................................................................................................86
5.2 Synthetic Processes ...............................................................................................................................88
5.3 Doping of Polyaniline ............................................................................................................................90
5.4 Models of the Structure of Polyaniline in the Doped State .................................................................92
5.5 Solid-State NMR Characterizations ......................................................................................................95
5.6 Research Objectives ............................................................................................................................97

VI. EXPERIMENTAL..................................................................................................................................99

6.1 Chemical Synthesis of Emeraldine Base (EB) Polyaniline .................................................................99
6.2 Polyaniline Synthesized in the Presence of a Template .................................................................100
6.3 Doped Polyaniline .............................................................................................................................102
6.4 Solid-State Nuclear Magnetic Resonance (SSNMR) ..........................................................................103
VII. RESULTS AND DISCUSSION .......................................................................................... 105

7.1  Structure of Doped Polyaniline ............................................................................. 105

7.2  Meta-cresol Exposures ....................................................................................... 110

7.3  Hydrogen Bond Investigation ............................................................................ 113

7.4  PANI-PAAMPSA ................................................................................................. 120

REFERENCES ............................................................................................................... 127


LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>10</td>
</tr>
<tr>
<td>1.4</td>
<td>11</td>
</tr>
<tr>
<td>1.5</td>
<td>18</td>
</tr>
<tr>
<td>2.1</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>24</td>
</tr>
<tr>
<td>2.4</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>30</td>
</tr>
<tr>
<td>2.6</td>
<td>32</td>
</tr>
<tr>
<td>2.7</td>
<td>34</td>
</tr>
<tr>
<td>2.8</td>
<td>35</td>
</tr>
</tbody>
</table>
4.13 SEM images of alumina nanofibers after calcination at 1200 °C in the closed oven .......................................................... 67

4.14 $^{27}$Al DP/MAS (left side) and $^{1}$H-$^{27}$Al CP/MAS (right side) NMR spectra of wet bake alumina nanofibers calcined at 525 °C (top spectra) and 1200 °C (bottom spectra) ................................................................. 69

4.15 $^{1}$H-$^{27}$Al CP/MAS NMR spectra of dry bake alumina nanofibers .................................................. 70

4.16 $^{27}$Al DP/MAS NMR spectra of alumina nanofibers calcined at 1200 °C with varied amounts of H$_2$O present: (A) 2 drops of H$_2$O, (B) 4 drops of H$_2$O, (C) 8 drops of H$_2$O, (D) 16 drops of H$_2$O, and (E) 30 drops of H$_2$O ................................................................. 72

4.17 Structures of (A) methyl phosphate (MePO$_4$, mixture of mono- and di-methyl phosphate) and (B) dimethyl methyl phosphonate (DMMP) ............ 74

4.18 $^{31}$P DP/MAS (left) and CPMAS (right) NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition ........................................ 75

4.19 $^{13}$C CP/MAS NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition ................................................................ 78

4.20 $^{27}$Al DP/MAS NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition ......................................................................... 79

4.21 $^{31}$P DP/MAS NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition, aged 2 months .............................................. 80

4.22 $^{31}$P DP/MAS (left) and CP/MAS (right) NMR spectra of (A) neat DMMP and DMMP deposited on the surface of alumina nanofibers calcined at (B) 525 °C, (C) 800 °C, and (D) 1000 °C prior to deposition ...................... 81

4.23 $^{27}$Al DP/MAS (left) and CP/MAS (right) NMR spectra of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, and (C) 1000 °C followed by DMMP deposition .............................................. 83
### 4.24 13C CP/MAS NMR spectra of DMMP deposited on the surface of alumina calcined at (A) 525 °C, (B) 800 °C and (C) 1000 °C prior to deposition...

### 5.1 Polyaniline structures

### 5.2 Protonation mechanism of the emeraldine base of polyaniline

### 5.3 Models of PANI:HCSA structure, as proposed by Łužny and co-workers

### 5.4 Proposed intermolecular interactions existing between polyaniline and HCSA (dopant) and the solvent, m-cresol (adapted from reference 231)

### 7.1 13C DP/MAS NMR spectrum of sonicated Polyaniline/HCSA cast from NMP

### 7.2 Conformational changes of the PANI/HCSA complex as a result of exposure to m-cresol vapors

### 7.3 13C CP/MAS NMR spectra of m-cresol exposures

### 7.4 1H-13C LGCP-FSLG HETCOR NMR spectrum of L-Tyrosine hydrochloride salt

### 7.5 1H-13C LGCP-FSLG HETCOR NMR spectrum of deuterated L-Tyrosine hydrochloride

### 7.6 1H-13C FSLG HETCOR NMR spectrum of L-Tyrosine hydrochloride salt

### 7.7 1H solution-state NMR spectra of N,N'-diphenyl-p-phenylenediamine cast from CHCl₃ (non-hydrogen bonding solvent) and DMSO (hydrogen bonding solvent)

### 7.8 1H-13C MELODI-HETCOR NMR spectrum of 15N labeled PANI cast from NMP

### 7.9 Pol(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA

### 7.10 13C CP/MAS NMR spectra of (A) PAAMPSA-45 (solid line) and PAAMPSA-724 (dotted line), (B) PANI-PAAMPSA-45 and (C) PANI-45
7.11 $^{15}$N CP/MAS NMR spectra of (A) PANI-PAAMSA (i) -724, (ii) -45, and 
(B) PANI (i) -724, (ii) -45 ............................................................................ 124
CHAPTER I

ALUMINA

1.1 History and Background

An aluminum compound, “alum” was first referred to by the Greeks in the fifth century B.C. In 80 A.D., an aluminous material named “alumen” was used by the Romans as a mordant and astringent\textsuperscript{1-3} and the name is believed to be the root word for alumina.\textsuperscript{4} Increased interest in aluminum oxides and hydroxides began in the 17\textsuperscript{th} century. The base of alum was suggested to be a distinct “earth” in 1722 by Hoffman\textsuperscript{5} and named “thonichte erde” or “terre argilleuse” (clay earth), by Pott.\textsuperscript{6} In 1754 it was shown that alum and clays contained a distinct compound, “alumine”,\textsuperscript{7,8} which was named by De Morveau in 1786 and later converted to the recognized English name, alumina.

Alumina or aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) is found abundantly in nature as minerals containing different forms of aluminum oxides and hydroxides. The most common source of alumina is the mineral bauxite. Bauxite was discovered by Pierre Berthier in 1821 and named after Les Baux in the Provence district of France. It is composed
primarily of aluminum hydroxides with a small percent of iron, silicates and titanium and must be refined in order to obtain pure (>99%) Al₃O₃. The name bauxite was later extended to cover weathered minerals containing higher percents of aluminum hydroxides⁹ and is now considered a general term for minerals containing a large percent of alumina and a low percent of alkaline earths and silica. Bauxite minerals are found in areas around the world and the type of aluminum hydroxide present in the minerals varies by location.

Before bauxite was defined, minerals containing aluminum hydroxides were being discovered. In 1798, a mineral found in India was described as having the composition, Al₂O₃ and named “corundum” by Greville.¹⁰ The mineral diaspore was described in 1801¹¹ and in 1802 was shown to have the structure Al₂O₃·H₂O.¹² Gibbsite, named in honor of the American mineralogist G. Gibbs, was discovered in 1820¹³ and the structure was determined by Torrey a few years later to consist of Al₂O₃·3H₂O.¹⁴ After the discovery and naming of bauxite, two other forms of aluminum hydroxide containing minerals were discovered, boehmite (böhmit) named after the discoverer, Böhm¹⁵,¹⁶ and nordstrandite, named after Van Nordstrand.¹⁷ Nordstrandite has been found in tropical red soils in West Sarawak¹⁸ and on the island of Guam.¹⁹ Another form of aluminum hydroxide was discovered and found to be an isomer of gibbsite.²⁰ Due to its rare natural abundance, this form is commonly synthesized and was named bayerite,²¹ for it was thought to be a product of the Bayer process. It was later found that gibbsite is the actual product of the Bayer process; however the name bayerite was never changed.

The various aluminum hydroxides found in bauxite minerals and those synthesized have been classified into four main categories, aluminum trihydroxides
(Al(OH)₃), aluminum oxide hydroxides (AlOOH), gelatinous aluminas (amorphous aluminas) and aluminum oxide (Al₂O₃). The minerals gibbsite, bayerite and nordstrandite are aluminum trihydroxides, while boehmite and diaspore are aluminum oxide hydroxides. Corundum is the pure form (found in nature) of aluminum oxide, whereas α-Al₂O₃ is the thermodynamically stable phase of aluminum oxide, formed upon calcining the various aluminum oxides and hydroxides at high temperatures.

The gelatinous aluminas are two-phase, synthetic aluminum hydroxides with the dominant phase being the solid phase and the other, a solution phase. The solid phase consists of colloidal aluminum hydroxides or oxide hydroxides and the solution phase is made up of water, a mixture of water and an organic solvent or air.¹ ² ² ⁹

Alumina is an extremely versatile material and its range of properties is best described by Francis C. Frary.² ³

Aluminum oxide and its hydrates present a variety of amazing contrasts. From the hardness of the sapphire to a softness similar to that of talc, from an apparent density of over 200 pounds to one of about 5 pounds per cubic foot, from high insolubility and inertness to ready solubility in acids or alkalies and marked activity, the properties can be varied over wide limits. Some forms flow and filter like sand; other are viscous, thin, unfilterable or even thixotropic. Crystals may be of any size down to a fraction of a micron in diameter, with various allotropic forms, and there are also amorphous forms. Some varieties have a very high adsorptive power, others none at all. Some are catalytically active, others inactive.

Owing to the diverse properties described above, aluminum hydroxides are used in a wide range of applications; as additives in adsorbents, abrasives and refractories, as well as their use as the pre-cursor for the production of alumina.¹ ² ³ ⁴ They are also used directly as industrial catalysts, catalyst supports, adsorbents, coatings, ceramics and soft abrasives.¹ ² ⁴-² ⁶ Gibbsite is used as an additive in flame retardants and smoke suppressants, toothpaste, paper and synthetic marble. When calcined, it is used in high
surface area sorbents and as an additive in glasses.\textsuperscript{27} Boehmite is additionally used in ceramics and as catalyst supports.\textsuperscript{28} Due to its thermal stability at temperatures exceeding 1800 °C, \(\alpha\text{-Al}_2\text{O}_3\) (corundum) is most commonly used in ceramic materials.\textsuperscript{1}

1.2 Modes of Production

The most commonly used process for the extraction of alumina from bauxite minerals is the Bayer process, discovered in 1888 by Karl Joseph Bayer.\textsuperscript{2} The resulting product from this process is crystalline gibbsite. The Bayer process involves four main steps: extraction of aluminum hydroxide minerals, separation of insoluble impurities, precipitation of crystalline gibbsite, and calcination of gibbsite. Extraction of aluminum hydroxides occurs at elevated temperatures, in a concentrated solution of NaOH (caustic soda) and the conditions are dependent upon the type of hydroxide present in the bauxite. For instance, extraction of gibbsite occurs in a 200 g/L NaOH solution at temperatures of 150 °C or less, whereas a NaOH concentration of 300 g/L is used in the extraction of boehmite and diaspore with temperatures greater than 200 °C and 300 °C, respectively. Boehmite and diaspore are purified by other means, as will be discussed later.

Decantation and filtration of the NaOH mixture are the methods used to separate the impurities contained within the bauxites. The filtered mixture, referred to as a “caustic aluminate liquor”, contains dissolved aluminum trihydroxide and is cooled and crystallized by the addition of gibbsite seed crystals. Separation of the seed crystals from the grown gibbsite crystals occurs via washing and filtration and is followed by drying
(calcination) of the material. The method of drying is dependent upon the type of alumina desired. A complete diagram of the Bayer process is shown in Figure 1.1.

Figure 1.1. Bayer Process (adapted from reference 2).
Other methods of processing aluminum hydroxides include, but are not limited to the sinter process, the combination process and the Zeigler process. The sinter process, introduced by Louis Le Chatelier in 1855 involves annealing bauxites at temperatures well above 900 °C in the presence of Na$_2$CO$_3$ (soda), producing NaAlO$_2$ to which separation and precipitation of an aluminum hydroxide liquor follows. Carbon dioxide gas is bubbled through the liquor. Precipitated residual aluminum hydroxide and silica contaminants are removed by annealing at temperatures between 150-200 °C and reacting the aluminum hydroxide with lime (CaO). The product is a much whiter material; a result of the sintering and removal of organic materials.

The combination process begins with Bayer extraction and is followed by the sinter process. Bauxites containing large amounts of silica are usually processed in this manner. The product is a white, non-organic, hydroxide material.

The aluminum hydroxide (aluminum alkoxide with a boehmite crystal structure) obtained from the Ziegler process is an intermediate product made during the synthesis of linear alcohols that is hydrolyzed, separated and dried.

1.3 Transition Aluminas: Bulk Properties

Transition aluminas are the most important forms of alumina, as their unique surface properties in conjunction with high surface areas makes them successful in many industrial applications, such as adsorbents and catalytic materials in hydrocarbon cracking, purification of gas oil fractions, control of combustion emissions, destruction of chemical weapons and other chemical processes. Transition aluminas
are metastable, intermediate forms of alumina, created by the dehydration/dehydroxylation (calcination) of aluminum hydroxides via annealing at high temperatures, before transforming into the thermodynamically stable form, $\alpha$-alumina. $\alpha$-alumina must not be confused with corundum alumina, while having the same crystalline structure as the *pure* mineral corundum, it is a *synthetic* alumina.$^{35}$ Dehydration involves the removal of physisorbed water molecules and occurs at relatively low temperatures, while dehydroxylation involves condensation of surface hydroxyl groups.$^{36}$ Dehydration/dehydroxylation methods are also referred to as calcination processes; as calcination is the method in which a material is annealed at high temperatures with subsequent removal of moisture.

The various transition aluminas formed are highly dependent upon the alumina pre-cursor used and the annealing temperature, as illustrated in Figure 1.2.

\[
\begin{align*}
\text{Boehmite} & \quad 300-400 \, ^\circ \text{C} \xrightarrow{\gamma} 750-850 \, ^\circ \text{C} \xrightarrow{\delta} 1000-1100 \, ^\circ \text{C} \xrightarrow{\theta} 1200 \, ^\circ \text{C} \xrightarrow{} \alpha-\text{Al}_2\text{O}_3 \\
\text{Bayerite} & \quad 230-650 \, ^\circ \text{C} \xrightarrow{\eta} 800-1000 \, ^\circ \text{C} \xrightarrow{\theta} 1000-1200 \, ^\circ \text{C} \xrightarrow{} \alpha-\text{Al}_2\text{O}_3
\end{align*}
\]

Figure 1.2. Thermal evolution of aluminum hydroxides, boehmite and bayerite in air (adapted from references 35 and 37).

Other factors influencing the types of transition aluminas produced upon calcination include the particle size and impurities/additives contained in the aluminum precursor and gases present during annealing.$^{23}$ As a result of the impact of these many factors, the thermal transformation sequences are complex and this has lead to controversy over the forms of the transition aluminas created. This is most clearly evident in the calcination of
gibbsite (hydrargillite), where numerous studies have shown that the thermal
transformation pathway is highly dependent upon the particle size and water vapor
present during calcination.\(^{28,38,39}\) It was observed by x-ray powder diffraction (XRD) and
infra-red (IR) spectra that \(\chi\)- and \(\kappa\)-\(\text{Al}_2\text{O}_3\) are produced upon annealing fine gibbsite
particles, before transformation into \(\alpha\)-\(\text{Al}_2\text{O}_3\) at 1200 °C. When coarse gibbsite particles
are annealed, two different pathways have been found to occur, one which produces the
transitional aluminas observed during the calcination of fine gibbsite particles and the
other which produces boehmite, followed by the transition aluminas \(\gamma\)-, \(\delta\)-, \(\theta\)-, and finally
\(\alpha\)-\(\text{Al}_2\text{O}_3\).\(^{23,27,40-44}\) Other studies have reported that the dehydration sequence of
hydrargillite (gibbsite) occurs with the formation of boehmite, followed by the transition
aluminas \(\eta + \kappa', \kappa, \text{ and } \alpha\)-\(\text{Al}_2\text{O}_3\).\(^{45}\) Alexanian\(^{46}\) reported the dehydration sequence of
hydrargillite to be boehmite, \(\gamma\)-, \(\delta\)-, \(\kappa\)-, and \(\alpha\)-\(\text{Al}_2\text{O}_3\), whereas Glemser and Rieck\(^{47}\)
reported a dehydration sequence of boehmite, \(\varepsilon\)-, \(\kappa\)-, and \(\alpha\)-\(\text{Al}_2\text{O}_3\). Sato \(\text{et al.}\)^{43,48}
reported that annealing fine particle agglomerates of hydrargillite produces \(\lambda\)-\(\text{Al}_2\text{O}_3\),
followed by \(\kappa\)-, \(\theta\)- and \(\alpha\)-alumina; whereas large, single crystals produce a mixture of
hydrargillite and boehmite, followed by a mixture of boehmite and \(\lambda\)-\(\text{Al}_2\text{O}_3\), which is
then followed by the transition aluminas \(\lambda\)-, \(\kappa\)-, \(\theta\)- and \(\alpha\)-\(\text{Al}_2\text{O}_3\). On the contrary, other
studies have shown that in vacuum, \(\rho\)-, \(\eta\)-, and \(\theta\)-alumina forms are produced before
transformation into \(\alpha\)-alumina, regardless of the gibbsite particle size.\(^{27,28}\) In spite of the
discrepancies, the formation of boehmite is a common step, before transformation into
the various transition aluminas. The transformation into boehmite is believed to be a
result of the large particle sizes of gibbsite, in which water molecules become trapped
within the crystal lattice.\(^{23,49,50}\) The transformation into boehmite also has been thought to
be a product of a reaction between χ-alumina and water released during the dehydration process.\textsuperscript{51,52}

1.4 Transition Aluminas: Surface Properties

The surfaces of the transition aluminas contain Brönsted acid and Lewis acid sites in the form of surface hydroxyl groups and coordinately unsaturated sites (cus), AlO\textsubscript{x} (x = 3, 4, 5), providing for their catalytic and reactive nature. The presence of both Brönsted and Lewis acid sites make the surfaces of transition aluminas the most complex of all metal oxide catalysts.\textsuperscript{26} Lewis acids sites are believed to be the result of thermal dehydroxylation mechanisms between adjacent octahedral aluminum hydroxyl groups in aluminum hydroxides and transition aluminas, accounting for lower coordinated aluminum species (3-, 4-, and 5- coordinated aluminum).\textsuperscript{26} While the catalytic activity of transition aluminas is complex, the interactions with Lewis acid and Brönsted acid sites are believed to be a major contribution to their reactivity. Hydrogen bonding between Brönsted acid sites and adsorbed molecules is proposed to be the mechanism for the catalytic activity observed in transition aluminas, while the acidity of Lewis acids is also a major contributor to their catalytic properties.\textsuperscript{26}

Several models have been proposed as to the surface structure of transition aluminas. One model, supported by infra-red spectroscopic data, proposes that five different types of hydroxyl configurations exist on the surfaces of transition aluminas and they have been grouped into three main types (I, II and III).\textsuperscript{26,53-56} Figure 1.3.
Type I hydroxyls are bonded to either an octahedrally coordinated or a tetrahedrally coordinated aluminum atom, whereas type II sites contain bridging hydroxyl groups with either two octahedrally coordinated aluminum atoms or one octahedral and one tetrahedral aluminum atoms. With type III hydroxyls, the oxygen atom is bridged between three octahedrally coordinated aluminum atoms.

The actual wavenumber assigned to the different types of hydroxyl groups and the reasons for these assignments (Figure 1.3) have received some debate. Peri\textsuperscript{53,54} attributed the five different OH band positions in the IR data to be a result of the number of oxide ions next to the hydroxyl group (next nearest neighbor theory). He assigned the highest wavenumber peak to hydroxyls with the most neighboring oxide ions (surrounded by four oxide ions) and the lowest wavenumber peak to hydroxyls that are not next to an oxide
A representation of the surface hydroxyl groups and their IR band assignments are shown in Figure 1.4.

![Figure 1.4](image_url)

**Figure 1.4.** Peri’s surface hydroxyl model and IR assignments of the five different types of hydroxyl groups (adapted from references 1 and 48).

Other studies have shown that the coordination number of the aluminum bonded to the surface hydroxyl groups (Figure 1.3) determines the OH-stretching frequencies. 57-59 Morterra *et al.* 57 assigned hydroxyl groups coordinated to tetrahedral Al\(^{3+}\) to wavenumbers in the range of 3760-3800 cm\(^{-1}\) and hydroxyls coordinated to both octahedral and tetrahedral Al\(^{3+}\) to 3700-3750 cm\(^{-1}\), while those coordinated only to octahedral Al\(^{3+}\) were assigned to wavenumbers between 3730-3740 cm\(^{-1}\). Studies by Tsyganenko and Filimonov 60 agree with those of Morterra in that assignments of the IR
hydroxyl bands are related to the specific aluminum coordination numbers. Knözinger and Ratnasamy, along with Jones relate the OH-stretching frequency with the net charge of the hydroxyl species, where higher wavenumbers have been assigned to the hydroxyl groups carrying the most negative net charge, and peaks with lower wavenumbers are assigned to groups having a more positive net charge. Therefore, hydroxyl band assignments are as follows: $I_b = 3800 \text{ cm}^{-1}$, $I_a = 3760-3780 \text{ cm}^{-1}$, $IIb = 3740-3745 \text{ cm}^{-1}$, $IIa = 3730-3735 \text{ cm}^{-1}$, $III = 3700 \text{ cm}^{-1}$, with net charges on the OH groups of -0.5, -0.25, 0, +0.25 and +0.5, respectively. In addition to the identification of the different types of surface hydroxyls, IR studies have provided information on hydrogen bond interactions between neighboring hydroxyl groups. These studies have provided information on the condensation mechanisms that occur during thermal treatments and the surface structure of different aluminas.

Another method that allows for the characterization of transition alumina surfaces is adsorbing small molecules onto the surface of the materials under study. The use of small molecules as molecular probes provides information on the coordinately unsaturated aluminum sites (cus), as well as the catalytic/reactive nature of the alumina materials. Carbon monoxide (CO) is an example of one of the molecular probes used. IR studies of CO adsorption on the $\gamma$- and $\eta$-transition aluminas have been reported. It has been shown that only upon dehydration of these transition aluminas, at temperatures greater than 673 K do CO species adsorb onto the surfaces. The presence of coordinately unsaturated tetrahedral aluminum sites ($\text{Al}^{IV}_{\text{cus}}$) also was observed to promote CO adsorption. IR studies of CO adsorption onto dehydrated $\gamma$-alumina surfaces revealed the formation of three different adsorbed CO species ($\text{CO}_A$, $\text{CO}_B$ and $\text{CO}_C$), indicating that
three different surface sites exist on \( \gamma \)-alumina. CO\(_B\) and CO\(_C\) species are believed to be associated with Al\(^{IV}\)\(_{\text{cus}}\) defect sites, giving IR bands at 2215-2220 cm\(^{-1}\) and 2235-2240 cm\(^{-1}\), respectively. Based on the frequencies of the IR bands representing the two different CO species; higher IR frequency, stronger interaction and lower IR frequency, weaker interaction, it was concluded that the CO\(_C\) species interact with the alumina surface more strongly than the CO\(_B\) species. The third species, CO\(_A\), was believed to be associated with Al\(^{IV}\)\(_{\text{cus}}\) sites located in sections of low-crystalline order and interacted weakly with the \( \gamma \)-alumina surface. However, it was discovered that adsorption at higher temperatures brought about an increase in the amount of CO\(_A\) that adsorbed onto the surface of the alumina, while the adsorption of CO\(_B\) and CO\(_C\) was unaffected.

The investigation of CO adsorption on the surfaces of \( \eta \)-alumina reveals that adsorbed species of the types CO\(_A\) and CO\(_C\) dominate the IR spectra, while CO\(_B\) is barely detected and in some cases not reported.\(^{62,63}\) The strength of the adsorption of the CO\(_C\) and CO\(_A\) species on the surfaces of \( \eta \)-alumina were found to be similar to that observed with the interaction of CO and the surfaces of \( \gamma \)-alumina. It was also illustrated that the strongly adsorbed CO\(_C\) species perturbed hydroxyl groups of type Ia and those particular sites have been designated as X-sites.\(^{56,63-66}\) The presence of surface X-sites were also observed upon adsorption of pyridine, ketones, nitriles\(^{67}\) and olefins,\(^{68}\) suggesting that the interaction of the X-sites with the adsorbents is the same, regardless of the molecule used.\(^{56}\) Based upon the similarities of the surface sites observed by IR studies of adsorbed molecular probes onto the selected transition aluminas, it has been concluded that the same types of surface OH configurations exist on the surface of both aluminas, regardless of their bulk structures.\(^{56}\)
Solid-state nuclear magnetic resonance (SSNMR) is another technique that has been used to study the surface structure and reactivity of transition aluminas. By using a series of SSNMR methods, separate investigations of the bulk and surface properties of these materials is possible. Morris and Ellis\textsuperscript{69} have used cross-polarization (CP) from surface protons to aluminum atoms in an effort to study the effect calcination had on the surface of $\gamma$-Al$_2$O$_3$. Before thermal treatment, two peaks were observed in the $^{27}$Al spectra, arising from tetrahedral (~68 ppm) and octahedral (~0 ppm) surface Al-OH species. Upon calcination, the resonance from tetrahedral aluminum sites broadened; a result of increased heterogeneity in the structure of the alumina sites, and with an increase in temperature the signal intensity for both octahedral and tetrahedral sites decreased. At a calcination temperature of 815 °C \textit{in vacuo}, a complete loss of the $^{27}$Al signal was observed. It was suggested that the loss of the hydroxyl proton was the reason for the loss of signal. However, O’Reilly has proposed that the $^{27}$Al signal was broadened to a very large extent as a result of large electric field gradients created by surface site distortion upon dehydroxylation methods.\textsuperscript{70} In later studies by Huggins and Ellis,\textsuperscript{71} they proposed that the loss of the signal in the NMR spectrum was a result of the complex nature of alumina surfaces brought about by changes in the symmetry of surface aluminum sites. These changes, caused by the movement of water molecules along the surface and dehydration/dehydroxylation methods, cause an increase in the aluminum quadrupole coupling constant and a loss in aluminum signal, thus rendering $^1$H-$^{27}$Al CP as an inaccurate representation of the true surface properties.

Cross-polarization from protons to oxygens ($^{17}$O) has provided useful information about the types of surface hydroxyl groups present on $\gamma$-Al$_2$O$_3$ and other transition
The $^1$H-$^{16}$O CP/MAS NMR spectra from boehmite and bayerite contained weak Al$_2$OH signals, which were assigned to Brønsted acid surface sites and used for comparison in the interpretation of the spectra from transition aluminas. In the CP spectrum from $\gamma$-alumina, signals consistent with hydroxyl oxygens of type IIB (Figure 2) were observed. Additional studies by Fitzgerald and co-workers using $^1$H combined rotation and multiple pulse (CRAMPS) spectroscopy, has allowed for the investigation of surface Brønsted acid Al-OH groups on pseudo-boemite materials. $^{26,36,73}$ $^1$H CRAMPS results showed three resonances at 3.0 ppm, 4.0 ppm and 8.2 ppm. The peak at 4.0 ppm was assigned to physisorbed water and the peaks at 3.0 and 8.2 ppm were assigned to AlOH and Al$_2$OH groups, respectively. Evacuation and dehydration procedures, followed by CRAMPS experiments provide information about the surface hydroxyl groups that are involved in condensation reactions. A significant reduction in the signal intensity of the Al$_2$OH resonance (8.2 ppm) indicates that the associated hydroxyl protons undergo condensation with neighboring Al$_2$OH groups. Upon more extreme dehydration conditions, a reduction in the peak representing AlOH (3.0 ppm) groups was observed, however the complete removal of the hydroxyl protons was not achieved.

Solid-state NMR studies on molecules adsorbed onto the surface of alumina have also provided insight into the surface properties and catalytic activity of these materials. Studies involving the adsorption of pyridine (Lewis base) onto the surface of $\gamma$-alumina have shown that there are two different Lewis acid sites that consist of coordinately unsaturated (cus) octahedral and tetrahedral sites. $^{69,74-76}$ Aluminum-27 NMR results showed that when ammonia is bound to the surface of dehydrated $\gamma$-alumina, there are four aluminum Lewis acid sites present; two 4-coordinate sites, one 5-coordinate site and
one 6-coordinate site. Upon rehydration of γ-alumina, one of the 4-coordinate aluminum sites disappears, while the other aluminum sites are unchanged. It was also observed that the chemisorption of molecular water produced reconstruction of the alumina surface, converting 4- and 5-coordinated aluminum sites to 5- and 6-coordinate aluminum sites, respectively.\textsuperscript{76}

In an effort to increase the surface area and enhance the chemical properties of alumina, alumina “fibrous” materials, nanometer size alumina particles\textsuperscript{77-80} and mesostructured aluminas\textsuperscript{81-84} have been synthesized by a variety of means. The diameters of these nano-aluminas are in the range of 2 nm-1 μm and the lengths range from 40 nm-10 μm. While these fibrous nano-alumina materials have large surface areas, macroscopic manipulation is difficult and the materials lack flexibility, thus limiting their potential applications. Therefore, producing flexible aluminum oxide materials with macroscopic handling capabilities, and incorporating high surface area is highly desired.

1.5 Alumina Nanofibers

Electrospinning has been around since the early 1900’s,\textsuperscript{85,86} however, recently it has attracted renewed interest. Electrospinning is a relatively simple and inexpensive process used to generate fibers in large quantities, compared to traditional methods that are costly, material dependent and have low yields. The process of electrospinning allows for the formation of sub-micron diameter (100-500 nm) fibers with lengths on the order of meters to kilometers.\textsuperscript{87} Enhanced surface area and control over the morphology and flexibility of the nanofibers produced are some of the benefits of this technique.
Electrospun nanofibers are currently used in diverse areas, such as membranes in batteries, photovoltaic cells, fuel cells, nanoelectronics, tissue and organ scaffolding, delivery of drugs, and filters. The most common electrospun materials are high molecular weight polymers, such as polyethylene oxide, polyacetonitrile, polyethylene, polypropylene and polystyrene. Owing to the ease and versatility of the electrospinning process, it has now branched out to include several different forms of materials, including ceramics and metal oxides.

In general, the electrospinning process begins when a high voltage is applied to an electrode immersed in a polymer solution that is contained in a pipette or syringe. Competition occurs between the surface tension of the polymer solution and the repulsive electric force created by the applied voltage, and the polymer solution begins to form a droplet at the end of the pipette (syringe) in the shape of a cone, referred to as a Taylor cone. When the electric field forces exceed that of the surface tension of the droplet, the polymer solution is forced from the pipette and travels in a circular manner, towards an oppositely charged collecting plate. The circular (spinning) pathway is a result of the repulsive forces present within the polymer solution. If these forces are large enough, then several pathways (jets) are formed creating nanofibers with smaller diameters. While traversing the distance between the pipette and collecting plate, the solvent evaporates and the material that reaches the collector are dry, or nearly dry, fibers. A schematic of the electrospinning apparatus is shown in Figure 1.5.
1.6 Research Objectives

The electrospinning process, typically used to create polymer fibers has been extended to produce alumina containing nanofibers. The electrospun nanofibers were spun from a solution of ethanol containing an aluminum precursor, aluminum acetate and a guide polymer, polyvinylpyrrolidone (PVP). The generated nanofibers were then calcined at temperatures ranging from 525 °C to 1200 °C, forming alumina nanofibers with average diameters of 500 nm. While several groups have used this approach to produce alumina nanofibers, different polymer and aluminum precursors were used in the starting material and calcination of the fibers was always performed at temperatures exceeding 900 °C. The characterization of the fabricated alumina nanofibers was also limited in that the methods employed consisted mainly of electron microscopy and X-ray diffraction techniques.
In this report, a detailed characterization of the alumina nanofibers using solid-state NMR spectroscopy is discussed. In addition to the NMR, these materials have been studied using the techniques of X-ray diffraction and scanning electron microscopy. These techniques are complimentary and the collective set of data allows for a comprehensive, molecular-level understanding of the nanofiber composition and structure.

The ideal goal for the fabrication of alumina nanofibers is to form alumina-based catalytic or chemically reactive materials. One potential application of these fibers, currently of high relevance is in the area of chemical warfare agent (CWA) detoxification. Various studies have shown that alumina nanoparticles are highly effective in binding and decomposing/detoxifying chemical warfare agents, as a result of the presence of edge and defect sites located on the surface of the materials. The alumina nanofibers generated are anticipated to show similar capabilities. Solid-state NMR spectroscopy was used to study the efficacy of the decomposition of a chemical warfare agent simulant, dimethyl methyl phosphonate (DMMP), which is a simulant of the g-agents, sarin and soman. Another phosphorus containing compound, methyl phosphate and its interaction with the surface of the alumina nanofibers was also studied.

This research was done in collaboration with Dr. Rex Ramsier’s research group in the Department of Physics at The University of Akron. Richard Tuttle, a graduate student in the Ramsier group fabricated the alumina nanofibers and conducted the XRD and SEM studies.
CHAPTER II

SOLID-STATE NUCLEAR MAGNETIC RESONANCE

2.1 Theory

Nuclear magnetic resonance (NMR) is a spectroscopic technique that takes advantage of the spin angular momentum of nuclei. Nuclei that have spin angular momentum are described as having “spin”. The magnitude of the spin angular momentum of a nucleus is represented by the spin quantum number, I, and is determined by the number of neutrons and protons that the nucleus contains. If the number of neutrons and protons of a nucleus are both odd, then it has an integer spin with values $I = 1, 2, 3$, etc., and if the number of neutrons plus the number of protons is odd, the nucleus has a half-integer spin with values $I = 1/2, 3/2, 5/2$, etc. However, if the number of protons and neutrons are both even, the nucleus has no spin ($I = 0$) and is NMR inactive. The nuclei commonly studied by NMR include $^1$H, $^{13}$C, $^{15}$N, $^{31}$P and $^{19}$F.

The magnitude of the spin angular momentum is described by the relationship

$$I = [I(I+1)]^{\frac{1}{2}} \hbar,$$

(1)
where \( \mathbf{I} \) is the overall spin angular momentum, \( I \) is the spin quantum number and \( \hbar = \frac{h}{2\pi} \), with \( h \) being Planck’s constant. Spin angular momentum, a quantum mechanical property, is quantized and has specific, discrete values. These values are governed by the magnetic quantum number, \( m \), with \( m = I, I-1, I-2 \ldots -I \), thus there are \( 2I+1 \) possible states for spin angular momentum. A nucleus with \( I = 1/2 \) for example, has two possible values, \( m = +1/2 \) and \( -1/2 \) and for a nucleus with \( I = 1 \), \( m = 1, 0, \) and \( -1 \) (spin angular momentum has three possible values).

In a classical mechanics description, the spin angular momentum of a nucleus is brought about by its rotation. As the nucleus is treated as a rotating, charged species it has a magnetic moment (\( \mu \)) associated with its spin angular momentum. Spin angular momentum and magnetic moments are both vector quantities and the two vectors are parallel. The direction of the vectors of spin angular momentum and the magnetic moments are also parallel to the rotation axis of the nucleus. Thus, the magnitude of the magnetic moment (\( \mu \)) and spin angular momentum (\( I \)) are directly proportional, equation 2,

\[
\mu = \gamma I
\]

(2)

where \( \gamma \) is the gyromagnetic ratio (charge per mass unit) and is specific for each nucleus. The sign (+/−) of the \( \gamma \) governs the orientation of the magnetic moment relative to the spin angular momentum vector. If \( \gamma \) is positive, \( \mu \) is parallel to the spin angular momentum and if \( \gamma \) is negative, it is anti-parallel.

In the absence of an external magnetic field, the magnetic moments are randomly oriented in space. In the presence of an applied magnetic field (\( B_0 \)), however, spin
angular momentum and its associated magnetic moment aligns with respect to the magnetic field. In NMR, the value of interest is the projection of the spin angular momentum along the Z-axis, with the Z-axis defined as the direction of the applied magnetic field ($B_0$). The projection of spin angular momentum (and $\mu$) and its possible states are $I_z$ and $m_z$, Figure 2.1. Nuclei with $I_z = \frac{1}{2} \hbar$ are labeled spin-1/2 nuclei and include $^1\text{H}$, $^{13}\text{C}$, $^{15}\text{N}$, $^{31}\text{P}$ and $^{19}\text{F}$.

![Diagram of spin angular momentum and magnetic moments](image)

**Figure 2.1.** The interaction of spin angular momentum and magnetic moments of a spin-1/2 nucleus with a magnetic field.

In addition to the alignment of spin angular momentum with the magnetic field, a torque is induced on the nucleus by $B_0$. This torque causes the nucleus to precess about $B_0$ with a frequency known as the Larmor frequency, whose magnitude is shown in equation 3.

$$\omega_0 = \gamma B_0$$

In the case when $I_z = \frac{1}{2} \hbar$, the magnetic moment of the nucleus can be aligned parallel (–) or anti-parallel (+) to $B_0$. These two orientations have different energies, producing a two level system, Figure 2.2.
Figure 2.2. Energy level diagram for a spin-½ nucleus in the presence of a magnetic field, $B_0$. When spin angular momentum is aligned parallel to $B_0$ (arrow pointed in the upward direction), it is in a lower energy state or the $\alpha$-state and if $I_z$ is aligned antiparallel to $B_0$ (inverted arrow), then it is in a higher energy state or the $\beta$-state.

The two states and their energy difference are a function of the magnitude of the magnetic moment of the nucleus and $B_0$, equation 4,

$$\Delta E = \gamma \hbar B_0 = \hbar \nu$$  \hspace{1cm} (4)

where $\nu$ is the Larmor frequency.

As NMR is a resonance technique, a transition (spin flip) of the nucleus from $m_z = +\frac{1}{2}$ to $m_z = -\frac{1}{2}$ must be achieved. This resonance phenomenon occurs by the application of electromagnetic radiation (photon), such that the frequency ($\nu$) of the photon is equal to $\Delta E = \hbar \nu$. During resonance, the nucleus adsorbs or emits a photon and the spin angular momentum changes by $\Delta m$, the allowed transitions in NMR. For a spin-$\frac{1}{2}$ system the allowed transitions are $\Delta m = \pm 1$, as shown in Figure 2.2. At typical field strengths of 200 MHz-750 MHz (4.7–17.6 T), the applied radiation required for resonance to occur is in the megahertz (MHz) or radio frequency (rf) regime. Rf radiation has both an oscillating magnetic and electric field component and in NMR the
nucleus interacts with the oscillating magnetic field component. The magnetic field from the rf radiation (B₁) must be applied perpendicular to the B₀ field in order for a spin-flip to occur.

The previous discussion applied to a single nucleus, however, in a many spin system in the presence of a magnetic field, a population difference of the nuclear spins (magnetic moments) exists. This population difference follows the Boltzmann distribution which is expressed as

\[
\frac{P_{+1/2}}{P_{-1/2}} = e^{\frac{-\Delta E}{k_b T}} = e^{\frac{-\hbar B_0}{k_b T}},
\]

where \(\Delta E\) is the energy difference between the possible energy states, \(k_b\) is the Boltzmann constant and \(T\) is the temperature. The Boltzmann distribution shows that the population of the spins in the lower energy state (\(P_{+1/2}\)) is slightly greater than the population of spins in the higher energy state (\(P_{-1/2}\)) and the sum of all the individual magnetic moments from the nuclei within a sample produces the bulk magnetization (\(M\)), Figure 2.3.

Figure 2.3. Many spin system represented as the bulk magnetization.
Upon application of rf radiation, on resonance ($\nu_{\text{rf}} = \nu_{\text{Larmor}}$), the spins can adsorb ($\Delta m = +1$) or emit ($\Delta m = -1$) radiation. However, as there are more nuclei in the $m_z = +1/2$ spin state, there is a net adsorption of rf radiation. It is important to note that the population difference of the spins is extremely small, 1 to 0.99997 or 3 out of 100,000 (at average field strengths); as a result NMR is a fairly insensitive technique. This low sensitivity can be overcome by studying nuclei with larger $\gamma$ values and using higher field strengths, as the signal intensity is related to the square of the magnetic field ($S = B_o^2$).

The application of rf radiation, perpendicular to $B_o$, causes the bulk magnetization vector ($\mathbf{M}$) to rotate around $B_1$ in a clock-wise direction. The effect of the application of rf on $\mathbf{M}$ is best illustrated by describing the spin system in terms of a rotating axis system (RAS). In the rotating axis system, the $x$ and $y$ axes rotate around the $Z$-axis (the direction of $B_o$) at a frequency equal to $\nu_{\text{rf}}$. In this representation the magnetic field from the rf radiation ($B_1$) appears static. The application of the rf radiation results in the bulk magnetization ($\mathbf{M}$) rotating around $B_1$. The angle that $\mathbf{M}$ is rotated by, the flip angle or nutation angle, is described by

$$\theta_{\text{rf}} = \omega_1 \tau_{\text{rf}} = \gamma B_1 \tau_{\text{rf}},$$

where $\omega_1$ is the frequency that $\mathbf{M}$ precesses around $B_1$ and $\tau_{\text{rf}}$ is the time in which the rf is applied. Typically a flip angle of $90^\circ$ is applied and is referred to as a $90^\circ \times$ or $y$ pulse, with $x$ or $y$ denoting the direction along which the $B_1$ field is applied. For example, application of a $90^\circ_x$ rf pulse or $\frac{\pi}{2}$ pulse, rotates the net magnetization ($\mathbf{M}$) onto the $y$-axis. After the magnetization has been rotated, it still precesses about $B_o$. The rotation of this vector within a coil generates an oscillating current that is recorded. This oscillating
signal is a free induction decay (FID). The FID is detected in the time domain and by use of Fourier transformations, equation 7, it is converted into the frequency domain spectrum.

\[ F(f) = \int T(t) e^{-\omega t} dt \]  

(7)

In modern NMR experiments, a static magnetic field is used and rf pulses are applied to achieve resonance. Application of short (\(\mu s\)) rf pulses irradiate the sample with a spread of radio frequencies. Nuclei with different Larmor frequencies that fall within the spread will be rotated away from \(B_0\) and onto the xy-plane of the rotating axis system. The FID recorded is then a sum of the different Larmor frequencies from the different nuclei. Fourier transforms convert this into the frequency spectrum we typically observe.

Continued application of the rf radiation results in the populations of the spin states becoming equal and no NMR signal is observed. Under these conditions the system is saturated, and there is no net adsorption of photons. After the spins have been perturbed by applying the rf pulse, the system returns to equilibrium, Boltzman distribution, through several relaxation processes. Spin-lattice relaxation occurs when energy is transferred from the nuclear spin system to the surrounding environment or lattice. Spin-lattice relaxation is brought about by molecular motions of nearby nuclei with magnetic moments, which give rise to fluctuating magnetic fields. When the frequency of the fluctuations match the Larmor frequency of the nuclei, the nuclear spins flip, energy transfer occurs and relaxation is achieved. Spin-lattice relaxation is a kinetic process, where \(k = \frac{1}{T_1}\) and \(T_1\) is the half-life. A second relaxation mechanism that is also present is spin-spin relaxation \((T_2)\) or transverse relaxation. This type of relaxation
mechanism does not involve energy transfer, instead it describes the time it takes for the spins to lose phase coherence, or to dephase. \( T_2 \) is related to the linewidth of the observed NMR signals as shown below:

\[
\Delta \nu_{1/2} = \frac{1}{\pi T_2},
\]

(8)

where \( \Delta \nu_{1/2} \) is the peak width at half height.

A typical NMR spectrum consists of a variety of peaks positioned at various frequencies. These resonances represent nuclei that are in different chemical environments, as such, the various peak positions are known as chemical shifts. Chemical shifts are a result of induced magnetic fields brought about by the electrons surrounding the nuclei. The electrons generate a magnetic field, or local field (\( \sigma \)), when introduced to an external magnetic field, \( B_0 \). The local field generated by the electrons opposes that of \( B_0 \), the shielding effect, and contributes to the total field felt by the nucleus. The resulting field felt by the nucleus is the total or effective field (\( B_{\text{eff}} \)) and is described by

\[
B_{\text{eff}} = B_0(1-\sigma).
\]

(9)

When the local field is small, the nuclei are shielded and the chemical shift occurs at lower frequency and when the field is large, the nuclei are de-shielded and the chemical shift occurs at higher frequency.
2.2 Solid-State Internuclear Interactions

The previous section focused on systems that are undergoing rapid isotropic tumbling, such as solutes in solution. Under these conditions, anisotropic parameters such as dipolar coupling and chemical shift anisotropy are greatly reduced in magnitude, approaching zero or yielding their isotropic values. However, in the case when rapid motion of the molecules is restricted, as is the case for solid samples, the anisotropic nature of these parameters is evident. The following is a discussion of the application of NMR to solid materials.

Chemical Shift Anisotropy (CSA)

As described above, chemical shift occurs as a result of the local magnetic fields generated by electrons surrounding the nucleus. In the case when the electron density surrounding the nucleus is not spherical, the effective field felt by the nucleus is dependent upon the orientations of the molecule with respect to the magnetic field. For example, when a nucleus has a spherical distribution of electrons, as is the case for a hydrogen atom, the local field from chemical shielding (σ) in equation 9, is orientation independent. However, with an ensemble of nuclei, the electron density around the nucleus is no longer spherical due to the formation of bonds and the local field is orientation dependent. The shielding (σ) is then a tensor quantity with a principal axis system related to the structure of the molecule.

The chemical shielding tensor contains both magnitude and direction and is expressed as

\[ \sigma = (\lambda_1^2\sigma_{11} + \lambda_2^2\sigma_{22} + \lambda_3^2\sigma_{33}) \]  \hspace{1cm} (10)
where $\sigma_{ii}$ are the three principle components and $\lambda_{ii}$ are the directional cosines of the CSA principle axes relative to the external magnetic field, $B_0$. If the nucleus is located at a site of axial symmetry, then $\sigma_{11} = \sigma_{22} \neq \sigma_{33}$ and if the nucleus is at a site with rhombic symmetry, then $\sigma_{11} \neq \sigma_{22} \neq \sigma_{33}$. The angular dependence of the shielding tensor results in nuclei with different spatial orientations, relative to $B_0$ having different chemical shifts.

For powder samples, where all orientations are possible, powder pattern line shapes are observed in the NMR spectrum, Figure 2.4.

![Figure 2.4. Powder lineshapes describing the position of the shielding tensor ($\sigma$) based upon the site of symmetry.](image)

In the solution-state, molecules undergo rapid isotropic tumbling and the effect of the motion averages the CSA tensor to its isotropic value, equation 11,

$$\sigma_{\text{iso}} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33})$$

leading to the observation of a resonance positioned at the isotropic chemical shift.
**Magic-Angle Spinning (MAS)**

The presence of the powder patterns (Figure 2.4) significantly reduces spectral resolution, as in many cases, the width of the lineshapes is large on the chemical shift scale. In order to reduce the linewidth the technique of magic-angle sample spinning (MAS) is commonly used. The magic-angle spinning method involves aligning the sample at an angle of 54.74° ($\theta_m$) with respect to the applied magnetic field ($B_o$) and spinning the sample. This angle is referred to as the magic-angle and just so happens to be half of the tetrahedral angle (109.5°), the angle of the body diagonal of a cube and the angle at which glaciers cut through mountains. Figure 2.5, shows a representation of a sample positioned at the magic-angle with respect to the external magnetic field, $B_o$.

![Diagram of rotor spinning at a set frequency along the magic-angle.](image)

**Figure 2.5.** Rotor spinning at a set frequency along the magic-angle.
Under magic-angle spinning conditions, the directional cosines ($\lambda_{ii}$) become time-dependent and as such the equation for chemical shift anisotropy becomes:

$$\sigma = \left[ \frac{1}{2} \sin^2 \beta (\sigma_{11} + \sigma_{22} + \sigma_{33}) + \frac{1}{2} (3\cos^2 \beta - 1) \right] \times \text{(functions of direction cosines)} \quad (12)$$

where $\beta$ is the angle between the rotation axis and the external magnetic field. When $\beta = 54.74^\circ$, the first term in equation 12 becomes $\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33})$, which is equivalent to $\sigma_{\text{iso}}$ and the second term becomes zero. Spinning the sample at the magic-angle is mathematically equivalent to the isotropic motion that occurs in solution. Also, under MAS conditions, the NMR spectrum consists of a peak at the isotropic chemical shift value.

Typical MAS speeds range from 5 kHz to 10 kHz at fields of 4.7 T to greater than 20 kHz at high fields (17.6 T and higher). When MAS is used, in addition to a peak at the isotropic chemical shift, peaks are present that are separated from the isotropic peak by integer multiples of the spinning speed. The relative intensity of these spinning sidebands traces the powder pattern line shape. Increasing the spinning speed increases the spacing between the peaks and reduces the number of spinning sidebands present, resulting in better resolution, less number of peaks (spinning sidebands) and larger signal intensity.

**Dipolar Coupling**

An NMR nucleus (S) feels the presence of neighboring NMR active nuclei (I) through the interaction of their magnetic moments. This through space interaction of the two magnetic moments is termed dipolar coupling. The field at a nucleus, S, is then the sum of the applied field ($B_0$) and the local dipolar coupling field, $B_D$. The magnitude of
the dipolar coupling is governed by the distance \((r)\) between the nuclei and the angle between \(B_0\) and the internuclear vector connecting the two nuclei \((\theta)\), Figure 2.6.

![Figure 2.6. Dipolar coupling between a heteronuclear spin pair, S and I.](image)

The strength of the dipolar coupling \((D)\) is defined in equation 13,

\[
D = -\frac{\mu_0 \gamma_I \gamma_S}{4\pi} \frac{h}{r^3} (3\cos^2\theta - 1) \tag{13}
\]

where \(\frac{\mu_0 \gamma_I \gamma_S}{4\pi} \frac{h}{r^3}\) is the dipolar coupling constant and \((3\cos^2\theta - 1)\) describes the angular dependency of the interaction. It can be seen that the larger the distance between the two nuclei, the weaker the dipolar coupling and the closer the nuclei are to each other the stronger the dipolar coupling.

**Dipolar Decoupling**

Heteronuclear dipolar coupling between nuclei of interest and nearby hydrogens \((^1H-X)\) can produce extremely broad NMR linewidths. For instance, in the case of C-H group, the dipolar coupling between \(^1H\) and \(^{13}C\) is 20 kHz, leading to linewidths on the order of 100 ppm at a field strength of 4.7 T. Since typical \(^{13}C\) NMR spectra cover a 200 ppm
ppm window, this line broadening renders the NMR spectrum useless and uninformative. There are, however, techniques to minimize these dipolar interactions. The most common method of removing $^1$H-X dipolar coupling is continuous wave (CW) decoupling, in which continuous, high power radio frequency is applied at the proton Larmor frequency throughout the NMR experiment. The application of continuous rf radiation to the protons, causes transitions between the $m = +\frac{1}{2}$ to $m = -\frac{1}{2}$ states to occur so rapidly that the strength of the dipolar interaction between the nuclei is averaged to approximately zero, resulting in significant narrowing of the peak width. Typical $^{13}$C linewidths under CW proton decoupling are a few ppm or less. Maximum proton decoupling is achieved by using high rf power, with regards to the limitations of the amplifier and probe. Other forms of decoupling have been developed and involve the application of a series of short, 90° rf pulses as is the case in MREV-8, WAHUHA, BR-24 and TPPM (Two Pulse Phase Modulation). The incorporation of MAS and decoupling schemes greatly enhances the resolution of the resonance lines, thus creating solution-like spectra and extending the use of solid-state NMR to a variety of applications.

Quadrupole Coupling

Unlike spin-1/2 nuclei, quadrupolar nuclei (spin greater than 1/2) are non-spherical as a result of the asymmetric charge distribution within the nucleus. A representation of the charge distribution within a quadrupolar nucleus, compared to a spin-1/2 nucleus is shown in Figure 2.7.
The amount that the nucleus deviates from spherical symmetry is measured by the electric quadrupole moment ($eQ$) of the nucleus. In addition to interactions of the nuclear magnetic moment with $B_0$ (Zeeman interactions) and local magnetic fields, the electric quadrupole moment interacts with electric field gradients ($eq$) present at the nucleus (shown as positive and negative signs surrounding the quadrupolar nucleus in Figure 2.7), as well. The magnitude of the interaction between the quadrupole moment of the nucleus and the electric field gradients is described by the quadrupole coupling constant, $C_Q = \frac{e^2qQ}{\hbar}$; the electric quadrupole moment is $eQ$ and $eq$ is the anisotropy of the electric field gradient tensor. The energy of the different spin states resulting from the interaction between the quadrupole moment of the nucleus and the electric field gradients are

$$E_m = \left( \frac{e^2qQ}{4I(2I-1)} \right) [3m^2 - I(I+1)\left(\frac{1}{2}(3\cos^2\vartheta - 1) + \frac{1}{2}\eta\sin^2\vartheta\cos2\varphi\right)],$$

with the quadrupolar interaction having an angular dependency, similar to that of chemical shift anisotropy. The effect of quadrupolar interactions on the Zeeman energy level splitting is shown in Figure 2.8.
It is important to note that quadrupolar interactions consist of contributions from both first and second order interactions. The first order quadrupolar interactions do not affect the central transition \( (m = + \frac{1}{2} \leftrightarrow -\frac{1}{2}) \), however, second order interactions affect all transitions, Figure 2.8. Large shifts in the energy levels with molecular orientation, especially for \( I = \pm \frac{3}{2} \) and \( I = \pm \frac{5}{2} \) states, results in very broad lines from these transitions. Because the central transition is unaffected by first order quadrupole coupling effects, it has a weak dependence on the molecular orientation. As a result, the central transitions are typically narrow and are routinely the focus of studies of quadrupolar nuclei.
As with chemical shift anisotropy and dipolar coupling, fast magic-angle spinning greatly reduces the first order quadrupole interactions, leading to substantial line narrowing of the peaks. Second order interactions, however, are not significantly reduced by MAS and as such, removal of these interactions requires other measures. The second order effect is inversely related to the magnetic field strength ($B_0$), thus collecting the NMR spectra of quadrupolar nuclei at higher field decreases line broadening from quadrupolar coupling. Quadrupolar nuclei are typically studied using very high magnetic field strengths, 17.4 T (750 MHz) or higher.

2.3 Solid-State NMR Methods

This section describes certain NMR methods used when performing solid-state NMR experiments.

*Direct Polarization (DP)*

The technique of direct polarization (DP) allows for the detection of all nuclei of the nuclear isotope under investigation ($^{13}$C, $^{31}$P, $^{15}$N, etc.). This is accomplished by the application of a single $\frac{\pi}{2}$ pulse, which flips the net magnetization onto the xy-plane followed by acquisition of the FID. DP allows for quantitative information to be obtained. If a recycle delay equal to $5\times T_1$ is used, a fully relaxed spectrum is obtained with peak intensities proportional to the number of nuclei of a specific type present within the sample. In an effort to separate the rf pulses from data acquisition, the spin-echo technique is used. In the spin-echo technique, the $\frac{\pi}{2}$ pulse is followed by a delay
(τ) equal to a rotor period, after which a 180° (π) pulse is inserted, with another delay (τ) equal to a rotor period, following that pulse. At the end of the second delay the FID is collected. A rotor period is the time it takes for the sample to complete one full revolution, under magic-angle spinning (MAS) conditions. The pulse sequence for a direct polarization echo experiment is shown in Figure 2.9.

![Figure 2.9. Bloch decay echo pulse sequence.](image)

**Cross-polarization (CP)**

Cross polarization is a technique that increases the signal intensity for nuclei with a low γ, such as 13C and 15N. This technique transfers magnetization (polarization) from abundant spins of nuclei with large gyromagnetic ratios (I) to dilute spins with smaller gyromagnetic ratios (S). The increase in signal to noise is proportional to the ratio of the gyromagnetic ratios of the spins (γ_I/γ_S). The CP process is most commonly used to transfer polarization from proton (1H) to carbon (13C) nuclei that are in contact through their dipolar coupling. 1H nuclei have a large gyromagnetic ratio, therefore they have a large energy difference (ΔE) between the m_z = ±1/2 spin states; 13C nuclei have a small γ and a smaller energy difference, in comparison to 1H. Polarization transfer occurs through an energy conserving, mutual spin-flip process. In this process, the 1H and 13C net magnetization vectors are rotated onto the xy-plane and the B1 field is applied along
the direction of the magnetization. The strength of the $B_1$ field for the $^1\text{H}$ and $^{13}\text{C}$ nuclei are adjusted, such that the magnetization precesses around $B_1$ at the same frequency. In other words, the energy difference ($\Delta E$) of both spin-states must be equal, as expressed in equation 16, and this is termed the Hartmann-Hahn match condition.

$$\gamma_C B_1(C) = \gamma_H B_1(H) \rightarrow \omega_{1(H)} = \omega_{1(C)}.$$  \hspace{1cm} (16)

Mutual $^1\text{H}$ and $^{13}\text{C}$ spin flips occur, resulting in the two polarizations becoming equal. The polarization transfer occurs with a rate constant $T_{1S}$ which is dependent on the strength of the dipolar coupling. When nuclei are closer and the dipolar coupling is stronger, the polarization transfer occurs at a higher rate. The cross-polarization pulse sequence is shown in Figure 2.10.

During this sequence, a $\frac{\pi}{2}$ pulse is applied to the protons, flipping the proton magnetization onto the x,y axis. Rf radiation is applied to the protons and carbons, under the Hartmann-Hahn condition until the polarizations become equal. The maximum
increase in signal intensity is 4, as $\frac{\gamma_H}{\gamma_C} = 4$. CP can also be performed as an echo experiment and is most often performed in conjunction with MAS.

**Cross-Polarization to Quadrupolar Nuclei**

Cross polarization from spin-1/2 nuclei to quadrupolar nuclei ($I > 1/2$) occurs in the same manner as CP between two spin-1/2 nuclei, except that the Hartmann-Hahn match condition must satisfy the relationship:

$$\omega_{1(I)} = (S + \frac{1}{2}) \omega_{1(S)}$$

when $\omega_{1(S)} \ll \omega_Q$  

where $\omega_Q$ is the quadrupolar coupling and $S$ is the spin quantum number of the quadrupolar nucleus. If $\omega_{1(S)} \gg \omega_Q$, then the Hartmann-Hahn match condition is the same as for spin-1/2 systems (equation 16). Unlike spin-1/2 systems, MAS has a large effect on the Hartmann-Hahn match condition, where the sample must be spun at very slow or fast spinning speeds. If spun at an intermediate speed then the nuclei behave as if their magnetization does not remain aligned along $B_1$. At very slow spinning rates, the spins are adiabatic (moving slow enough that the system remains in thermal equilibrium) and at very rapid rates the quadrupolar interaction (like dipolar coupling) is averaged to zero and is essentially time independent and thus the magnetization of the nuclei remain aligned along $B_1$.

**Heteronuclear Correlation Spectroscopy**

Atomic connectivities between dipolar coupled nuclei can be obtained by the use of two-dimensional (2-D) heteronuclear correlation (HETCOR) techniques. A 2-D NMR experiment consists of four time periods: preparation period, evolution period, mixing period and a detection period. In the 2-D HETCOR experiment (using $^1H-^{13}C$
correlations as an example), the preparation period consists of the application of a rf pulse which rotates the $^1$H magnetization such that it is aligned along a specific direction in the xy-plane.

During the evolution period multiple pulses are applied to suppress $^1$H-$^1$H homonuclear dipolar couplings, and the $^1$H nuclei precess according to their individual chemical shifts. Typical multiple pulse sequences are MREV-8\textsuperscript{118,119,120,121,122} or BLEW-12,\textsuperscript{126,127,128} which use a series of 90° pulses that cause the protons to precess about an effective field that is tilted at either 45° (MREV-8) or 63° (BLEW-12) from the Z-axis ($B_o$). It is therefore necessary to incorporate a composite pulse at the end of the evolution period to return the magnetization to the xy-plane. During the evolution period, the $^1$H-$^{13}$C heteronuclear dipolar interactions are suppressed by the use of the BB-12 sequence. Simultaneous use of Blew-12 and BB-12 allows for protons and carbons to evolve solely under their individual chemical shifts.

During the mixing period dipolar coupling between the $^1$H and $^{13}$C is reintroduced and polarization transfer from protons to carbons occurs. In order to achieve selective polarization transfer, several techniques, including windowless isotropic mixing (WIM-24) can be employed. The use of WIM-24 suppresses $^1$H-$^1$H homonuclear dipolar interactions during cross polarization, so that only the interactions between $^{13}$C and spatially close $^1$H are observed.

The carbon magnetization is detected during the final period of the sequence and the resulting spectrum shows carbon chemical shifts in one-dimension and proton chemical shifts in the second-dimension, with cross-peaks (correlations) occurring between dipolar coupled nuclei. As the dipolar coupling is dependent on the internuclear
distance (r), cross peaks indicate nuclei that are near each other. Figure 2.11 shows the pulse sequence for a heteronuclear correlation experiment.

![Diagram of pulse sequence](image)

Figure 2.11. Heteronuclear correlation experiment incorporating BLEW-12 and BB-12 dipolar decoupling schemes.

The HETCOR experiment described above is most efficient when performed at low field strengths and with slow MAS. Many systems, such as polymers, proteins and other bio-materials require greater resolution in the proton dimension and as such developments geared towards improving proton resolution have been undertaken. One such method uses a frequency-switched Lee-Goldberg (FSLG) sequence that is applied to the protons during the evolution period and works effectively at high fields in conjunction with fast MAS. During the frequency-switched Lee-Goldberg (FSLG) homonuclear decoupling scheme, the net magnetization of the protons is rotated onto an axis that is inclined at the magic-angle. This is achieved by the application of off-resonance rf irradiation. Precession of the magnetization at the magic-angle removes $^1$H-
$^1$H homonuclear dipolar interactions and the protons precess according to their individual chemical shifts. The Lee-Goldburg condition is shown in Figure 2.12.

![Figure 2.12. Schematic of the Lee-Goldburg Condition.](image)

Incorporation of a selective cross polarization scheme that takes advantage of the Lee-Goldburg condition, allows for polarization transfer only between closely associated protons and carbons and is termed Lee-Goldburg cross polarization (LG-CP).

Generally, overlap of the strongly coupled one-bond $^1$H-$^{13}$C correlations dominate the HETCOR spectrum and can mask information from longer range dipolar couplings. Introducing a REDOR (rotational-echo double resonance) front end and selective cross polarization (LG-CP), in addition to Lee-Goldburg homonuclear decoupling, greatly suppresses cross peaks from one-bond dipolar couplings, leaving the cross-peaks arising from medium to long distance couplings for observation. Such a sequence is referred to as MELODI-HETCOR$^{131}$ and suppression of one-bond $^1$H-$^{13}$C couplings is achieved by incorporating 180° pulses on the carbon channel preventing the refocusing of $^{13}$C-$^1$H dipolar interactions, this sequence is shown in Figure 2.13.
Figure 2.13. MELODI-HETCOR pulse sequence.
CHAPTER III

EXPERIMENTAL

3.1 Alumina Nanofiber Synthesis and Electrospinning Conditions

Alumina nanofibers were electrospun from a solution containing a mixture of aluminum acetate stabilized with boric acid, 10% in ethanol and water. The aluminum acetate, polyvinylpyrrolidone (PVP) and absolute ethanol were purchased by STREM chemicals, Sigma-Aldrich and Pharmco Products, respectively and used as received. An aluminum acetate mixture was made by adding 5 grams of aluminum acetate into an ethanol/water solution containing 13 mL of ethanol and 10 mL of water. The mixture was stirred and kept overnight to allow for complete dissolution of the aluminum acetate. The PVP solution was made with by adding 1 gram of PVP to 10 mL of ethanol. The mixture was stirred until the polymer was completely dissolved. The aluminum acetate and PVP solutions were combined and this solution was used for electrospinning.

The electrospinning apparatus contained a power supply, collecting plate and sample holder. A portion of the aluminum acetate/PVP mixture, approximately 1 mL
was placed in a pipette that was positioned such that the tip of the pipette was angled downward towards the collecting plate. A copper wire, connected to the power supply was placed into the solution, and the power supply was set to a potential in the range of 25 to 30 kV. The collecting plate, held at ground potential was wrapped in aluminum foil.

3.2 Alumina Nanofiber Formation and Annealing Conditions

Two ovens were used to anneal the nanofibers, an ashing furnace and a box furnace. The ovens were pre-heated to 250 °C before the actual annealing process began. The as-spun fibers were placed into the oven and heated to temperatures of 525 °C, 800 °C, 1000 °C, or 1200 °C for 2 hours. After the 2 hours, the oven was shut off and allowed to cool until the temperature of the oven reached approximately 100 °C.

For the water vapor experiments, drops of water from the end of a pipette ranging from 2 to 30 drops were collected in a small ceramic evaporating dish and set in the box furnace. As-spun fibers were then heated to 1200 °C for two hours, for each set of water droplets.

Richard Tuttle and Ayesha Chowdry, Master students in the Physics Department, under the advisement of Dr. Rex Ramsier, produced the electrospun nanofibers and calcinated the as-spun nanofibers.
3.3 Phosphorus Deposition

Methyl phosphate (MePO$_4$) deposition was accomplished by carefully spreading out 100 mg of the annealed alumina nanofibers, allowing for maximum phosphate coverage. Methyl phosphate, purchased from TCI America (containing a mixture of mono and dimethyl phosphates) was added drop wise (4 ml) until the nanofibers were covered with methyl phosphate. The samples sat for 1 hour, covered with a watch glass to avoid outside contamination. The material was then washed with 500 mL of methanol, using a Buchner funnel (43 mm diameter plate). The washed material was subsequently collected and dried in a vacuum oven at 75 °C for 30 minutes.

Dimethyl methyl phosphonate (DMMP) was purchased from STREM chemicals and used as received. Deposition was carried out by placing a 100 mg alumina nanofiber sample into a 50 mL round bottom flask. The flask was purged with N$_2$ for ~1 minute and 2.5 mL of DMMP was added to the nanofibers creating a slurry. The flask was again purged with N$_2$ and swirled for ~2 minutes. The mixture sat for 1.5 hrs, during which it was occasionally swirled. 25 mL of methylene chloride (CH$_2$Cl$_2$) was added to the flask, purged with N$_2$ and swirled. After 30 minutes, the mixture was washed and filtered with ~250 mL of CH$_2$Cl$_2$ using a Buchner funnel. The filtrate was collected in a 250 mL filter flask containing 100 mL of a 40% (w/v) NaOH solution. The washed material was then collected and allowed to air dry for approximately 15 minutes. The treated alumina nanofiber samples were stored in scintillation vials for 2-3 months, after which additional data was collected.
3.4 Characterization Methods

The characterization methods used to study the alumina nanofibers are described in this section.

*Scanning Electron Microscopy (SEM)*

SEM was performed using a JOEL JEM-5310 instrument that operated at 25 kV and 60 mA. A sample of the nanofibers was placed on double-sided conducting carbon tape, which was then attached to a sample holder. The sample was then coated with a thin layer of Pd alloy by sputtering to reduce charging effects. The SEM images were collected by Richard Tuttle.

*X-ray Diffraction (XRD)*

The XRD spectra were collected on a Philips PQ1719 instrument, operating at 40 kV and 35 mA. The samples were ground to form a powder, mounted on a glass slide and treated with acetone. The XRD diffraction patterns were collected by Richard Tuttle.

*Solid-State Nuclear Magnetic Resonance (SSNMR)*

$^1$H- $^{13}$C/$^{31}$P cross-polarization (CP) magic-angle spinning (MAS) and $^{31}$P direct polarization (DP) experiments were performed on a Varian Unity$^{+}$ plus 200 (4.7T) spectrometer, operating at 50.77 MHz for $^{13}$C and 81.73 MHz for $^{31}$P. A Doty Scientific VT CP-MAS wide bore probe was utilized. The samples were packed into 7 mm silicon nitride rotors using kel-F end caps and spun at MAS rates ranging from 5 kHz ($^{13}$C, $^{31}$P)-6 kHz ($^{31}$P). 1024-2048 data points were collected for both the $^{13}$C and $^{31}$P experiments and continuous wave (CW) decoupling was with a field strength of ~52 kHz employed. Typical pulse widths of 5 µs were used for $^{13}$C and $^{31}$P data collection. A recycle delay of
2 seconds was used when collecting the $^{1}H-^{13}C$ CP/MAS spectra of aluminum acetate, PVP, as-spun nanofibers and annealed alumina nanofiber spectra and 5 seconds for $^{13}C$ CP experiments of the phosphorus treated materials. For $^{31}P$ DP and CP experiments, 30 and 10 second recycle delays were used, respectively. Cross-polarization times were 1 ms and 3 ms for $^{13}C$ and $^{31}P$ CP experiments, respectively. Typically, line broadening of 20 Hz was used before Fourier transformation and up to the first three points in the FID was calculated via linear prediction.

$^{27}Al$ experiments, both DP and CP MAS experiments, at 195.35 MHz were performed on a 17.6 T Varian INOVA spectrometer. A Doty Scientific DSI-971 HXY probe was utilized and samples were spun at 13 kHz. The samples were packed in 4 mm silicon nitride rotors using aurum end caps. Typical pulse widths of 1-2 µs and 5 µs were used for $^{27}Al$ DP and CP experiments, respectively and 8192 data points were collected. Recycle delays of 1-2 seconds were used to collect $^{27}Al$ DP spectra. For the $^{1}H-^{27}Al$ CP/MAS experiments, optimized conditions were established as outlined by Pines et al. Cross-polarization times of 100-150 µs were employed, along with a 1 second relaxation delay. Either back linear prediction (correcting the first 55 points in the FID) or left shifting the FID by 2-4 points was used. Only the central transitions ($I^{\pm1/2}$) were characterized.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Electrospun Nanofibers

The production of nanofibers via electrospinning processes is a straightforward method for producing fibers with sub-micron diameters from a wide range of polymers.\textsuperscript{103-109} This work has been extended by combining electrospinning of polymers with metal-oxide precursors and thermal treatment to produce a variety of metal-oxide nanofibers.\textsuperscript{110-114} Most recently we have reported the production of alumina fibers with average diameters of \textasciitilde500 nm and aspect ratios exceeding $10^3$. These alumina fibers also have the advantage of macroscopic handling capabilities.\textsuperscript{133} The synthetic approach to these fibers has the potential of providing alumina fibers with interesting and enhanced catalytic and adsorbent properties, when compared to other alumina structures. Alumina and other metal-oxide nanofibers have been characterized previously, using microscopy and X-ray diffraction techniques, predominantly.\textsuperscript{110-114} These studies, however, only included fiber characterization after calcination, to generate the metal oxide. We have extended these studies to fibers prior to calcination, as well as undertaking a molecular

49
level characterization of the fibers after calcination. The as-spun nanofibers consist of
aluminum acetate and polyvinylpyrrolidone (PVP) and their formula and structures are
shown in Figure 4.1.

![Figure 4.1. Formula of aluminum acetate and structure of polyvinylpyrrolidone.](image)

Aluminum Acetate

\[ \text{Al(OH)}_2(\text{CH}_3\text{COO}) \]

Polyvinylpyrrolidone

(PVP)

A scanning electron micrograph (SEM) image of the as-spun nanofibers is shown in
Figure 4.2, where the high aspect ratios and narrow diameters (500 nm on average) of the
nanofibers are clearly observed.
Characterization of the electrospun nanofibers by solid-state NMR (SSNMR) indicates that beyond fiber formation, no additional chemistry occurs during the electrospinning process. The $^{13}$C cross-polarization (CP) SSNMR spectra in Figure 4.3 are from the starting materials, PVP and aluminum acetate, and the as-spun nanofibers.
It is observed that the spectrum of the as-spun nanofibers is simply a sum of the acetate groups and polyvinylpyrrolidone, clearly showing that no reactivity of these species has occurred during electrospinning. The fact that electrospinning does not cause chemical changes to the materials is further confirmed in the $^{27}$Al direct polarization (DP) NMR spectra, Figure 4.4, as the $^{27}$Al NMR spectra from the as-spun nanofibers (4.4 B) and aluminum acetate (4.4 A) are nearly identical.
Figure 4.4. $^{27}\text{Al}$ DP/MAS NMR spectra of (A) aluminum acetate and (B) as-spun nanofibers. Only the central ($\pm \frac{1}{2}$) transitions are shown and the samples were spun at 13 kHz.

4.2. Nanofibers Calcined at 1200 °C

The as-spun fibers are calcined at elevated temperatures to remove the organic starting materials, the acetate group in aluminum acetate and PVP, as well as to produce alumina. The removal of PVP with increasing calcination temperatures is evident from the $^{13}\text{C}$ NMR spectra in Figure 4.5.
Figure 4.5. $^{13}$C CP/MAS NMR spectra of (A) as-spun nanofibers and alumina nanofibers calcined at (B) 525°C, (C) 800°C, (D) 1200°C, (E) empty rotor (background signal).

At a temperature of 525 °C (Figure 4.5 B), the majority of the polymer has been pyrolyzed and removed, evident by the absence of the peaks in the aliphatic region spanning from 10-50 ppm. Monitoring the residual carbonyl peak, positioned at 164.7 ppm shows that as the temperature is increased the fraction of the polymer in the nanofibers continues to decrease, and by 1200 °C no polymer is detected. The broad peaks spanning from 0-100 ppm are from instrumental background signals, confirmed by the top spectrum which is a spectrum from the empty sample rotor. The observation that chemical changes have occurred to the polymer during the calcination process is indicated by the change in the chemical shift of the carbonyl carbon, from 178.0 ppm to 164.7 ppm, in the spectrum of the nanofibers after calcination at 525 °C.
The conversion of aluminum acetate present in the fibers into \( \alpha \)-alumina, upon calcination at 1200 °C, was confirmed by X-ray diffraction (XRD) studies of the nanofibers, Figure 4.6.

![XRD data](image)

Figure 4.6. XRD data of (A) as-spun nanofibers and (B) calcined alumina nanofibers at 1200 °C (collected by Ricky Tuttle).

The sharp, narrow Bragg peaks in the XRD data from the nanofibers indicate the formation of a crystalline material and the 20 positions of the peaks are very similar to those reported previously for \( \alpha \)-alumina. The conversion into \( \alpha \)-\( \text{Al}_2\text{O}_3 \) is further supported by the similarities between the \( ^{27} \text{Al} \) NMR spectra of the nanofibers calcined at 1200 °C and commercially available \( \alpha \)-alumina powder, shown in Figure 4.7 A and B, respectively.
Figure 4.7. $^{27}$Al DP/MAS NMR spectra of (A) nanofiber calcined at 1200 °C and (B) commercially available α-alumina. Only the central (±½) transitions are shown and the samples were spun at 13 kHz. The spinning sidebands are labeled with an asterisk.

For both materials, the NMR spectra contain a main peak centered at 15.0 ppm, which is consistent with 6-coordinate alumina sites and a weak peak at 67.4 ppm, from a small population of 4-coordinate sites.

Upon calcination of the nanofibers at 1200 °C and subsequently forming α-alumina nanofibers, the large aspect ratios are reduced, as observed in the SEM image of the alumina nanofibers, Figure 4.8.
While the average diameter of the nanofibers does not appear to be largely affected by calcination, the fibers become very brittle. The reduction in flexibility of the fibers is likely a result of a high degree of crystallinity.

4.3 Transition Aluminas

It has been well established that thermally treating aluminum oxide materials produces a variety of transition aluminas before reaching the thermodynamically stable, \( \alpha \)-alumina phase.\(^{1,2,35,37}\) These transition aluminas are formed by dehydration and dehydroxylation mechanisms, where dehydration is the process of water removal and dehydroxylation involves the condensation of hydroxyl groups.\(^{36}\) The types of transition aluminas created are dependent upon the alumina precursor, particle size, impurities,
gases present and temperature at which calcination takes place.\textsuperscript{23} For instance, if the alumina precursor is boehmite, $\gamma$-$\text{Al}_2\text{O}_3$ and $\delta$-$\text{Al}_2\text{O}_3$ are formed at temperatures between 300- 450 °C and 600-850 °C, respectively; whereas if bayerite is the alumina precursor, $\eta$-$\text{Al}_2\text{O}_3$ and $\theta$-$\text{Al}_2\text{O}_3$ are formed at 230 °C and 850 °C, respectively.\textsuperscript{1,23,134} It also has been shown that the transformation mechanism of basic aluminum acetate proceeds in the following manner: amorphous alumina at 700 °C, $\gamma$-$\text{Al}_2\text{O}_3$ at 800 °C, a mixture of $\gamma$- and $\delta$-$\text{Al}_2\text{O}_3$ at 1000 °C, $\delta$-$\text{Al}_2\text{O}_3$ at 1050 °C, a mixture of $\delta$-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$ at 1100 °C and finally, $\alpha$-$\text{Al}_2\text{O}_3$ at 1200 °C.\textsuperscript{135,136}

The as-spun nanofibers were calcined at various temperatures and characterized to determine which transition alumina states they pass through prior to forming $\alpha$-alumina. As the starting materials consists of aluminum acetate stabilized with boric acid and polyvinylpyrrolidone (PVP), and not the usual aluminum oxides or hydroxides of boehmite and bayerite,\textsuperscript{1,134,137,138} the transition aluminas formed may be different from alumina materials produced by using traditional methods. The complimentary techniques of solid-state NMR and XRD are used in these studies. The use of both XRD and NMR provides information about both the crystalline transition phases (XRD and NMR) and the non-crystalline transition phases (NMR) produced during thermal treatment. In some cases, the studies of alumina materials by solid-state NMR have suffered from substantial peak overlap and poor spectral resolution.\textsuperscript{23,71,134,139} This is the result of collecting the $^{27}$Al NMR data at low and mid magnetic field strengths. The low resolution prohibits the direct assignment of different chemical shifts and distribution of alumina coordination numbers with specific transition alumina phases. However, complimentary results from
$^{27}$Al NMR, collected at high fields (9.4 T) correlated with XRD results have made distinct assignments of the various transition alumina phases possible.$^{134,139}$ The $^{27}$Al direct polarization magic-angle spinning (DP/MAS) NMR spectra from the alumina nanofiber samples calcined at 525 °C, 800 °C, 1000 °C and 1200 °C are shown in Figure 4.9.

![Figure 4.9](image)

Figure 4.9. $^{27}$Al DP/MAS NMR spectra of the calcined alumina nanofibers in the open oven. (A) 525 C, (B) 800 C, (C) 1000 C, (D) 1200 C, (E) $\alpha$-alumina powder. Only the central ($\pm \frac{1}{2}$) transitions are shown and the samples were spun at 13 kHz. The spinning sidebands are labeled with an asterisk.

Alumina sites differing in coordination numbers are readily observed from the $^{27}$Al NMR data. The peaks in the region spanning from -20 to 11 ppm, 30-35 ppm and 55-70 ppm represent 6- (octahedral), 5- (pentahedral) and 4-(tetrahedral) coordinate aluminum.
species, respectively. As the calcination temperature is increased, rearrangement of the types of aluminum coordination sites occur, shown by the reduction in the intensity of the peaks from 4- and 5-coordinate aluminum sites, as well as a narrowing and a shift towards lower field of the peak from 6-coordinate aluminum.

The $^{27}$Al NMR spectrum from nanofibers heated at 525 °C (Figure 4.9 A) contains three resonances at 69.9, 36.8 and 6.8 ppm, arising from 4, 5 and 6 coordinate aluminum sites, respectively. The fraction of 4- and 5-coordinate aluminum sites in these nanofibers is far greater than what has been observed for traditional aluminas calcined at this temperature, where the $\gamma$-alumina phase is typically produced. The largest difference is the fact that the nanofibers have a much larger fraction of 5-coordinate aluminum sites. While the presence of a large fraction of penta-coordinated sites in alumina materials is atypical, it has been reported to exist in a few minerals, such as andalusite, grandidierite, yoderite, augelite, and senegalite, as well as in synthesized AlPO$_4$ materials. It also has been observed that the grinding of gibbsite and boehmite produces 5-coordinate aluminum sites, which are not present in the unground minerals. In a second study on the structure and surface properties of ground and calcined gibbsite and boehmite aluminum minerals, it was found that ground boehmite contained a larger fraction of 5-coordinate aluminum species, compared to ground gibbsite, both before and after calcination processes. It has been proposed that the particle size of the material before calcination is an important factor in controlling the population of 5-coordinate aluminum species. The 5-coordinate aluminum species are proposed to reside on the surface of the boehmite particle, attributing to its catalytic activity. Since the nanofiber diameter does not change
significantly during calcination, alumina particles generated have sizes less than 500 nm. The alumina particles present are then as small, or smaller, than the ground materials previously studied.\(^{23,38,49,50}\) Based upon the similarities in the \(^{27}\)Al direct polarization spectra of Figure 4.9 A and those reported in the literature,\(^{23,38,49,50}\) we propose that the alumina in the nanofibers calcined at 525 °C have a structure very similar to that observed when ground boehmite is calcined at 400 °C, suggesting the aluminum acetate is initially converted into boehmite with thermal treatment. The intensities of the 4- and 5-coordinate aluminum species present in the electrospun, calcined nanofibers are slightly higher than those reported by Chen \textit{et al.}\(^ {38}\) for boehmite and this is attributed to the facts that the calcined nanofibers are amorphous and that at 525 °C the nanofibers still contain residual PVP which may cause structural differences within the alumina framework.

Calcination at 800 °C followed by characterization by XRD, shows that the alumina nanofibers contain a mixture of \(\gamma\)- and \(\theta\)-aluminas, Figure 4.10.
The formation of γ- and θ-aluminas is consistent with ground boehmite calcined at temperatures ranging from 800 °C to 1000 °C. In contrast, when aluminum acetate is calcined at 800 °C, only the γ-alumina phase is observed. Comparison with the NMR data from Pecharromán et al., the nanofibers calcined at 1000 °C, Figure 4.9 C likely contain γ- and θ-alumina phases and possibly a small amount of α-alumina (as α-alumina has been reported to exist at this temperature in other aluminous materials) but at different ratios than in the nanofibers calcined at 800 °C. This is again consistent with the calcination of the aluminum acetate in the nanofibers resulting in the formation of boehmite, as the transition aluminas produced during calcination are as follows: γ-Al₂O₃ to δ-Al₂O₃ to θ-Al₂O₃ to α-Al₂O₃.\textsuperscript{35,37}
4.4 The “Dry” Bake Method

The presence of water vapor during the calcination process has a profound effect on the transition aluminas produced. In one study, the grain size of the starting alumina precursor (gibbsite) had an impact on the vapor pressure of water inside the crystals, during the early stages of dehydration. It was discovered that large gibbsite particles caused a build up of vapor pressure, due to the fact that water molecules could not escape from the crystal lattice but with small gibbsite particles there was very little vapor pressure build up, as the water molecules were able to escape readily from the lattice. High vapor pressure was also found to alter the dehydration sequence, introducing a boehmite phase in the early stages of the calcination sequence. Another study showed that the presence of water vapor during dehydration played an important role in the formation of α-alumina, as well as the transition aluminas produced. The impact of water vapor on the transition alumina formation upon calcination of the as-spun nanofibers was investigated. The results in the previous section were from nanofibers calcined in an oven open to the atmosphere, referred to as the “wet” bake method. Fibers also have been calcined in a closed oven, minimizing the amount of water vapor present. This method is referred to as the “dry” bake method and the characterization of these fibers are discussed in the following section.

The $^{27}$Al direct polarization NMR spectra of the alumina nanofibers formed by calcination in the closed oven are shown in Figure 4.11.
Figure 4.11. $^{27}$Al DP/MAS NMR spectra of the calcined alumina nanofibers in the closed oven. (A) 525 °C, (B) 800 °C, (C) 1000 °C, (D) 1200 °C, (E) α-alumina powder. Only the central (±½) transitions are shown and the samples were spun at 13 kHz. The spinning sidebands are labeled with an asterisk.

Upon comparison with the data from the wet bake method, Figure 4.9, it is clear that calcination of the nanofibers via the dry bake method alters the composition and structure of the alumina nanofibers produced, indicated by changes in the chemical shifts, peak intensities and line shapes. After calcination at 525 °C (Figure 4.11 A), the $^{27}$Al spectrum of the nanofibers contains resonances at 69.4 ppm, 39.4 ppm and 10.2 ppm, from tetrahedral, pentahedral and octahedral aluminum species, respectively. The distribution of these aluminum sites differs from those observed in the $^{27}$Al spectrum of the nanofibers formed at 525 °C via the wet bake method in that the populations of the 4- and 5-coordinate aluminum sites are smaller in the nanofibers formed via the dry bake
method. The line shapes and intensities of the 4-, 5- and 6-coordinate sites even more closely compare with the NMR data from ground boehmite calcined at 400 °C.\textsuperscript{38} The lack of Bragg peaks in the XRD data from this sample, Figure 4.12 B, reveals that the nanofibers calcined at 525 °C are non-crystalline.

![XRD data of (A) as-spun nanofibers and calcined alumina nanofibers in the closed oven at (B) 525 °C, (C) 800 °C, (D) 1000 °C, (E) 1200 °C (collected by Ricky Tuttle).]

Figure 4.12. XRD data of (A) as-spun nanofibers and calcined alumina nanofibers in the closed oven at (B) 525 °C, (C) 800 °C, (D) 1000 °C, (E) 1200 °C (collected by Ricky Tuttle).

The \textsuperscript{27}Al NMR spectrum for the alumina nanofibers calcined at 800 °C, Figure 4.11 B, contains a higher fraction of 5-coordinate aluminum sites, in comparison to the wet bake fibers. The peak on the upfield side of the tetrahedral resonance (67.8 ppm) is less pronounced and the ratios of the two 6-coordinate peaks differ, as well. The formation of a mixture of $\gamma$- and $\theta$-Al$_2$O$_3$ at 800 °C is indicated from the XRD results, Figure 4.12 C, which is similar to that observed for nanofibers formed via the wet bake
method at the same temperature. In the case of the nanofibers calcined at 1000 °C, the
$^{27}$Al NMR spectrum, Figure 4.11 C, is more dependent on the calcination conditions.
The tetrahedral aluminum resonance at 53.4 ppm is greatly reduced and larger
populations of octahedral aluminum sites are in the environment giving rise to the
downfield resonance at 12.8 ppm in the dry bake sample versus the resonance at 8.1 ppm
in the spectrum of the wet bake sample. Consistent with previous studies,$^{134}$ the
increased calcination temperature results in the formation of $\theta$- and $\alpha$-alumina phases, as
observed by XRD studies, Figure 4.12 D. Overall, as the calcination temperature
increases the changes in the $^{27}$Al NMR spectra (Figure 4.11 B-D) include reductions in
the intensities of the resonances from 4- and 5-coordinate sites occurs, along with a
narrowing and shift towards lower field of the peak from 6-coordinate aluminum sites.
These trends are similar to those observed for fibers formed under the wet bake method.
Again, the changes in the $^{27}$Al NMR data with calcination temperature correlate with the
changes observed in the NMR spectra of calcined boehmite.$^{134}$

Observed in the $^{27}$Al NMR spectrum of the nanofibers calcined at 1200 °C
(Figure 4.11 D) is a larger population of tetrahedral aluminum sites, in comparison with
the NMR spectrum for the nanofibers calcined under the wet bake conditions, as well as
the spectrum of commercially available $\alpha$-Al$_2$O$_3$ (Figure 4.11 E). The presence of a
greater population of tetrahedral aluminum species demonstrates that the nanofibers have
not been completely driven to the $\alpha$-alumina phase. This fact is confirmed by the XRD
data in Figure 4.12 E, where the presence of $\theta$-Al$_2$O$_3$ is detected along with the $\alpha$-Al$_2$O$_3$
phase.
An SEM image of the alumina nanofibers calcined at 1200 °C, under dry bake conditions is shown in Figure 4.13.

![SEM image of alumina nanofibers calcined at 1200 °C](image)

Figure 4.13. SEM images of alumina nanofibers after calcination at 1200 °C in the closed oven (micrographs collected by Ricky Tuttle).

The nanofibers shown are very similar to the as-spun fibers in that they have high aspect ratios. The bulk properties of these fibers are also different, as the fibers are flexible on the macroscopic level. The Bragg peaks in the XRD spectra of Figure 4.12 are broader than those observed in the data from the wet bake method, showing that the crystal sizes are smaller. The lower overall crystallinity and smaller crystallites might explain the enhanced flexibility of the nanofibers produced in the absence of excess water vapor. The fact that the fibers are flexible and contain high aspect ratios is promising for a variety of applications.
4.5 Surface Characterization of the Alumina Nanofibers

Functional aspects of the alumina nanofibers, such as catalytic activity, depend on the surface structure of the fibers, however, detailed investigations of the surfaces of metal-oxide nanofibers have not yet been reported. The surfaces of the alumina nanofibers created by both wet and dry bake methods have been characterized by using the NMR method of proton to aluminum cross-polarization ($^1$H-$^{27}$Al CP). With this technique, the peaks in the $^{27}$Al NMR spectrum will arise only from aluminum sites that are in close proximity to protons (~ 6 Å). The surface of the alumina nanofibers contains surface hydroxyl groups and it is at these sites where interactions and catalytic processes occur, thus the information gained will be vital in understanding the chemical reactivity of the nanofibers.

The $^1$H-$^{27}$Al CP/MAS spectra of the nanofibers calcined at 525 °C and 1200 °C via the wet bake method are shown in Figure 4.14.
Figure 4.14. $^{27}$Al DP/MAS (left side) and $^1$H-$^{27}$Al CP/MAS (right side) NMR spectra of wet bake alumina nanofibers calcined at 525 °C (top spectra) and 1200 °C (bottom spectra). Spectra were collected at a magnetic field of 4.7 T with a MA spinning speed of 6 kHz. Only the central ($\pm \frac{1}{2}$) transitions are shown.

It is quite clear from the spectra that the surface structures differ greatly from the bulk. The CP/MAS spectrum of the alumina nanofibers calcined at 525 °C contains predominately 6-coordinate aluminum species (1.7 ppm), while the spectrum from the bulk contains significant amounts of 4- and 5-coordinate aluminum, in addition to the 6-coordinate species. As the calcination temperature increases, the number of surface protons decreases, shown by the loss of signal intensity in the CP/MAS spectrum for the alumina fibers calcined at 1200 °C. This phenomenon is expected, as at high temperatures, surface hydroxyl groups condense (dehydroxylation), forming water molecules which are then removed during the calcination process, reducing the number of surface protons.$^{36,71}$
The $^1\text{H} - ^{27}\text{Al}$ CP/MAS NMR spectra from the surfaces of the calcined alumina nanofibers formed via the dry bake method are shown in Figure 4.15.

Figure 4.15. $^1\text{H} - ^{27}\text{Al}$ CP/MAS NMR spectra of dry bake alumina nanofibers. (A) 525 C, (B) 800 C, (C) 1000 C, (D) 1200 C, (E) $\alpha$-alumina powder. Only the central ($\pm \frac{1}{2}$) transitions are shown and the samples were spun at 13 kHz.

These spectra are similar to those obtained from the nanofibers calcined via the wet bake method, where at low temperatures a large population of 6-coordinate aluminum species is observed (5.15 ppm), accompanied by the presence, however in smaller quantities compared to the bulk material, of 4- and 5-coordinate aluminum sites. The main
difference between the surfaces of the nanofibers obtained by the two calcination methods is observed in the $^{27}$Al CP/MAS spectra of the nanofibers calcined at 1200 °C. The surface of the dry bake nanofibers calcined at 1200 °C (Figure 4.15 D) contain a larger amount of surface hydroxyls (two peaks at 60.1 ppm and 10.8 ppm, tetrahedral and octahedral aluminum sites, respectively) than the surface of the nanofibers formed via the wet bake method and commercially available $\alpha$-Al$_2$O$_3$ powder.

The NMR and XRD studies of the bulk composition and structure indicate that the calcination method has a significant impact on these properties. However, the surface structure of the fibers is far less affected by the water vapor level during calcination. It is important to note the chemical shift differences between the $^{27}$Al CP/MAS spectra from the fibers generated using the two calcination methods does not indicate different aluminum species, but rather is a result of second order quadrupolar effects and the magnetic field strength. The spectra from wet bake method were collected at lower field than the spectra from the dry bake method.

4.6 Water Vapor and Its Effect on the Formation of $\alpha$-Alumina

As water is known to affect the rate at which $\alpha$-alumina is formed,$^{49,50,138}$ varied amounts of water were added during the dry bake process to see if simply increasing the vapor pressure of water in the oven would impact the alumina phase generated. This study was limited to samples calcined at 1200 °C, as the $\alpha$-alumina material is the most well characterized material. The $^{27}$Al DP/MAS spectra from alumina nanofibers calcined at 1200 °C with various amounts of water are shown in Figure 4.16.
Figure 4.16. $^{27}$Al DP/MAS NMR spectra of alumina nanofibers calcined at 1200 °C with varied amounts of H$_2$O present: (A) 2 drops of H$_2$O, (B) 4 drops of H$_2$O, (C) 8 drops of H$_2$O, (D) 16 drops of H$_2$O, (E) 30 drops of H$_2$O. Only the central ($\pm \frac{1}{2}$) transitions are shown and the samples were spun at 13 kHz. The spinning sidebands are labeled with an asterisk.

In each spectrum a peak is observed at ~67 ppm from tetrahedrally coordinated alumina sites. If the material is converted completely to $\alpha$-alumina, the intensity of this peak will be significantly reduced. There are several possible reasons why the fibers are not converted to $\alpha$-alumina; one being the design of the oven and flow of oxygen through out the system during thermal treatments. The wet bake method was performed in an ashing furnace with a hole in the top allowing for a constant flow of oxygen throughout the
calcination process, while the dry bake method was performed in a box furnace containing small slits as vents, minimizing the flow of oxygen throughout the system. It may be that a constant source of oxygen, in addition to water vapor is required in order for transition into the $\alpha$-phase to occur. Another reason may be that water vapor must be present throughout the entire calcination process and not just at the beginning of heating. Water may only catalyze the cleavage of the acetate groups in the initial stages of the reaction before escaping the oven and restricting the complete formation of $\alpha$-alumina. Regardless of the reason, simply adding water to the oven did not drive the nanofibers completely to the $\alpha$-phase at 1200 °C, however, flexible nanofibers with large aspect ratios were created in the absence of water vapor and these factors are what set apart our nanofibers from previously made alumina materials and as such will be the nanofibers of focus for the duration of this chapter.

4.7 Surface Reactivity of the Alumina Nanofibers Prepared Via the “Dry” Bake Method

Adsorption of phosphorus compounds on the surface of inorganic oxides\textsuperscript{150-157} is a commonly used method to gain insight into their chemical properties and surface reactivity. The ability of the alumina nanofibers to adsorb and decompose phosph(on)ates has been investigated, as this chemistry is relevant to the area of personal protection. For example, most of the nerve agents that have been developed, as well as pesticides and some industrial toxins are organophosphorus esters. The g-agents GB (sarin), GD (soman) and GF have the structure (RO)PO(CH\textsubscript{3})(F). Defunctionalization of toxic phosphonates by halogen, ester, or sulphur bond scission renders them either much
less toxic or non-toxic. It is well-established that alumina nanoparticles\textsuperscript{34,158} adsorb and in some cases decomposes phosph(on)ates. High surface reactivity has been shown to occur on nanoscale crystalline particles as a result of the presence of many edge and defect sites.\textsuperscript{159}

Two different phosphorus species, methyl phosphate (MePO\textsubscript{4}) and the g-agent simulant dimethyl methyl phosphonate (DMMP), Figure 4.17, were deposited on the calcined alumina nanofibers discussed in the previous section.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of (A) methyl phosphate (MePO\textsubscript{4}, mixture of mono- and dimethyl phosphate) and (B) dimethyl methyl phosphonate (DMMP).}
\end{figure}

For identification purposes, the samples will be referred to in the format MePO\textsubscript{4}-X or DMMP-X, corresponding to the phosphorus compounds being studied and the temperature of fiber calcination.

\textit{Methyl Phosphate Deposition}

\textsuperscript{31}P NMR DP/MAS and CP/MAS spectra of the methyl phosphate (MePO\textsubscript{4}) treated nanofibers are shown in Figure 4.18.
Figure 4.18. $^{31}$P DP/MAS (left) and CPMAS (right) NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition.

The spread of chemical shifts and breadth of the peaks shows that the surfaces of the alumina nanofibers are heterogeneous and a variety of alumina-phosphate interactions are present. The DP/MAS spectra of MePO$_4$-1000 and MePO$_4$-1200, Figure 4.18, are dominated by a broad peak centered at -1.7 ppm and 0 ppm, respectively. These broad resonances are assigned to physisorbed methyl phosphate molecules, as the $^{31}$P chemical shifts are similar to those observed for neat methyl and di-methyl phosphate resonances at 1.5 ppm and 2.9 ppm, respectively. The broadening of the peaks relative to that observed in solution indicates that the methyl phosphate has hindered motion from interacting with the fiber surface and that there are a variety of interactions occurring between the physisorbed phosphate molecules and the alumina surfaces. The minor change in chemical shift, relative to the pure compounds, indicates that there is no chemisorption to the fibers. There is also presence of physisorbed phosphate molecules in the $^{31}$P DP spectra of the 525 °C and 800 °C, however, at much lower levels.
The absence of the peaks between 0 and -1.7 ppm in the corresponding $^1$H-$^{31}$P CP/MAS spectra confirm the assignment of these resonances to physisorbed species. The polarization transfer from protons to phosphorus nuclei is only effective when there is moderate to strong dipolar coupling interaction between the nuclei. When the molecules are undergoing large amplitude motion, the magnitude of the dipolar coupling is greatly reduced and the cross-polarization is inefficient. The physisorbed molecules are more mobile than molecules chemically bound to the surface of the nanofibers, greatly reducing the efficiency of cross-polarization and yielding the low intensity, broad resonance observed for the sample calcined at 1200 °C. Given that adsorption on the surface of various oxides occurs via hydrolysis of the phosphate species, the larger population of physisorbed species observed in the alumina nanofibers calcined at higher temperatures shows that these nanofibers have low surface reactivity toward phosphates. This is consistent with the $^1$H-$^{27}$Al CP NMR data that showed there are few surface hydroxyl sites present upon calcination at 1000-1200 °C.

The $^{31}$P NMR spectra from three nanofiber samples calcined at lower temperatures (525 °C, 800 °C and 1000 °C), Figure 4.18, also contain peaks in the region at -6.4 and -16 ppm in both the DP and CP MAS spectra. These peaks arise from phosphate species bound (chemisorbed) to the surface of the alumina nanofibers. Numerous NMR studies of phosphates interacting with inorganic oxides and silica materials have been reported. It has been illustrated that when phosphates interact with inorganic oxide surfaces through one (mono-dentate) and two (bi-dentate) P-O-Al linkages, chemical shifts ranging from -4 ppm to -8 ppm are observed in the $^{31}$P spectra, with shifts towards higher field as the number of P-O-Al linkages...
It has been recently suggested, however, that chemical shielding tensors and chemical shift anisotropy may be more sensitive to geometrical changes than isotropic chemical shifts.\textsuperscript{165,166} Mueller and co-workers\textsuperscript{167} have recently reported that the magnitude of the anisotropy of the chemical shift tensor may be a more accurate way of determining the chemical environment of phosphates. They demonstrated that while the chemical shift change between a mono- and bi-dentate bound mononucleotide complex are unresolved, there are substantial changes in the $^{31}\text{P}$ chemical shift anisotropy. Interactions of phosphates with silica materials, show similar chemical shift trends as seen when phosphates interact with aluminum oxides, where an increase in the number of P-O-Si interactions causes an upfield shift of the $^{31}\text{P}$ resonance.\textsuperscript{151,152,160,161} The fact that the $^{31}\text{P}$ chemical shift may, or may not change with the number of P-O-Al bonds, it is not possible to assign specific structures to the peaks in the reported $^{31}\text{P}$ NMR data. Based upon these findings, the peaks ranging from $\sim -5$ to $\sim -10$ ppm are attributed to both mono- and bi-dentate phosphate interactions with the surfaces of the calcined alumina nanofibers. The fact that P-O-Al bonds form between the phosphates and the alumina surface shows that these nanofibers are reactive and have potential uses in catalytic processes. Nevertheless, phosphate interactions with the surface of the alumina nanofibers appear not to catalyze the cleavage of all of the P-O-CH$_3$ bonds, as seen by the $^{13}\text{C}$ resonance at 54.1 ppm in the $^{13}\text{C}$ CP/MAS NMR spectrum from the methyl groups of the phosphate ester, Figure 4.19. The broad peaks in the top spectrum of Figure 4.19, spanning from $\sim 30$-100 ppm are again, simply background signals.
The peaks at approximately -16 ppm in the $^{31}$P NMR spectra for MePO$_4$-525, 800 and 1000 (Figure 4.18) lie in the chemical shift range of phosphate groups interacting with the alumina surface via three P-O-Al linkages (tri-dentate).$^{150,151,160,163,164}$ This reaction results in the formation of AlPO$_4$ species and the dissolution of aluminum from the nanofiber matrix.$^{163,164,168-173}$ Upon examination of the $^{27}$Al DP/MAS spectra in Figure 4.20, a narrow peak occurs at approximately -16 ppm, along with the formally assigned 4-, 5-, and 6-coordinate aluminum species. The presence of this peak is attributed to the formation of octahedral AlPO$_4$ or dissolved alumina.
Figure 4.20. $^{27}$Al DP/MAS NMR spectra of methyl phosphate deposited on the surface of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, (C) 1000 °C and (D) 1200 °C prior to deposition. Only the central ($\pm \frac{1}{2}$) transitions are shown and the samples were spun at 13 kHz. The spinning sidebands are labeled with an asterisk.

Based on the fact that the methyl group is still present in Figure 4.19, the formation of octahedral AlPO$_4$ is highly unlikely; therefore the peaks at -16 ppm in both the $^{27}$Al and $^{31}$P NMR spectra are assigned to dissolution of aluminum from the nanofiber matrix.

The DP/MAS $^{31}$P NMR spectra of methyl phosphate treated alumina nanofibers that have aged for two months are shown in Figure 4.21.
Comparison with the NMR results from the fresh samples shows that the reaction between the methyl phosphate and the nanofibers has continued. The decrease in intensity of the peaks between 0 and -1.7 ppm in the $^{31}$P spectrum reveals that a portion of the physisorbed methyl phosphate has reacted and become chemically bound to the surface of the alumina nanofibers. With longer reaction time, it appears that the preferred binding modes between the alumina surfaces and the phosphorus species are through two and three P-O-Al linkages.

**Dimethyl Methyl Phosphonate Deposition**

The $^{31}$P DP and CP MAS spectra from the phosphonate DMMP deposited on the surface of calcined (525 °C, 800 °C and 1000 °C) alumina nanofibers are shown in Figure 4.22.
Figure 4.22. $^{31}$P DPMAS (left) and CPMAS (right) NMR spectra of (A) neat DMMP and DMMP deposited on the surface of alumina nanofibers calcined (B) 525 °C, (C) 800 °C, and (D) 1000 °C prior to deposition.

Again, the NMR data are consistent with a variety of interactions between DMMP and the alumina nanofiber surfaces; a result of surface heterogeneity. The resonances observed at 33.7 ppm and 35.8 ppm represent physisorbed DMMP, as these chemical shifts correlate to that from neat DMMP, shown in the bottom spectra of Figure 4.22. As was the case for samples treated with methyl phosphate, the absence of these peaks in the $^1$H-$^{31}$P CP/MAS NMR data indicates that the physisorbed species have some mobility.

It is important to consider differences between the structures of methyl phosphate and dimethyl methyl phosphonate, Figure 4.17; three oxygens are bound to the central phosphorus atom of DMMP, where MePO$_4$ has four oxygens bound to the phosphorus. The chemical differences affect the way in which the molecules interact with the surface of alumina materials. The three resonances at 27.0 ppm, 20.2 ppm and 8.3 ppm are from chemisorbed phosphonate species, as they are still present in the $^1$H-$^{31}$P CP/MAS spectra. Studies have reported NMR chemical shifts of phosphonate species bound to oxide...
surfaces and an upfield chemical shift is observed with increasing P-O-X attachment. For instance, Gao and co-workers showed that single ester linkages (mono-dentate) cause an upfield chemical shift of 5 ppm, two ester linkages (bi-dentate) cause an upfield shift of 14 ppm and three ester linkages (tri-dentate) cause a 24 ppm upfield shift, relative to the free (neat) phosphonate molecule resonance. These results correlate very well with the data from DMMP, Figure 4.22. Therefore the peaks with chemical shifts of 27.0 ppm, 20.2 ppm and 8.3 ppm are assigned to mono-, bi- and tri-dentate bound phosphonate species, respectively.

In examining the $^1$H-$^{31}$P CP/MAS spectra (right side of Figure 4.22), preferential binding to the alumina surface is through one and two P-O-Al linkages, similar to the case with methyl phosphate treated alumina nanofibers. In the CP/MAS spectrum of DMMP-525, a portion of the mono-dentate bound phosphonate (27 ppm) has decreased in intensity, in relation to that observed in the $^{31}$P DP spectrum, Figure 4.22 (right side). This decrease in intensity is most likely a result of motion which causes inefficient proton to phosphorus polarization transfer, as previously discussed. With only one P-O-Al linkage, the phosphonate species have a greater degree of freedom and are not seen in the cross-polarization spectrum. The CP/MAS spectrum of DMMP-800, Figure 4.22, shows a greater affinity towards mono-dentate interactions with the alumina surface, in comparison with the spectra from DMMP-525 and DMMP-1000 in which bi-dentate is the favored interaction. Also, the peak from tri-dentate interactions has decreased in the $^{31}$P CP/MAS spectrum of DMMP-525, compared to its corresponding DP/MAS spectrum, suggesting that the interactions through three P-O-Al linkages are not as strong as those in DMMP-800.
Adsorption of DMMP on aluminum oxides has also been reported to form AlPO₄ as a by-product in the decomposition process, however, under adverse conditions, such as temperatures exceeding 300 °C. Reports on NMR chemical shifts of aluminophosphonates produced by reactions of chemical warfare agents with aluminum oxides show $^{31}$P chemical shifts between 14-15 ppm and $^{27}$Al chemical shifts between -12 to -18 ppm from dissolved alumina. These peaks are not seen in either the $^{31}$P spectra or the $^{27}$Al spectra from the DMMP treated alumina fibers, Figure 4.23, indicating no dissolution of the alumina surface has occurred.

Figure 4.23. $^{27}$Al DPMAS (left) and CPMAS (right) NMR spectra of alumina nanofibers calcined at (A) 525 °C, (B) 800 °C, and (C) 1000 °C followed by DMMP deposition. Only the central (±½) transitions are shown.

There is no evidence of reactivity between the cleaved methoxy group and the alumina nanofiber surface, as there are no new peaks in the $^{13}$C CP/MAS spectra of the DMMP treated materials, Figure 4.24.
The peaks present at 50.6 and 10.8 - 12.2 ppm are from P-O-CH₃ and P-CH₃ groups, respectively. The methanol produced as a result of the decomposition of DMMP is likely removed during washing of the sample after exposure to DMMP. The sharp peak at 163.5 ppm is a result of residual PVP. At higher calcination temperatures this peak diminishes, signifying complete pyrolysis of the polymer.

Numerous studies on the adsorption and interactions of phosphorus acids on inorganic oxides have been reported. These reports describe the reaction processes that occur and by-products produced when phosphonate species in the gas phase are adsorbed on alumina surfaces. It is proposed that the decomposition mechanism of DMMP is as follows: $\text{DMMP} \rightarrow \text{methyl methylphosphonate} \rightarrow \text{methyl phosphonate or methyl phosphonic acid}$. It was also reported that there are two forms of adsorption, molecular and dissociative. Based upon the peak from P-CH₃ and P-O-CH₃ groups in the $^{13}$C NMR spectra, Figure 4.24, the decomposition and reaction process,
most likely follows the pathway described by Templeton et al.\textsuperscript{157} and Cao et al.\textsuperscript{179} in which DMMP decomposes into methyl methylphosphonate and then into methyl phosphonate or methyl phosphonic acid.

Comparison of the two phosphorus containing compounds and their interaction with the surfaces of the calcined alumina nanofibers shows that methyl phosphate (MePO\textsubscript{4}) interacts more strongly with the alumina surfaces than does dimethyl methylphosphonate (DMMP). It was shown that MePO\textsubscript{4} interacts so strongly with the alumina surfaces, such that dissolution of the surface occurs, where DMMP mildly interacts with the alumina surface through molecular and dissociative means.
CHAPTER V

POLYANILINE

5.1 Background of Polyaniline

Polyaniline (PANI) is one of the oldest known synthetic conducting polymers. It was first synthesized in 1834, by Friedrich Ferdinand Runge\textsuperscript{181} and analyzed by J. Fritzscbe in 1840.\textsuperscript{182} In 1862, H. Letheby\textsuperscript{183} documented physical and chemical responses of aniline with respect to oxidation via an electrochemical process. Following Letheby’s report, a series of investigations on the chemical and electrochemical oxidation of aniline transpired.\textsuperscript{184-197} It was not, however, until the mid 1980’s and early 90’s that the investigation and characterization of polyaniline accelerated.

Polyaniline falls into the category of a “synthetic metal” or an “intrinsically conducting polymer” in that it exhibits both metallic and polymer characteristics.\textsuperscript{198,199} In the words of Alan MacDiarmid, an intrinsically conducting polymer (ICP) is “an organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility, etc. commonly associated with a conventional polymer.”\textsuperscript{198,199} Not only was PANI the first polymer to be
processable in its stable, metallic form, but its inexpensive monomer, straight forward synthesis, high yield and environmental stability marked its importance in a number of industrial applications.\textsuperscript{200} Polyaniline has been used in rechargeable batteries, electrochromic windows, light-emitting devices (LED’s), actuators, photovoltaic cells, transistors, and as coatings for corrosion protection.\textsuperscript{199-204}

Polyaniline exists in three different oxidation states; the leucoemeraldine, pernigraniline and emeraldine forms. The leucoemeraldine and pernigraniline forms are the fully reduced and oxidized forms, respectively. The leucoemeraldine form of polyaniline consists of alternating benzene rings (reduced units) separated by secondary amine nitrogens and the pernigraniline form consists of alternating benzene and quinoid rings (oxidized units), separated by imine nitrogens. The emeraldine form is the half-oxidized form, consisting of alternating reduced and oxidized repeat units. The structures of the different oxidation states of PANI are shown in Figure 5.1.
The emeraldine base form of polyaniline has received the most attention, as this is the form that is produced during the synthesis of the polymer and is the form that becomes highly conductive upon doping. The emeraldine base may be cast as a free-standing film that has a high degree of flexibility, when cast from N-methyl pyrrolidinone (NMP), cresols, dimethylsulfoxide (DMSO) or formic acid.\textsuperscript{205}

5.2 Synthetic Processes

Polyaniline can be synthesized by a variety of means; however, processes involving the chemical and electrochemical oxidative polymerization of aniline are the most common modes of synthesis. The electrochemical oxidation of aniline involves the formation of emeraldine hydrochloride polyaniline films on a metal or conducting glass
electrode. The reaction takes place in an acidic medium (typically in 1M HCl) upon applying a potential difference between the electrodes. The resulting emeraldine hydrochloride is collected and washed with HCl or distilled water to remove unreacted aniline and then dried. The chemical oxidation of aniline also takes place in an acidic medium (usually 1M HCl) with aniline being oxidized by a chemical oxidant, such as ammonium peroxydisulfate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\). The emeraldine hydrochloride form of PANI is collected, washed and filtered and then dried. Regardless of the synthetic method used, the salt form of PANI can be deprotonated by a strong base, such as ammonium hydroxide to produce the emeraldine base form of PANI.

The preferred structure of polyaniline consists of para-substituted aniline repeat units, as this structure has been shown to produce materials with higher conductivities. In order to promote para-directed attachment (head-to-tail coupling) of the phenyl rings, linear polyacids have been used as templates. In this method, aniline is associated with the polyacid template through the interaction of the anilinium cation and the acid anion. Upon addition of the oxidant PANI is produced via a coupling of the anilinium through a zipper like process. The presence of excess acid groups generates a water soluble, conducting form of PANI. An extension of this process, involves the use of a peroxidase enzyme, such as horseradish peroxidase (HRP), palm tree peroxidase or soybean peroxidase to catalyze the oxidative coupling of the aniline units to create polyaniline.
5.3 Doping of Polyaniline

The emeraldine base form of polyaniline is an insulator with conductivities typical of organic polymers, $\sim 10^{-10}$ S/cm.\textsuperscript{198,199} However, the doping of PANI converts the polymer into a semiconductor or a conductor. Doping is a reversible process in which an insulator or semiconductor, with a low conductivity is converted to a material with high conductivity. Two main doping processes exist, redox and non-redox doping. In redox doping, the number of electrons in the polymer backbone is altered. Redox doping can be either p- or n-type reactions, in which the polymer backbone is oxidized or reduced by chemical or electrochemical means, respectively. Emeraldine base PANI undergoes non-redox doping, as the number of electrons in the polymer is unchanged. In this case, the polymer is protonated via a protonic acid at the two imine nitrogen sites of each PANI repeat unit. Protonation at the imine nitrogen sites introduces localized positive charges (bipolarons) on the imine nitrogens, Figure 5.2.
Figure 5.2 Protonation mechanism of the emeraldine base of polyaniline.

Through internal electronic re-arrangement, stable, delocalized polysemiquinone radicals are formed, as well as the conversion (reduction) of the quinoid ring into a benzenoid ring.\textsuperscript{217,218} Stability of this electronic state is brought about by resonance throughout the polymer backbone and the high conductivity of the dope PANI is achieved through the delocalization of charge and spin throughout the polyaniline chain. The highly conductive nature of PANI, a result of the delocalization of charge, has been observed in the crystal structure of the aniline tetramer, which has been determined.\textsuperscript{219}
The emeraldine base form of PANI was actually the first polymer to be doped by non-redox processes and is environmentally stable and exhibits conductivities ($10^3$ S/cm) approaching that of copper ($10^6$).\textsuperscript{199,220} Typically, the emeraldine base form of polyaniline is doped by immersion into an acidic medium, such as 1M HCl.\textsuperscript{199,200,206,221} The conductivity of PANI is related to the doping level, with the highest conductivity observed when all the imine nitrogen sites are protonated. Several types of acids have been used to dope polyaniline, including but not limited to halogen acids (HCl, HBr, HF), sulfonic (camphorsulfonic, dodecylbenzene sulfonic) and phosphonic acids (tertbutylphosphonic). It has also been discovered that in the doped (protonated) state, high molecular weight PANI is soluble in organic solvents and can readily be processed into films.\textsuperscript{222}

5.4 Models of the Structure of Polyaniline in the Doped State

The structure and conductivity of doped polyaniline is greatly affected by the acid, solvent and processing methods employed during doping. Depending upon the solvent chosen, PANI adopts either a “compact” or “extended” coil conformation, affecting the conductivity observed.\textsuperscript{223} The change in conformation of the polymer from a compact coil to an extended coil can be monitored by the change in viscosity of the mixture, UV-vis spectra and conductivity of the cast films. In the presence of a “poor” solvent, such as chloroform, polyaniline adopts the compact coil conformation and a reduction in viscosity of the mixture is observed. When the polymer is cast from poor solvents, the polymer films have low crystallinity and low conductivity. UV-vis studies
of doped polyaniline cast from chloroform show evidence of localized bi-polarons, consistent with a material of low conductivity.\textsuperscript{223,224} In the presence of a “good” solvent, such as \textit{m}-cresol, polyaniline adopts the extended coil conformation and an increase in viscosity is observed. Films cast from good solvents are found to contain crystalline regions and the conductivity is higher than films cast from poor solvents. UV-vis studies of doped polyaniline cast from \textit{m}-cresol show evidence of a free carrier tail from delocalized bipolarons, confirming that the material has a high conductivity.

The interactions between the polymer, acid and solvent affect the structure and conductivity of the doped system; however, the relationship between structure and conductivity is still poorly characterized. The most well studied system is that of polyaniline doped with camphorsulfonic acid (HCSA), in which the crystalline portions of this material have been characterized by X-ray diffraction techniques (XRD).\textsuperscript{225-227} As the X-ray diffraction data contain only a few Bragg peaks that are broad, it is not possible to obtain an exact structure of the doped polymer. Based upon the XRD data, \L\u{z}ny \textit{et al.} proposed two structures describing the PANI/HCSA system.\textsuperscript{228} The first structure (Model A) consists of alternating layers of PANI chains separated by layers of HCSA molecules. The second structure (Model B) consists of PANI chains which form channels where HCSA molecules are located, extending in two dimensions. A schematic of \L\u{z}ny’s models are shown in Figure 5.3.
Figure 5.3. Models of PANI:HCSA structure, as proposed by Łużny and co-workers.

The cylinders represent polyaniline chains and the black circles represent camphorsulfonic acid molecules.

Winokur and co-workers\textsuperscript{229} also proposed a lamellar structure, in which there are layers of polymer chains with acid molecules forming layers parallel to the polymer chains; much like Model A proposed by Łużny et al.\textsuperscript{228}

Investigation of the structure of doped polyaniline has been extended to include the characterization of specific intermolecular interactions for PANI/HCSA films cast from \textit{m}-cresol. Ikkala \textit{et al.} proposed two models for the structure of this complex which contains specific intermolecular interactions.\textsuperscript{230,231} One model involves hydrogen bonding of the sulfate group of camphorsulfonic acid with the phenolic hydrogen on \textit{m}-cresol, and the other model suggests that the carbonyl carbon of HCSA hydrogen bonds with the phenolic hydrogen of \textit{m}-cresol, Figure 5.4.
Figure 5.4. Proposed intermolecular interactions existing between polyaniline and HCSA (dopant) and the solvent, *m*-cresol (adapted from reference 231).

Ikkala *et al.* also has proposed that along with the hydrogen bond interactions there may also be interactions among the phenyl groups of the polymer and solvent (*m*-cresol) in the form of \( \pi \)-stacking.\(^{231}\) Presently, there is no spectroscopic evidence to show which, or if either of these models is correct, or if specific hydrogen bonds within the bi-molecular complex exists.

5.5 Solid-State NMR Characterizations

Solid-state NMR (SSNMR) has proven to be a very useful tool in the characterization of polymers, providing information about their structure and morphology.\(^{232,233}\) Cross-polarization magic-angle spinning (CP/MAS) NMR has
provided a way to characterize the different forms of polyaniline. Hjertzberg *et al.*\textsuperscript{234} and Kaplan and co-workers\textsuperscript{235} used $^{13}$C CP/MAS NMR and cross-depolarization (CDP) experiments to show that the emeraldine base form consists of alternating reduced and oxidized repeat units. The broad linewidths in the $^{13}$C spectra, on the order of 10 ppm have been attributed to structural heterogeneity of the polymers.\textsuperscript{235}

In the doped form, the emeraldine hydrochloride salt, a broad resonance with a width of approximately 60 ppm was observed in $^{13}$C CP/MAS NMR spectra.\textsuperscript{235} The single, broad resonance was reported as being a result of heterogeneity in charge delocalization throughout the polyaniline chain, arising from structural disorder.\textsuperscript{235,236} Solid-state NMR studies have also revealed that complete charge delocalization, or a fully metallic state, is not achieved in doped polyaniline, as a result of structural disorder. Instead there are “metallic” regions within the polymer separated by amorphous regions.\textsuperscript{236-239} These “metallic” regions are not observed by NMR, as the presence of unpaired electrons produce extremely broad resonances which dominate the NMR spectrum, thus leaving only the amorphous regions visible. Espe and co-workers studied polyaniline doped with HF using $^{13}$C, $^{15}$N and $^{19}$F NMR experiments.\textsuperscript{239} A reduction in the signal intensity of the peaks in the $^{13}$C and $^{15}$N NMR spectra (~ two-thirds) was observed, a result of the presence of paramagnetic electrons. From the $^{19}$F and $^{15}$N REDOR data it was determined complete delocalization of charge throughout the backbone of HF-doped PANI was not achieved due to structural disorder.

$^{15}$N NMR has also provided important information regarding the structure and oxidation state of doped and undoped polyaniline. The presence of “end group” amine nitrogens were detected in the $^{15}$N NMR spectra of isotopically labeled $^{15}$N polyaniline in
the emeraldine base form, supporting the idea that PANI polymerization occurs via head-
to-tail coupling and providing information about the molecular weight of the polymer. Protonation at the imine nitrogen sites was also confirmed by NMR studies. In the
undoped form, the $^{15}$N NMR spectra contain two resonances at $\sim 326$ ppm and 65 ppm, consistent with imine and secondary amine nitrogens, respectively and in the doped form
the peak from the imine nitrogen shifts upfield (to $\sim 102$ ppm), consistent with protonsation at that site. Also a broad resonance is observed in the $^{15}$N spectra as a result of a wide distribution of protonated imine nitrogens with their charge delocalized throughout the PANI backbone.

5.6 Research Objectives

The selection of the dopant and solvent greatly affects the magnitude of the conductivity of polyaniline and has been attributed to the structural changes of the polymer between the open and compact coil conformations. However, details of the structures present with different acid/solvent combinations have not yet been reported. The focus of this work is to begin identifying the specific interactions present between the solvent/acid and polyaniline, in particular the investigation of the hydrogen bond between the polymer/acid/solvent. Solid-state 2-D NMR heteronuclear correlation (HETCOR) experiments have been employed to identify the hydrogen bond interactions between polyaniline and the solvent, N-methylpyrrolidone (NMP). Solid-state NMR was also used to characterize the structure of polyaniline synthesized in the presence of a polyacid template, poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAAMPSA) and
investigate the effect molecular weight of the PAAMPSA has on the conductivity and structure of polyaniline.
6.1 Chemical Synthesis of Emeraldine Base (EB) Polyaniline

The emeraldine base (EB) form of polyaniline, both $^{15}\text{N}$ labeled and unlabeled was used as received from Santa Fe Science and Technology, Inc. The material was synthesized by dissolving 20 mL of aniline (labeled or unlabeled) in 250 mL of 1.0M HCl. The solution was then cooled to 0-2 °C using an ice bath. A solution of peroxydisulfate (45 g of in 250 mL of 1.0 M HCl) was added drop wise to the aniline solution over a period of 1 hour with vigorous stirring and the reaction proceeded for 3 hours after complete addition of the oxidant. The polymer was collected via filtration, using a Buchner funnel and washed with 1.0 M HCl until a colorless filtrate was observed. The polymer was then washed three times with 100 mL of de-ionized water to remove oligomeric impurities. The emeraldine base was formed by stirring the emeraldine hydrochloride in 500 mL of 1.0 M NH$_4$OH for 1 hour. The material was collected via filtration, using a Buchner funnel and washed with 0.1 M NH$_4$OH, until a colorless filtrate was observed. The emeraldine base powder was then dried under
dynamic vacuum for 72 hours at room temperature. The molecular weight of the polyaniline was estimated to be 50,000 g/mol, based on gel permeation chromatography.

6.2 Polyaniline Synthesized in the Presence of a Template

2-Acrylamido-2-methyl-1-propanesulfonic acid, 99% (AAMPSA) and potassium persulfate, 99+% were purchased from Aldrich and dried in a vacuum oven overnight before use in the synthesis of poly-AAMPSA. Aniline, 99.9% and ammonium per oxydisulfate, 98.2% purchased from Fisher Scientific were dried over molecular sieves and under vacuum overnight, respectively. A high molecular weight PAAMPSA, 10.3 wt% in water (M_w = 800 kg/mol) was purchased from Scientific Polymer Products, Inc. and used in the synthesis of PANI. It was precipitated in tetrahydrofuran and dried in a vacuum oven at 55°C overnight before use. ¹⁵N aniline (99.7+%), purchased from Cambridge Isotope Laboratories, Inc. was used, without further purification for ¹⁵N Solid-State NMR experiments.

PAAMPSA was synthesized by the free-radical polymerization of AAMPSA (monomer) and carried out in deionized water. The molar ratio of monomer (AAMPSA) to initiator (potassium persulfate) was varied to obtain PAAMPSA with different molecular weights. For clarification purposes, the different PAAMPSA templates are referred to as PAAMPSA-X, where X refers to the poly(ethylene oxide), PEO-equivalent weight-average molecular weight of the polymer in kg/mol. The low molecular weight PAAMPSA, PAAMPSA-45 was synthesized using a monomer to initiator molar ratio of 1:0.4, with the total concentration of monomer and initiator in the aqueous solution
equaling 10 M. The solution was purged with nitrogen for 30 min before the flask was placed in an oil bath preheated to 75°C to initiate polymerization. The polymerization was carried out for 5 hours, after which the reaction medium was precipitated in tetrahydrofuran to recover PAAMPSA. The polymer acid was then dried in a vacuum oven at 55°C overnight.

The PANI-PAAMPSA complex was created by the oxidative polymerization of polyaniline in the presence of PAAMPSA.\textsuperscript{205,236} 5.8 g of PAAMPSA (0.028 mol) was dissolved in 375 mL of deionized water. 2.6 g of aniline (0.028 mol) was then added to the PAAMPSA solution and stirred at room temperature for 1 h. 5.8 g of the oxidizing agent, ammonium peroxydisulfate, (0.025 mol) was dissolved in 25 mL of deionized water and both solutions were purged with nitrogen for 30 min. The PAAMPSA-aniline solution was then cooled in an ice water bath before the ammonium peroxydisulfate solution was added drop wise at a rate of approximately 1.25 mL/min. The reaction medium was kept at ice water temperature and stirred vigorously for the first 6 hours of the reaction. The reaction was allowed to proceed overnight to ensure complete conversion. Acetone was added slowly to the polymer suspension to recover the polymer complex, after the 24 hour reaction took place. The supernatant was decanted and then the rest of the mixture was filtered to obtain a green powder. The samples were then dried in the vacuum oven at 50°C overnight. For \textsuperscript{15}N Solid-State NMR experiments, \textsuperscript{15}N aniline was polymerized according to the procedures above. Again to avoid confusion, these materials are referred to as PANI-PAAMPSA-X, with X being the PEO-equivalent weight-average molecular weight of the PAAMPSA template, in kg/mol, that was used during PANI synthesis.
The PANI-PAAMPSA complex was deprotonated by removal of the PAAMPSA template by addition of excess ammonium hydroxide. A 2 wt% PANI-PAAMPSA solution was added to deionized water and stirred for 5 days. Excess ammonium hydroxide was then added to the PANI-PAAMPSA solution and stirred for 48 hours. The dispersion was centrifuged for 1 hour at 4500 rpm to recover the solids, which were then washed with water and dried in a vacuum oven at 50°C. The dedoped material is referred to as PANI-X, where X again denotes the PEO-equivalent weight-average molecular weight of the initial PAAMPSA template, in kg/mol.

The template assisted synthesis of PANI and PAAMPSA was carried out by Joung Eun Yoo, a graduate student in the department of chemical engineering at the University of Texas at Austin, Austin, TX.

6.3 Doped Polyaniline

Polyaniline was doped with camphorsulfonic acid (HCSA) by preparing a 1% wt/wt solution of $^{15}$N labeled emeraldine base PANI and HCSA in N-methylpyrrolidinone (NMP). Approximately 0.4 g of $^{15}$N labeled EB PANI and ~0.5 g of HCSA, creating a molar ratio of 1:2 (PANI:Acid) were ground together. The ground material was then slowly added to ~40 g of NMP, with stirring on a magnetic stir plate. The mixture was then sonicated or stirred for 2 days and then filtered into a glass Petri dish using a disposable, 5 cc syringe with a Whatman filter (0.45 µm pore size) attached on the end. The doped PANI solution was placed into a vacuum oven at 60 °C for 24
hours to remove the solvent. The doped PANI film was scraped off via a razor blade and
dried overnight under dynamic vacuum.

6.4 Solid-State Nuclear Magnetic Resonance (SSNMR)

Spin count experiments and PANI-PAAMPSA data were collected on a Varian
Unity\textsuperscript{Plus} 200 (4.7 T) spectrometer, operating at 50.77 MHz for \textsuperscript{13}C and 20.47 MHz for
\textsuperscript{15}N. A Doty Scientific VT CP-MAS wide bore probe was utilized. The samples were
packed into 7 mm silicon nitride rotors, using Kel-F end caps and spun at 5 kHz. \textsuperscript{13}C
chemical shifts were referenced with respect to hexamethyl benzene ($\delta$ \textsuperscript{13}C\textsubscript{methyl} = 17.3
ppm, $\delta$ \textsuperscript{13}C\textsubscript{TMS} = 0 ppm). Typical carbon pulse widths were 5 µs and continuous wave
decoupling (CW) was employed using a field strength of approximately 52 kHz.

\textit{Spin Count Experiments}

The mass of the samples were recorded before data collection. Fully relaxed \textsuperscript{13}C
NMR spectra of the doped film and \textsuperscript{15}N labeled EB PANI powder were collected with
relaxation delays of 30 seconds ($> 5 \times T_1$). Back linear prediction was employed when
processing the doped film, correcting the first 3 points of the FID. A fully relaxed \textsuperscript{13}C
spectrum of neat HCSA was also collected, using a relaxation delay of 60 seconds. No
linear prediction was used in the processing of the EB PANI powder or HCSA samples.
In all the spectra, 1024 data points and approximately 2200-3000 transients were
collected. Line broadening of 20 Hz was applied to the data before Fourier
transformation. Integrations of the area of the peaks were performed and baseline
correction was used.
PANI-PAAMPSA

$^{13}$C cross-polarization spectra (CP) were collected using a CP time of 1 ms cross-polarization and a relaxation delay of 2 seconds. $^{15}$N Solid-State NMR spectra were collected using a relaxation delay of 5 seconds, and $^{15}$N chemical shifts were referenced with respect to ammonium nitrate ($\delta^{15}\text{NH}_{4}^{+} = 0$ ppm). Pulse widths of 7.5 µs and CW decoupling of 52 kHz were used. Line broadening of 20 Hz was added before Fourier transformations and the first eight points of the FID were corrected via linear prediction.

Heteronuclear Correlation (HETCOR) Experiments

The HETCOR experiments were performed on a 17.6 T Varian INOVA spectrometer, using a Doty Scientific DSI-971 HXY probe, tuned to two channel mode. The $^{13}$C chemical shifts were referenced to HMB ($\delta^{13}\text{C}_{\text{methyl}} = 17.3$ ppm, $\delta^{13}\text{C}_{\text{TMS}} = 0$) ppm and $^{13}$C parameters were calibrated using HMB. $B_1$ fields for $^1$H and $^{13}$C were 62.5 kHz and 50.3 kHz, respectively. $^1$H chemical shifts were referenced to uniformly labeled $^{13}$C L-alanine ($\delta^1H_{\text{methyl}} = 20.6$ ppm) and the $^1$H parameters were also calibrated using the labeled alanine. A two pulse phase modulation (TPPM) decoupling scheme was employed.

For the medium to long distance HETCOR (MELODI-HETCOR) experiment, a rotational echo double resonance (REDOR) front end is employed, along with Lee-Goldburg cross-polarization and frequency shifted Lee-Goldburg (fslg) decoupling. Therefore, the spinning speed must be selected such that it is an integer increment of the fslg period. The samples were spun at 12202 Hz and packed into 4 mm silicon nitride rotors using aurum end caps. The rotors were packed such that the sample size was 2 mm in length and positioned in the center of the rotor, using KBr as end spacers.
7.1 Structure of Doped Polyaniline

Polyaniline, in the emeraldine base form is an insulating polymer. Upon doping (protonation) with a protonic acid, polyaniline becomes a conducting polymer whose conductivity approaches that of copper.\textsuperscript{199,220} Doping occurs at the imine nitrogen sites with two acid molecules associated with each repeat unit of polyaniline, yielding the maximum conductivity.\textsuperscript{199,200,217,218} Several models have been proposed for the structure of this system based on XRD data,\textsuperscript{228-231} however, no experimental evidence has been reported to confirm these structures. Models proposed by Ikkala \textit{et al.}\textsuperscript{230,231} suggest specific interactions occur between polyaniline, the dopant and the solvent, in particular hydrogen bonding. In these particular models, polyaniline was doped with camphorsulfonic acid and cast from \textit{m}-cresol, resulting in a system with high conductivity. Based upon the models proposed by Ikkala and co-workers, it is the focus of this work to begin investigating the specific interactions that occur within the doped
polyaniline system. The particular system under characterization is polyaniline doped with camphorsulfonic acid and cast from NMP, as this system has reasonable conductivity allowing for characterization by NMR methods.

Doped polyaniline films cast from NMP, typically are made via stirring polyaniline and the dopant in a solution of NMP. However, when the films are cast a portion of the material is lost, as the final mass of the material collected is less than the mass of the starting material. In order to investigate the structure of doped PANI by NMR, it is important that the sample is as homogeneous as possible and that the polymer is fully doped. The presence of excess acid also needs to be minimized such that characterization of the structure does not include studies of acid molecules that are not interacting with the doped polymer.

Initial efforts to generate doped PANI films cast from NMP resulted in doped films containing only 55-60 % of the starting material. In this case the polyaniline solution was produced by stirring the solution for 2 days. In an effort to increase the percent yield of the dope PANI film, sonication was employed instead of stirring. It was observed that the yield of the material increased to 90 % when the sonication method was employed. The percent yield values took into account residual NMP (15-20 % by weight) that typically remains in films cast from this solvent.

As it was determined, the sonication method provides a means of minimizing the amount of material lost during filtration and film formation; however, there is still a small amount of material that is lost during this process. It is important to determine whether or not the mass loss is a result of losing undoped polyaniline. If the mass loss is a result of filtering out undoped polyaniline, then the resulting film contains a portion of excess
acid. Solid-state NMR spin counting experiments provide a way to determine the mole ratio of acid molecules to polymer repeat units. The $^{13}$C direct polarization (DP) NMR spectrum from PANI doped with HCSA and cast from NMP after a period of sonication, is shown in Figure 7.1. The structures of the solvent, NMP and the dopant, HCSA are shown within the figure.

Figure 7.1. $^{13}$C DP/MAS NMR spectrum of sonicated Polyaniline/HCSA cast from NMP.

The peaks at 218 ppm and 175 ppm are from the carbonyl carbons of camphorsulfonic acid and N-methylpyrrolidinone, respectively. The broad region spanning from 80 ppm to 160 ppm are the carbons from doped polyaniline and the aliphatic carbons from both NMP and HCSA are located in the region spanning from 0-80 ppm.

The mole ratios of polyaniline to camphorsulfonic acid in the stirred and sonicated methods were compared. Four fully relaxed $^{13}$C NMR spectra were collected;
\[^{15}\text{N}\] labeled emeraldine base PANI powder, neat camphorsulfonic acid (HCSA) and HCSA doped PANI films cast from an NMP solution prepared via stirring and sonication. Each sample was weighed before the NMR experiments were performed and solid-state NMR peak intensities from fully relaxed spectra were corrected for differences in sample mass and the number of transients collected. From this data, a signal intensity per mole of material can be determined. These results, in turn, are used to calculate the PANI to acid mole ratio. The mole ratios of NMP and HCSA were determined based upon the integrated value for each of the carbonyl peaks, as they represent one carbon atom per molecule. The signal intensity from doped polyaniline in the films was determined by integrating the doped PANI region, spanning from 80-160 ppm and adding in the regions from the corresponding spinning sidebands. The spinning sidebands were determined by integrating the region containing the carbonyl carbons of both HCSA and NMP, spanning from 165-260 ppm, as this region also contains a spinning sideband from the doped polyaniline resonance. The integrated areas of the carbonyl resonances from NMP and HCSA where subtracted from this region and the resulting area was multiplied by two, as there are two spinning sidebands attributed to the dope PANI signal (the other side band is located underneath the aliphatic region of the acid). The integrated value of the NMP carbonyl peak (175 ppm) was multiplied by 5 to determine the total signal intensity per mole of NMP. The total signal intensity per mole of HCSA was determined by adding the integrated area of the carbonyl peak for HCSA (218 ppm) to the integrated value of the aliphatic carbons (region spanning from 0 to 80 ppm); minus the value from the spinning sideband of the doped PANI signal. The moles of the acid and polymer in the doped films were calculated using equation 1.
The mole ratio of HCSA to PANI was then determined and compared to the theoretical mole ratio of 2 HCSA molecules per 1 PANI repeat unit. From the spin count results, it was determined that the doped PANI film obtained from the stirring method resulted in a mole ratio of 1 polyaniline repeat unit to 4.6 HCSA molecules and in the sonicated sample a mole ratio of 1 polyaniline repeat unit to 2.8 HCSA molecules. It is important to note that the integration values of the carbonyl resonances of NMP and HCSA included a portion of the spinning sideband intensity from the doped PANI signal. This in turn results in an over determination of the amount of HCSA present. The addition to the integration value is approximately 10-20 %, thus the actual mole ratio of HCSA to polymer is closer to 2.2 to 2.5 for the sonicated sample. The results from the spin count experiments indicate that the large mass loss observed when doped polyaniline films are formed via stirring is due to a loss of undoped polyaniline, leaving behind a large amount of excess HCSA. In contrast, when sonication is employed, the resulting film contains a mole ratio very near that of the experimental value of 2:1 (HCSA:PANI). As the $^{13}$C NMR spectrum from the PANI/HCSA material does not show any evidence of undoped PANI, Figure 7.1, it is proposed that a portion of the polymer did not dissolve during sonication and stirring and is removed during the filtration step.
7.2 Meta-cresol Exposures

Polyaniline, doped with camphorsulfonic acid and cast from \( m \)-cresol, has been reported to have the expanded coil conformation and one of the highest reported conductivities for polyaniline, ranging from 300-1000 S/cm.\(^{205,222}\) Several studies have monitored the change of the polymer from a compact coil conformation, having low conductivity to an extended coil conformation with high conductivity, upon exposure of the polymer to \( m \)-cresol vapors.\(^{214,215}\) In these studies polyaniline doped with camphorsulfonic and cast from CHCl\(_3\) were exposed to \( m \)-cresol vapor, a secondary dopant, for varied amounts of time. UV-vis spectroscopy was used to track the changes from a low conducting material with a \( \lambda_{\text{max}} \) of \(~850\) nm to that of a high conducting material, showing a free carrier tail extending out to the near IR region.

In order to convert PANI doped with HCSA to a more extended coil conformation while still keeping the conductivity reasonably low, a similar approach was undertaken. Polyaniline, doped with camphorsulfonic acid and cast from an NMP solution was exposed to \( m \)-cresol vapors for various amounts of time. The changes in the electronic structure of doped PANI, upon exposure to \( m \)-cresol vapors are illustrated in Figure 7.2.
Figure 7.2. Conformational changes of the PANI/HCSA complex as a result of exposure to $m$-cresol vapors.
The conformational changes of the PANI/HCSA complex were monitored via $^{13}$C CP/MAS solid-state NMR, Figure 7.3.

Figure 7.3. $^{13}$C CP/MAS NMR spectra of $m$-cresol exposures. (A) no $m$-cresol exposure. Exposed to $m$-cresol vapors for (B) 1 hour, (C) 5.5 hours, (D) 8 hours, (E) 13.5 hours, (F) 36 hours, and (G) 46.5 hours.

PANI doped with HCSA, cast from NMP and with no exposure to $m$-cresol is shown in the bottom spectrum of Figure 7.3. The aliphatic carbons from the primary dopant (HCSA) lie in the region spanning from 0-80 ppm and the broad resonance in the region from 80-190 ppm is from the aromatic carbons of doped PANI. This broad peak has been observed previously as it is attributed to a heterogeneous distribution of the positive charge of the doped polymer. The weak resonances located at ~180 ppm and 217 ppm are the carbonyl carbons of NMP and HCSA, respectively. As the exposure time to the
$m$-cresol vapors increases, a narrowing of the aliphatic HCSA peaks is observed. This narrowing is a result of the polymer/complex becoming more ordered. This ordering of the doped system is expected as the $m$-cresol becomes incorporated into the system.$^{223,224}$ The incorporation of $m$-cresol into the system is shown by the small, sharp peaks observed in the aromatic region (100-170 ppm) of the spectrum, Figure 7.3 F.

The large reduction in the signal intensity of the peaks in Figure 7.3 E signifies a conversion from a low conducting material to that with high conductivity. As the exposure time to $m$-cresol vapors increases, the reduction in signal intensity continues and upon exposure to the vapors for 46.5 hours the signal intensity has reduced by a factor of approximately 20. The loss in signal intensity may also be a result of the skin depth effect. It has been shown that in conducting materials, the adsorption of rf inside a conducting sample is exponentially attenuated. As a result, spins that are located in the middle of the sample experience a reduced flip angle, causing a loss in signal intensity.$^{241}$

7.3 Hydrogen Bond Investigation

The goal of this work is to investigate the specific interactions present in the doped PANI system, beginning with the investigation of the hydrogen bond between PANI and the acid and/or solvent. Solid-state NMR heteronuclear correlation (HETCOR) experiments have provided detailed information concerning polymer interactions, in particular hydrogen bond interactions. White and Mirau$^{242}$ used HETCOR to observe hydrogen bonding between two miscible polymers, poly(vinylphenol) (PVPh) and polyacrylates. The intermolecular correlation between the
phenolic proton of PVPh and the carbonyl carbon of poly(methyl acrylate) (PMA) was detected, paving the way to directly measure hydrogen bond interactions between miscible polymer blends and other materials.

Before beginning studies on the complex system of PANI doped with HCSA, a model compound known to contain a hydrogen bond, L-tyrosine hydrochloride, was first investigated. Previous applications of HETCOR NMR have observed a $^{1}H-^{13}C$ correlation that has been proposed to arise from a hydrogen bond between two tyrosine molecules. The structure of L-tyrosine·HCl is shown in Figure 7.4, along with the corresponding $^{1}H-^{13}C$ LGCP-FSLG HETCOR NMR spectrum.

Figure 7.4. $^{1}H-^{13}C$ LGCP-FSLG HETCOR NMR spectrum of L-Tyrosine hydrochloride.
The incorporation of a Lee-Goldburg cross-polarization (LGCP) scheme allows for selective $^{1}H$ to $^{13}C$ polarization transfer, which suppresses spin diffusion so only one-bond heteronuclear correlations are observed. From the spectrum in Figure 7.4, correlations from directly dipolar coupled protons and carbons are observed. It is the correlation of the proton located at 12.2 ppm with the carbon positioned at 150 ppm that is of most interest, as this is the hydrogen bond interaction between the carboxylic acid proton of one tyrosine molecule with the phenolic carbon of another tyrosine molecule, verifying the ability to detect intermolecular interactions. The HETCOR results are in good agreement with previously reported NMR assignments and heteronuclear correlations of L-tyrosine·HCl.$^{243}$

In an effort to verify that this correlation truly originates from a hydrogen bond, L-tyrosine·HCl was deuterated and the LGCP-FSLG HETCOR experiment was carried out, Figure 7.5.
The broad and distorted correlations observed in the aromatic region of tyrosine are a result of dipolar interactions with deuterium. In the $^{1}$H-$^{13}$C LGCP HETCOR spectrum of the deuterated tyrosine, the hydrogen bond correlation is absent, confirming that the correlation seen in Figure 7.4 is a result of the hydrogen bond between the carboxylic acid proton and an adjacent phenol carbon in L-tryrosine hydrochloride.

Using the HETCOR technique, it is also possible to observe both long-range and short-range heteronuclear ($^{1}$H-$^{13}$C) interactions. This is accomplished by simply using a general cross-polarization scheme, instead of LGCP, Figure 7.6. In the HETCOR NMR spectrum, both one bond and multiple bond interactions are observed.
Numerous reports have provided evidence that hydrogen bonding occurs between neighboring PANI chains, as well as between PANI and the solvent, in both the solution and solid-state.\textsuperscript{244-250} In order to begin looking for the hydrogen bond interaction(s) in the polyaniline system, a simple system consisting of PANI cast from an NMP solution was first characterized. This system contains residual NMP that hydrogen bonds to the amine nitrogens of PANI. In order to determine the expected $^1$H chemical shift of the hydrogen bonded amine nitrogens of PANI, $^1$H solution-state NMR spectra were collected of the tetramer of polyaniline (one repeat unit) in a non-hydrogen bonding and a hydrogen bonding solvent. The $^1$H NMR spectra are shown in Figure 7.7.
Figure 7.7 $^1$H solution-state NMR spectra of N,N’-diphenyl-p-phenylenediamine cast from CHCl$_3$ (non-hydrogen bonding solvent) and DMSO (hydrogen bonding solvent).

From Figure 7.7, NH protons of the tetramer in the non-hydrogen bonded state are located at ~5.7 ppm and when the tetramer is hydrogen bonded to DMSO, the peak from the NH protons is shifted downfield to 7.9 ppm. It is therefore expected that in the solid-state $^1$H-$^{13}$C HETCOR experiment, the hydrogen bond correlation between the amine nitrogens of polyaniline and the carbonyl carbon of NMP should be found in the vicinity of 7-8 ppm ($^1$H) and 175 ppm ($^{13}$C). The HETCOR data, Figure 7.8, show the correlation between the $^{13}$C of PANI and aromatic protons as well as the correlations between the aliphatic carbons and protons of NMP.
Figure 7.8. $^1$H-$^{13}$C MELODI-HETCOR NMR spectrum of $^{15}$N labeled PANI cast from NMP.

However, no correlation was observed in the expected region for a hydrogen bond between NMP and PANI. There are a few reasons as to why the hydrogen bond is not seen, one is that it does not exist, however there is experimental evidence that has been reported on the existence of hydrogen bonding between the polymer and NMP. The other reason is that the structural heterogeneity commonly observed in PANI results in a distribution of hydrogen bond lengths. The change in the hydrogen bond will result in a change in both the proton and carbon chemical shifts. This distribution will then result in
significant broadening of the peak. This may result in low enough signal-to-noise that the peak cannot be observed.

7.4 PANI-PAAMPSA

Doping of polyaniline with small protonic acids has paved the way for its use in a variety of industrial applications. The problem, however is that once in the conducting form, solubility in common solvents decreases drastically and thus solution and melt processability is very difficult, near impossible to achieve. It has been found that oxidative polymerization of aniline monomers in the presence of a polymer acid template (polyacid), allows for the formation of water-dispersible, conductive polyaniline that is readily processable.\textsuperscript{196,211,250,251} In addition to the ease of processability, the polyacid provides a means of chemical stability and is not volatile, like many of the small molecule acids used as dopants.

In this study, polyaniline was synthesized in the presence of poly(2-acryl-amido-2-methyl-1-propanesulfonic acid), PAAMPSA. The structure of PAAMPSA is shown in Figure 7.9.

![Poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA. The carbons are labeled as a-f.](image)

Figure 7.9. Poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA. The carbons are labeled as a-f.
PAAMPSA was chosen as it is a strong acid in both the polymer and monomer forms and as such promotes para-directed polyaniline repeat units and low defect densities. Various molecular weights of PAAMPSA were used in the template assisted synthesis of PANI and the conductivity of the PANI-PAAMPSA system was found to be affected by the molecular weight of the polyacid. It was observed that a decrease in molecular weight of PAAMPSA caused an increase in conductivity. The molecular weights of the polyacid varied from 45 kg/mol to 724 kg/mol and are referred to in this text as PAAMPSA-$X$, where $X$ is the molecular weight of PAAMPSA in kg/mol.

Solid-state $^{13}$C CP/MAS NMR was employed to study the structure of the PANI-PAAMPSA complex. The $^{13}$C NMR spectra of PAAMPSA, the PANI-PAAMPSA complex and the de-doped form of PANI-PAAMPSA are shown in Figure 7.10.
Figure 7.10. $^{13}$C CP/MAS NMR spectra of (A) PAAMPSA-45 (solid line) and PAAMPSA-724 (dotted line), (B) PANI-PAAMPSA-45 and (C) PANI-45. The PAAMPSA carbons are labeled with respect to Figure 7.9 and the polyaniline carbons are labeled with respect to the inset.

The chemical shift assignments for PAAMPSA-45 (Figure 7.10 A) were based upon previously reported $^{13}$C NMR studies.$^{252,253}$ The carbon assignments correlate to the structure shown in Figure 7.9. Subtle differences in the peak line widths and intensities are observed between the $^{13}$C NMR spectra of PAAMPSA-45 (solid line, spectrum A) and PAAMPSA-724 (dotted line, spectrum A). The line widths in the $^{13}$C NMR spectrum of PAAMPSA-724 appear to be slightly broader than that of PAAMPSA-45 and are most likely due to local disorder in PAAMPSA-724.$^{254}$ The increase in local disorder in the PAAMPSA template is directly correlated with the observed decrease in
conductivity of PANI-PAAMPSA, in that the conductivity decreases from 1.1 S/cm (PANI-PAAMPSA-45) to 0.45 S/cm (PANI-PAAMPSA-724). The decrease in conductivity, as a result of local disorder emphasizes the importance of the local structure of the polyacid template in determining the electrical properties of the final material.

The $^{13}$C solid-state NMR spectrum of PANI-PAAMPSA-45 is shown in Figure 7.10 B. The peaks in the region spanning from 10 to 70 ppm are from the aliphatic carbons and the peak at 175 ppm is from carbonyl carbon of PAAMPSA. The broad resonance spanning from 100 and 160 ppm arises from the presence of the distribution of positive charges along the polymer chains, consistent with doped PANI.$^{238,255}$

The $^{13}$C NMR spectrum of the dedoped form of PANI-PAAMPSA-45 is plotted in Figure 7.10 C. The spectrum confirms that the polyaniline created is in fact para-directed, as the chemical shift assignments in the de-doped form are consistent with previous reports on polyaniline,$^{234,235}$ suggesting the formation of linear PANI chains with low defect densities. The peaks in the aliphatic region between 10 and 70 ppm indicate the presence of a small amount of residual PAAMPSA after de-doping, as it is difficult to completely remove the polymer acid template during the dedoping process.

$^{15}$N Solid-State NMR provides a way to directly observe the extent of doping, as doping occurs at the imine nitrogen sites converting those sites to protonated amine sites. The $^{15}$N Solid-State NMR spectra of PANI-PAAMPSA-724 and PANI-PAAMPSA-45 are shown in Figure 7.11.
In the $^{15}$N NMR spectrum of PANI-PAAMPSA-724, a small, broad resonance located at ~322 ppm is observed, as a result of residual unprotonated imine nitrogens.\textsuperscript{241,256} The presence of the residual imine nitrogens indicates that PANI-PAAMPSA-724 is not completely doped. Confirmation of the incomplete doping of PANI-PAAMPSA-724 is confirmed by the conductivity measurements of the sample before and after exposure to HCl vapor, in which an increase in conductivity is achieved upon exposure to the vapors.

In contrast, the $^{15}$N NMR spectrum of PANI-PAAMPSA-45 (Figure 7.11 A ii) is consistent with fully doped polyaniline, as the conversion of imine nitrogens to protonated amine nitrogens has been achieved, shown by the absence of a resonance at ~320 ppm. The conductivity measurements also suggests that the sample is completely doped as-synthesized, whereby when exposed to HCl vapors, no increase in conductivity is observed.
In lieu of the fact that PANI-PAAMPSA-724 is not completely doped, its conductivity (0.4 S/cm) is higher than those previously reported for PANI that were chemically-\(^{213,252,257}\) and enzymatically-synthesized\(^ {241,258,259}\) on other polyacid templates. The reason for the enhanced conductivity is believed to stem from differences in the local structure of the different material systems. In the \(^{15}\)N NMR spectra of both PANI-PAAMPSA-724 and PANI-PAAMPSA-45 (Figure 7.11 A), the single peak that is centered around 115 ppm, midway between the chemical shifts for protonated imine and amine nitrogens is assigned to the protonated amines whose charges are delocalized along the PANI-PAAMPSA backbone.\(^ {241,255,260}\) The relatively symmetrical shape of the peaks observed at ~115 ppm suggests that very few, if any defect sites resulting from “kinks” in the polymer chain are present. In only one other instance was a single resonance observed in the \(^{15}\)N NMR spectrum of a template-synthesized PANI,\(^ {241}\) in which PANI was enzymatically-synthesized on a PSS template. Typically, multiple peaks are observed in this region of the \(^{15}\)N NMR spectrum, suggesting the presence of multiple nitrogen environments.\(^ {241,260}\) For example, the \(^{15}\)N NMR spectrum of PANI that is enzymatically-synthesized on a poly(vinylphosphonic acid) template exhibits a series of peaks between 30 to 200 ppm.\(^ {241,255,260}\) The sharp peaks at 139.7 ppm and 67 ppm have been assigned to protonated imine nitrogens and uncharged secondary amine nitrogens, respectively. The chemical structures of these PANI systems contain localized cation species situated on individual imine nitrogens, resulting in lower conductivities. It is not fully understood what controls the local nitrogen environment during the template synthesis of PANI, however it is believed that the extent of charge delocalization throughout the PANI-PAAMPSA system (not typically observed in other polyacid PANI
systems) is responsible for the increase in conductivity in these materials compared to other PANI systems.

In addition to the peaks associated with the protonated amine nitrogens in Figure 7.11 A, a sharp, intense peak at 26 ppm is observed. Based on the chemical shift (~26 ppm), this resonance has been assigned to unreacted anilinium.\cite{256} When PANI-PAAMPSA is washed and precipitated repeatedly, the intensity of the anilinium peak reduces significantly. Further more, the assignment of this peak is confirmed by the fact that it completely disappears upon deprotonation with excess ammonium hydroxide (Figure 7.11 B). The $^{15}$N NMR spectra of dedoped PANI-724 and PANI-45 are shown in Figure 7.11 B. Observed in the spectrum of deprotonated PANI-PAAMPSA are imine nitrogens and amine nitrogens located at 320 ppm and 73 ppm, respectively. These resonances are in good agreement with previously reported data of de-protonated PANI.\cite{240,261}

In conclusion, polyaniline synthesized in the presence of a polyacid, in particular poly(2-acryl-amido-2-methyl-1-propanesulfonyl acid), PAAMPSA has been characterized by $^{13}$C and $^{15}$N solids-state NMR. It was found that the molecular weight of the polyacid has an impact on the doping and conductivity of the polymer. It was also shown that synthesis in the presence of PAAMPSA does not affect the para-directed polymerization of polyaniline, in fact less defect sites are formed and a water-soluble, readily processable and environmental friendly polyaniline material is created.
REFERENCES


42. Sato, T. J. Appl. Chem. 1964, 14, 303-308.


64. Fink, P. Z. Chem. 1967, 7, 324.


109. Chun, I. *Dissertation* The University of Akron, **1995**.


133. Tuttle, R. W.; Chowdury, A.; Bender, E. T.; Ramsier, R. D.; Cross, J. L.; Espe, M. P. *submitted.*


