

**DETERMINATION AND EVALUATION OF ELECTRICAL PROPERTIES OF
METAL-CONTAINING CONDENSATION POLYMERS**

by

Amitabh J. Battin

A Dissertation Submitted to the Faculty of

The Charles E. Schmidt College of Science

in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

Florida Atlantic University

Boca Raton, FL

August 2009

Copyright by Amitabh Battin 2009

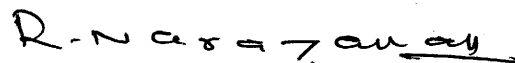
**DETERMINATION AND EVALUATION OF ELECTRICAL PROPERTIES OF
METAL-CONTAINING CONDENSATION POLYMERS**

by

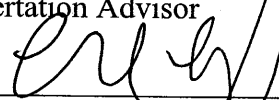
Amitabh Battin

This dissertation was prepared under the direction of the candidate's dissertation advisor, Dr. Ramaswamy Narayanan, Department of Chemistry and Biochemistry, and has been approved by the members of his supervisory committee. It was submitted to the faculty of the Charles E. Schmidt College of Science and was accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

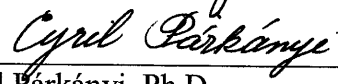
SUPERVISORY COMMITTEE:



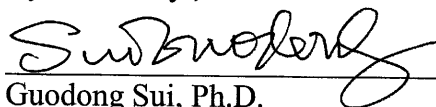
Ramaswamy Narayanan, Ph.D.
Dissertation Advisor



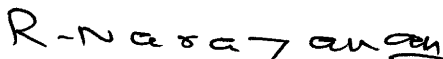
Charles Carraher, Ph.D.



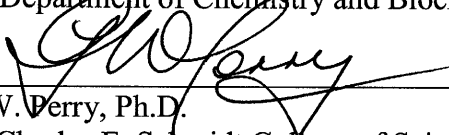
Cyril Parkányi, Ph.D.



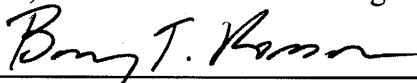
Guodong Sui, Ph.D.



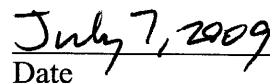
Ramaswamy Narayanan, Ph.D.
Chair, Department of Chemistry and Biochemistry



Gary W. Perry, Ph.D.
Dean, Charles E. Schmidt College of Science



Barry T. Rosson, Ph.D.
Dean, Graduate College


Date

ACKNOWLEDGEMENTS

I would sincerely like to express my appreciation and gratitude to my dissertation advisor Dr. Ramaswamy Narayanan for his constructive criticism, support and guidance which created a positive impact on my scientific career. As my mentor, he always encouraged me to think like a research scientist and helped me in moving forward in my life.

I would like to express special thanks to my committee members (Dr. Charles Carraher, Dr. Cyril Párkányi and Dr. Guodong Sui) for investing their valuable time and efforts, support and guiding me through my doctoral program. I thank my colleagues, faculty and staff from the chemistry department for their utmost support and assistance. My special acknowledgments to Dr. Jayarama Perumareddi, Dr. Patricia Snyder and Dr. Predrag Cudic for their valuable input in my research projects. I am thankful to the professors from the physics department Dr. Fernando Medina and Dr. Andy Lau for their advice and guidance in my research projects.

My special appreciation to Dr. Rajendra Gupta, Dr. Abhijit Pandya, President Brogan and all the administration of Florida Atlantic University for their assistance and support.

ABSTRACT

Author : Amitabh Battin

Title: Determination and Evaluation of Electrical Properties of Metal-Containing Condensation polymers

Institution: Florida Atlantic University

Dissertation Advisor: Dr. Ramaswamy Narayanan

Degree : Doctor of Philosophy

Year: 2009

Doped electrically conductive polymers are one of the critical materials that have allowed the current technological revolution. Essentially all of today's applications of doped conductive polymers involve vinyl-related polymers. While the application of conductive polymers is rapidly increasing there is need for additional materials with different electrical behaviors. The current focus is on studying condensation polymers that contain a metal atom and the possibility of undergoing entire chain delocalization of electrons. The different series of organometallic condensation polymers were synthesized by employing interfacial polycondensation technique and characterization of these products were carried out using standard techniques like light scattering photometer, fourier transform infrared spectroscopy (FTIR), matrix assisted laser desorption ionization time

of flight mass spectroscopy (MALDI TOF MS) and nuclear magnetic resonance spectroscopy (NMR). The electrical measurements were carried out employing Genrad 1650-B impedance spectroscopy. Prior studies conducted in this area have led to the pathway of looking at two aspects; first, surveying 60 metal-containing polymers that can undergo entire chain delocalization studying the effect of different substituents on their electrical properties and secondly, doping selected candidates employing iodine. The products derived from 2-nitro-1,4-phenylenediamine and N-methyl-1,4-phenylenediamines with titanocene dichloride exhibited about 10^3 to 10^5 fold magnitude increases in the electrical conductivity on doping with iodine, moving it near conductive region. This increase is dependent on the concentration of the iodine and is cyclic. The results support the starting premise that selected metal-containing condensation polymers can be doped to increase their electrical conductivity. Further investigation is warranted to see if metal-containing condensation polymers can be important materials in the electronic industry. This research sets the stage for studying not only metal-containing polymeric materials but also to investigate the ability to increase the conductivity of other condensation polymers such as nylons and polyesters through doping.

DEDICATION

I would like to dedicate my dissertation work to my loving parents (Mr. Jaiprakash Battin and Mrs. Ashalata Battin) for their encouragement and moral support throughout my doctoral program. I would like to thank my sister (Ms. Anagha Battin) for continuously keeping me motivated at all times. I sincerely thank my in-laws (Mr. Arvind Kapote and Mrs. Jayshree Kapote) for their support. And finally last but not least I wish to express my gratitude to my lovely wife (Mrs. Anita Battin) who spend sleepless nights and always stood besides me and kept my energy levels high with utmost confidence.

I would also like to dedicate this manuscript to my late grandparents (Mr. Narayan Battin and Mrs. Chandrabhaga Battin) for their blessings and providing me a goal in my life.

**DETERMINATION AND EVALUATION OF ELECTRICAL PROPERTIES OF
METAL-CONTAINING CONDENSATION POLYMERS**

| | |
|---|-----|
| LIST OF FIGURES | xii |
| LIST OF TABLES | xx |
| CHAPTER 1. INTRODUCTION | 1 |
| 1.1 Overview..... | 1 |
| 1.1.1 Electrical Conductivity..... | 2 |
| 1.2 Polyacetylenes: charge transport mechanism..... | 5 |
| 1.3 History and discovery of polyacetylenes..... | 7 |
| 1.4 Applications of conductive polymers..... | 9 |
| 1.5 Background and significance of organometallic polymers..... | 13 |
| 1.6 Hypothesis..... | 15 |
| CHAPTER 2. EXPERIMENTAL | 17 |
| 2.1 Materials and Methodology..... | 17 |
| 2.2 Synthesis..... | 18 |
| 2.2.1 Synthesis of organotin polymers from substituted 4, 6 – diaminopyrimidines..... | 18 |
| 2.2.2 Synthesis of samples especially studied for doping..... | 19 |
| 2.3 Physical Characterization..... | 20 |
| 2.3.1 Solubility of polymers..... | 20 |
| 2.3.2 Molecular weight determination using light scattering photometry..... | 21 |

| | |
|---|-----------|
| 2.3.3 Fourier transform infrared spectroscopy (FTIR)..... | 23 |
| 2.3.4 Nuclear magnetic resonance spectroscopy (^1H and ^{13}C NMR)..... | 24 |
| 2.3.5 Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI TOF MS)..... | 24 |
| 2.4 Determination of particle size..... | 24 |
| 2.5 Measurement of electrical properties..... | 25 |
| 2.5.1 Equations for calculation of dielectric constant, dielectric loss and dissipation factor for the materials..... | 26 |
| CHAPTER 3. RESULTS..... | 29 |
| 3.1 Surveying of undoped Group IVB metallocene - containing polymers..... | 33 |
| 3.1.1 Group IVB metallocene - containing polymers..... | 33 |
| 3.1.2 Group IV B metallocene polyethers..... | 34 |
| 3.1.2(2) Electrical properties of titanocene polyethers from hydroquinone and hydroquinone derivatives with titanocene dichloride..... | 35 |
| 3.1.3 Group IVB metallocene polyesters..... | 40 |
| 3.1.4 Group IVB metallocene phenylsulfonephthalein polydyes..... | 43 |
| 3.1.5 Cobalticene - containing products..... | 46 |
| 3.1.6 Organotin polydyes..... | 47 |
| 3.2 Dibutyltin pyrimidine compounds..... | 50 |
| 3.2.1 Structural characterization of dibutyltin pyrimidine compounds..... | 50 |
| 3.2.2 Fourier Transform Infrared Spectroscopy (FTIR) for determination of functional groups in organotin polyamines..... | 54 |

| | |
|--|-----|
| 3.2.3 MALDI TOF MS for determination of ion fragments..... | 61 |
| 3.2.4 Structure elucidation of 4,6-diaminopyrimidine and dibutyltin dichloride polymer by ^1H and ^{13}C NMR spectroscopy..... | 80 |
| 3.2.4(1) Proton (^1H NMR)..... | 80 |
| 3.2.4(5) Carbon (^{13}C NMR)..... | 83 |
| 3.2.5 Electrical properties of dibutyltin pyrimidines..... | 85 |
| 3.3 Doping Experiments..... | 89 |
| 3.3.1 Surface and bulk doping studies for 2-nitro-1, 4-phenylenediamine titanocene dichloride polymer..... | 89 |
| 3.3.2 Surface conductivity studies for 2-nitro-1, 4-phenylenediamine titanocene dichloride polymer..... | 92 |
| 3.3.3 Cumulative doping..... | 93 |
| 3.3.4 Individual doping..... | 99 |
| 3.3.5 Recycling tests..... | 100 |
| 3.3.6 Bulk conductivity studies for 2-nitro-1, 4-phenylenediamine and titanocene dichloride..... | 106 |
| 3.4 Standard deviation plots (n=3) and comparison of conductivity of 2-nitro-1,4-phenylenediamine titanocene dichloride polymer in undoped and 10% iodine phase..... | 106 |
| 3.4.1 Standard deviation plots (n=3) for 2-nitro-1,4-phenylenediamine/ titanocene dichloride polymer containing 10% iodine concentration..... | 106 |

| | |
|---|-----|
| 3.5 Standard deviation plots (n=3) for 2-nitro-1,4-phenylenediamine/ titanocene dichloride polymer with varying iodine concentrations..... | 112 |
| 3.5.1 Comparison plots for 3%, 5%, 10% and 15% iodine concentrations for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer..... | 112 |
| 3.6 Study of variety of metal atoms (Sn, Zr and Hf) containing 10% iodine and their effect on electrical conductivity..... | 124 |
| 3.6.1 Effect of metal atom on the electrical conductivity..... | 124 |
| 3.6.2 Effect of tin on conductivity of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride product..... | 124 |
| 3.6.3 Effect on conductivity by changing the nature of the Group IVB metal..... | 125 |
| 3.7 Electron donating and electron withdrawing substituents and their effect on electrical conductivity..... | 127 |
| 3.7.1 Effect on conductivity for 2-methoxy-1,4-phenylenediamine and titanocene dichloride product..... | 128 |
| 3.7.2 Effect on conductivity for 1,4-phenylenediamine and titanocene dichloride product..... | 129 |
| 3.7.3 Effect on conductivity for the product of 2,5-dichloro-1,4-phenylenediamine and titanocene dichloride..... | 130 |
| 3.7.4 Effect on conductivity for the product of N-methyl -1,4-phenylenediamine and titanocene dichloride..... | 131 |
| 3.8 Determination of degradation rate for 2-nitro-1,4-phenylenediamine and titanocene dichloride containing 10% iodine..... | 132 |

| | |
|--|------------|
| 3.8.1 Degradation study for 2-nitro-1,4-phenylenediamine and titanocene dichloride product containing 10% iodine concentration..... | 132 |
| 3.9 Structural Analysis..... | 133 |
| 3.9.1 Determination of functional groups for the 1,4-phenylenediamine-derived polymers employing IR spectroscopy..... | 134 |
| 3.9.2 Determination of ion fragments for metal-containing polymers derived from various 1,4-phenylenediamines employing MALDI MS..... | 146 |
| 3.9.3 Molecular weight determination of 1,4-phenylenediamines by light scattering photometry..... | 156 |
| 3.10 Physical characterization summary..... | 157 |
| CHAPTER 4. DISCUSSION & SUMMARY..... | 158 |
| 4.1. Hypothesis..... | 158 |
| 4.2 Specific aims..... | 158 |
| 4.3 Discussion..... | 159 |
| 4.4. Critical Issues..... | 167 |
| 4.5 Future Directions..... | 168 |
| 4.6 Summary..... | 172 |
| REFERENCES..... | 173 |

LIST OF FIGURES

| | |
|--|----|
| 1.1.1(1) Electrical conductivity chart..... | 2 |
| 2.2.1(1) Flowchart for synthesis of organotin polymers..... | 19 |
| 2.2.2(1) Synthesis of polymer from reaction of 2-nitro-1, 4 – phenylenediamine and titanocene dichloride..... | 20 |
| 3.1.1(1) Cyclopentadiene groups present in a distorted tetrahedral fashion..... | 33 |
| 3.1.2(1) Reaction of hydroquinone and its derivatives with titanocene dichloride..... | 34 |
| 3.1.2(4) Conductivity plot for hydroquinone and titanocene dichloride as a function of applied frequency..... | 36 |
| 3.1.2(5) Structure of the product of hydroquinone and titanocene dichloride..... | 36 |
| 3.1.2(6) Conductivity plots for hydroquinone and its derivatives as a function of applied frequency..... | 37 |
| 3.1.2(8) Conductivity plot for tetrachlorohydroquinone and zirconocene dichloride as a function of applied frequency..... | 39 |
| 3.1.2(9) Conductivity plot for phenylhydroquinone and dibutyltin dichloride as a function of applied frequency..... | 40 |
| 3.1.3(1) Synthesis of Group IVB metallocene polyesters..... | 40 |
| 3.1.3(2) Conductivity plot for the titanocene polyesters as a function of applied frequency..... | 41 |
| 3.1.4(1) Flavazin L and Cp_2TiCl_2 product..... | 43 |

| | |
|--|----|
| 3.1.4(2) Acid Red 88 and Cp_2TiCl_2 product..... | 43 |
| 3.1.4(3) Crocein Orange G and Cp_2ZrCl_2 product..... | 44 |
| 3.1.4(4) Orange II and Cp_2ZrCl_2 product..... | 44 |
| 3.1.4(5) Acid Yellow II and Cp_2HfCl_2 product..... | 44 |
| 3.1.4(6) Conductivity plot for phenylsulfonephthalein dyes and various organometallic dihalides as a function of applied frequency..... | 45 |
| 3.1.5(1) Cobalticene hexafluorophosphate and Ph_2SnCl_2 product..... | 46 |
| 3.1.5(2) Cobalticene hexafluorophosphate and Ph_3BiCl_2 product..... | 46 |
| 3.1.5(3) Cobalticene hexafluorophosphate and Ph_3SbCl_2 product..... | 46 |
| 3.1.5(4) Conductivity plot for cobalticene hexafluorophosphate polyesters with organometallic dihalides as a function of applied frequency..... | 47 |
| 3.1.6(1) Organotin polymer from Eosin Y (R = Phenyl)..... | 48 |
| 3.1.6(2) Organotin polymer from Eosin Y (R = Methyl)..... | 48 |
| 3.1.6(3) Phloxine B and Ph_2SnCl_2 product..... | 48 |
| 3.1.6(4) Rose Bengal and Ph_2SnCl_2 product..... | 49 |
| 3.1.6(5) Conductivity plot for the series of organotin polydyes as a function of applied frequency..... | 49 |
| 3.2.1(1) Structure of polypyrrole..... | 50 |
| 3.2.1(2) Synthesis of organotin polyamines..... | 51 |
| 3.2.2(2) IR spectrum for dibutyltin dichloride monomer..... | 56 |
| 3.2.2(3) IR spectrum of 4-chloro-2,6-diaminopyrimidine monomer..... | 57 |
| 3.2.2(5) IR spectra for 4-chloro-2,6-diaminopyrimidine/dibutyltin dichloride polymer..... | 59 |

| | |
|---|----|
| 3.2.3(3) MALDI MS for 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride..... | 64 |
| 3.2.3(4) Ion fragment cluster at 565 daltons for 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride..... | 65 |
| 3.2.3(5) Structural assignment for the ion fragment cluster at 565 Da..... | 65 |
| 3.2.3(6) Computer simulation for ion fragment cluster at 565 Da containing one 2,4-diamino-6- hydroxy-5-nitrosopyrimidine unit and two dibutyltin units..... | 66 |
| 3.2.3(7) Expanded MALDI MS for the ion fragment cluster at 618 Da..... | 67 |
| 3.2.3(8) Tentative assignment centered at 618 Da..... | 67 |
| 3.2.3(9) Computer simulation for ion fragment cluster at 618 Da..... | 68 |
| 3.2.3(10) MALDI MS for ion fragment cluster at 636 Da..... | 69 |
| 3.2.3(11) Structural assignment for the ion fragment cluster at 636 Da..... | 70 |
| 3.2.3(12) Computer simulation for ion fragment cluster at 636 Da containing two dibutyltin moieties connected to 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and NH moiety..... | 70 |
| 3.2.3(13) MALDI MS for ion fragment cluster at 795 Da..... | 71 |
| 3.2.3(14) Structural assignment for the ion fragment cluster at 795 Da..... | 72 |
| 3.2.3(15) Computer simulation for ion fragment cluster at 795 Da containing two dibutyltin moieties connected to two 2,4-diamino-6-hydroxy-5-nitrosopyrimidine plus one sodium ion..... | 72 |
| 3.2.4(2) ¹ H NMR spectrum for 4,6-diaminopyrimidine..... | 80 |
| 3.2.4(3) ¹ H NMR spectrum for dibutyltin dichloride..... | 81 |

| | |
|---|-----|
| 3.2.4(4) ^1H NMR spectrum for the product of 4,6-diaminopyrimidine and dibutyltin dichloride..... | 81 |
| 3.2.4(6) ^{13}C NMR spectrum for 4,6-diaminopyrimidine hemisulfate..... | 84 |
| 3.2.4(7) ^{13}C NMR spectrum for dibutyltin dichloride..... | 84 |
| 3.2.4(8) ^{13}C NMR spectrum for the product of 4,6-diaminopyrimidine and dibutyltin dichloride..... | 85 |
| 3.2.5(1) Conductivity plot for 4,6-diaminopyrimidine derivatives and dibutyltin dichloride as a function of applied frequency..... | 86 |
| 3.3.1(2) Reaction between 2-nitro-1,4-phenylenediamine and titanocene dichloride..... | 92 |
| 3.3.3(3) Comparison of undoped vs. sample exposed to iodine vapors for 5 seconds for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer as a function of applied frequency..... | 96 |
| 3.3.3(4) Results for single experiment (n=1) for surface conductivity as a function of cumulative doping with iodine vapors for different doping intervals..... | 97 |
| 3.3.4(1) Data for single experiment (n=1) showing the effect on surface conductivity by individual doping with iodine vapors for different doping intervals..... | 100 |
| 3.3.5(1) Surface conductivity measurements at different doping intervals at 0.4 KHz..... | 101 |
| 3.3.5(2) Surface conductivity measurements at different doping intervals at 1 KHz..... | 101 |
| 3.3.5(3) Surface conductivity measurements at different doping intervals at 2 KHz..... | 102 |

| | |
|--|-----|
| 3.3.5(4) Surface conductivity measurements at different doping intervals at 5 KHz..... | 102 |
| 3.3.5(5) Surface conductivity measurements at different doping intervals at 10 KHz..... | 103 |
| 3.4.1(3) Conductivity plot for repeat experiments (n=3) for the undoped sample as a function of applied frequency..... | 108 |
| 3.4.1(6) Conductivity plot for repeat experiments (n=3) for polymer containing 10% iodine as a function of applied frequency..... | 110 |
| 3.4.1(9) Conductivity values for repeat experiments (n=3) for samples containing 10% iodine heated for 10 seconds as a function of applied frequency..... | 112 |
| 3.5.1(2) Conductivity for repeat experiments (n=3) for unheated samples mixed at varying iodine amounts as a function of applied frequency..... | 114 |
| 3.5.1(4) Conductivity for repeat experiments (n=3) for samples mixed at varying iodine amounts heated for 10 seconds as a function of applied frequency..... | 115 |
| 3.5.1(6) Conductivity for repeat experiments (n=3) for samples mixed with varying iodine amounts heated for 20 seconds as a function of applied frequency..... | 117 |
| 3.5.1(8) Conductivity for repeat experiments (n=3) for samples mixed with varying iodine amounts heated for 30 seconds as a function of applied frequency..... | 118 |

| | |
|--|-----|
| 3.5.1(10) Conductivity for repeat experiments (n=3) for samples mixed with varying iodine amounts heated for 60 seconds as a function of applied frequency..... | 119 |
| 3.5.1(12) Conductivity for repeat experiments (n=3) for samples mixed with varying iodine amounts heated for 480 seconds as a function of applied frequency..... | 121 |
| 3.5.1(13) Conductivity for repeat experiments (n=3) for sample with 3% iodine concentration heated at different intervals as a function of applied frequency..... | 122 |
| 3.5.1(14) Conductivity plot for samples containing 10% iodine heated at different intervals as a function of applied frequency..... | 122 |
| 3.5.1(15) Conductivity for repeat experiments (n=3) for sample with 15% iodine concentration heated at different intervals as a function of applied frequency..... | 123 |
| 3.6.2(1) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride containing 10% iodine heated at different time intervals..... | 125 |
| 3.6.3(1) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and zirconocene dichloride containing 10% iodine heated at different times..... | 126 |
| 3.6.3(2) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and hafnocene dichloride containing 10% iodine heated for different periods..... | 127 |

| | |
|--|-----|
| 3.7.1(1) Conductivity plot (single experiment) for the product of 2-methoxy-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different periods..... | 128 |
| 3.7.2(1) Conductivity plot (single experiment) for the product of 1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different intervals..... | 129 |
| 3.7.3(1) Conductivity plot (single experiment) for the product of 2,5-dichloro-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different times..... | 130 |
| 3.7.4(1) Conductivity plot (single experiment) for the product of N-methyl-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different time intervals..... | 131 |
| 3.8.1(1) Conductivity plot (single experiment) representing the degradation rate for the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride by placing in the open atmosphere for different time durations..... | 133 |
| 3.9.1(3) IR spectrum for 2-nitro-1, 4-phenylenediamine monomer..... | 137 |
| 3.9.1(4) IR spectrum for 2-nitro-1,4-phenylenediamine and titanocene dichloride..... | 138 |
| 3.9.1(5) IR spectrum for 2-nitro -1,4-phenylenediamine and titanocene dichloride doped with iodine..... | 139 |
| 3.9.2(1) MALDI MS for 2-nitro-1,4-phenylenediamine and titanocene dichloride in the undoped state over the mass range of 100 to 500 Da..... | 147 |

| | |
|---|-----|
| 3.9.2(2) MALDI MS for 2-nitro-1,4-phenylenediamine and titanocene dichloride | |
| in the doped state over the mass range of 100 to 500 Da..... | 148 |
| 3.9.2(6) MALDI MS for N-methyl-1,4-phenylenediamine and titanocene dichloride | |
| in the undoped state over the mass range of 100 to 500 Da..... | 152 |
| 3.9.2(7) MALDI MS for N-methyl-1,4-phenylenediamine and titanocene dichloride | |
| in the doped state over the mass range of 100 to 500 Da..... | 153 |
| 3.9.2(9) Significant ion fragments derived from the matrix | |
| (α -cyano-hydroxy cinnamic acid) (CHCA)..... | 155 |
| 4.3.1(2) Possible mechanistic scheme for the substitution of iodine | |
| on the phenylene ring..... | 166 |
| 4.5.1(1) Reaction between 2-nitro-1,4-phenylenediamine and | |
| terephthaloyl chloride..... | 169 |
| 4.5.1(2) Illustration of chain growth termination through the | |
| use of monofunctional reactants..... | 170 |

LIST OF TABLES

| | |
|---|----|
| 2.3.2(1) Standards for light scattering photometer..... | 23 |
| 2.5.1(1) Parameters involved in calculation of bulk conductivity..... | 27 |
| 3.1.2(3) Electrical properties for hydroquinone and titanocene dichloride as a function of applied frequency..... | 35 |
| 3.1.2(7) Conductivity for titanocene polyether products as a function of electron density on the phenylene moiety..... | 38 |
| 3.1.3(3) Conductivity for terephthalic acid products as a function of electron density on the phenylene moiety..... | 42 |
| 3.2.1(3) Product yields, molecular weights and chain lengths for the dibutyltin polyamines..... | 51 |
| 3.2.1(4) Results for solubility tests for the series of dibutyltin pyrimidines in various attempted polar liquids..... | 53 |
| 3.2.2(1) IR assignments dibutyltin dichloride and Sn-N moiety..... | 55 |
| 3.2.2(4) IR bands from 4-chloro-2,6-diaminopyrimidine and dibutyltin dichloride polymer..... | 58 |
| 3.2.3(1) Isotopic abundances of tin..... | 62 |
| 3.2.3(2) Major ions for 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride..... | 63 |

| | |
|---|----|
| 3.2.3(16) Significant ion fragments from 2, 4-diamino-6-hydroxypyrimidine and dibutyltin dichloride..... | 74 |
| 3.2.3(17) Isotopic abundance matches for ion fragment 2U-Bu containing two tin atoms from 2,4,-diamino-6-hydroxypyrimidine and dibutyltin dichloride..... | 75 |
| 3.2.3(18) Isotopic abundance matches for ion fragment 3U-Bu containing three tin atoms from 2,4,-diamino-6-hydroxypyrimidine and dibutyltin dichloride..... | 76 |
| 3.2.3(19) Ion fragments from 4,6-diaminopyrimidine and dibutyltin dichloride between 500 to 5000 Da..... | 77 |
| 3.2.3(20) Isotopic abundance matches for ion fragments containing two tin atoms from 4,6-diaminopyrimidine and dibutyltin dichloride..... | 78 |
| 3.2.3(21) Isotopic abundance matches for ion fragments containing three tin atoms from 4,6-diaminopyrimidine and dibutyltin dichloride..... | 79 |
| 3.2.5(2) Electrical conductivity results for series of undoped samples..... | 87 |
| 3.3.1(1) Results for samples exposed to iodine vapors..... | 91 |
| 3.3.3(1) Electrical properties for undoped 2-nitro-1,4-phenylenediamine/ titanocene dichloride polymer as a function of applied frequency..... | 94 |
| 3.3.3(2) Electrical properties for 2-nitro-1,4-phenylenediamine/ titanocene dichloride polymer exposed to iodine vapors for 5 seconds as a function of applied frequency..... | 95 |
| 3.3.3(5) Weight increases of the test polymer disk exposed to iodine vapors as a function of doping time..... | 99 |

| | |
|--|-----|
| 3.3.5(6) Summary of surface conductivity values at different doping intervals at 1 KHz frequency..... | 104 |
| 3.4.1(1) Electrical properties for the undoped product of 2-nitro-1,4-phenylenediamine and titanocene dichloride as a function of applied frequency..... | 107 |
| 3.4.1(2) Log conductivity and standard deviation values for undoped sample as a function of applied frequency..... | 107 |
| 3.4.1(4) Electrical properties for 2-nitro-1,4,-phenylenediamine and titanocene dichloride containing 10% iodine as a function of applied frequency without heating..... | 109 |
| 3.4.1(5) Log conductivity and standard deviation values for samples containing 10% iodine as a function of applied frequency..... | 109 |
| 3.4.1(7) Electrical properties for 2-nitro-1,4,-phenylenediamine and titanocene dichloride containing 10% iodine heated for 10 seconds as a function of applied frequency..... | 111 |
| 3.4.1(8) Standard deviation results for the polymer containing 10% iodine heated for 10 seconds as a function of applied frequency..... | 111 |
| 3.5.1(1) Bulk conductivity results for unheated samples containing varying iodine concentrations as a function of applied frequency..... | 113 |
| 3.5.1(3) Bulk conductivity results for samples containing varying iodine concentrations heated for 10 seconds as a function of applied frequency..... | 115 |
| 3.5.1(5) Bulk conductivity results for samples containing varying iodine concentrations heated for 20 seconds as a function of applied frequency..... | 116 |

| | |
|--|-----|
| 3.5.1(7) Bulk conductivity results for samples containing varying iodine concentrations heated for 30 seconds as a function of applied frequency | 117 |
| 3.5.1(9) Bulk conductivity results for samples containing varying iodine concentrations heated for 60 seconds as a function of applied frequency | 119 |
| 3.5.1(11) Bulk conductivity results for samples containing varying iodine concentrations heated for 480 seconds as a function of applied frequency | 120 |
| 3.9.1(1) IR assignments for titanocene dichloride | 135 |
| 3.9.1(2) IR assignments for 2-nitro-1,4-phenylenediamine monomer and undoped and doped products with titanocene dichloride | 136 |
| 3.9.1(6) IR assignments for the undoped and doped products from 2-nitro-1,4-phenylenediamine and zirconocene dichloride | 141 |
| 3.9.1(7) IR assignments for the undoped and doped products from 2-nitro-1,4-phenylenediamine and hafnocene dichloride | 143 |
| 3.9.1(8) IR assignments for N-methyl-1,4-phenylenediamine monomer and undoped and doped products with titanocene dichloride | 144 |
| 3.9.2(3) Significant ion fragments in the mass range of 100 to 500 Da for the undoped and the doped products of 2-nitro-1,4-phenylenediamine and titanocene dichloride | 149 |
| 3.9.2(4) Significant ion fragments in the mass range of 100 to 500 Da for the undoped and doped product of 2-nitro-1,4-phenylenediamine and zirconocene dichloride | 150 |

| | |
|---|-----|
| 3.9.2(5) Significant ion fragments in the mass range of 100 to 500 Da for the undoped and doped product of 2-nitro-1,4-phenylenediamine and hafnocene dichloride..... | 151 |
| 3.9.2(8) Significant ion fragments in the mass range of 100 to 500 Da for the undoped and the doped product of N-methyl-1,4-phenylenediamine and titanocene dichloride..... | 154 |
| 3.9.3(1) Molecular weight and chain length for the metallocene polyamines..... | 156 |
| 4.3.1(1) General conductivity values for the polymer samples surveyed..... | 160 |

CHAPTER 1. INTRODUCTION

1.1 Overview

Until the advent of conducting polymers, polymers were considered nonconductive materials and widely used as insulating materials in industry [1]. In 1975, MacDiarmid and Heeger began studying the metallic properties of inorganic poly(sulfur nitride) [2]. They shifted their efforts to polyacetylene after visiting with Shirakawa [3]. These partnerships lead to the creation of polyacetylene that became a conductor through doping [4]. It signaled the beginning of the development of conductive polymers. In 2000 their efforts were recognized by being awarded the Nobel Prize in developing the field of conducting polymers [5]. Today, conductive polymers are used as electrochemical capacitors [6], corrosion inhibitors [7], electromagnetic shielding [8, 9] and in smart windows [10] that vary the amount of light passing through them. Second generation of conductive polymers is used as transistors [11, 12] and light emitting diodes [13, 14]. Conductive polymers have a number of advantages over metals as conductive materials including ease of processing of complex designs and low density. They generally suffer in comparison to metal-based conductors in having a limited current capacity and being sensitive to moisture and oxygen [15]. Today's polymeric conductors are based on vinyl polymers such as polyacetylene, polyaniline and polypyrrole. The topic of conducting polymers has been recently reviewed [16-25].

1.1.1 Electrical conductivity

The electrical conductivity of the materials varies widely. General limits of the divisions of conductivity are given in **Figure 1.1.1(1)**

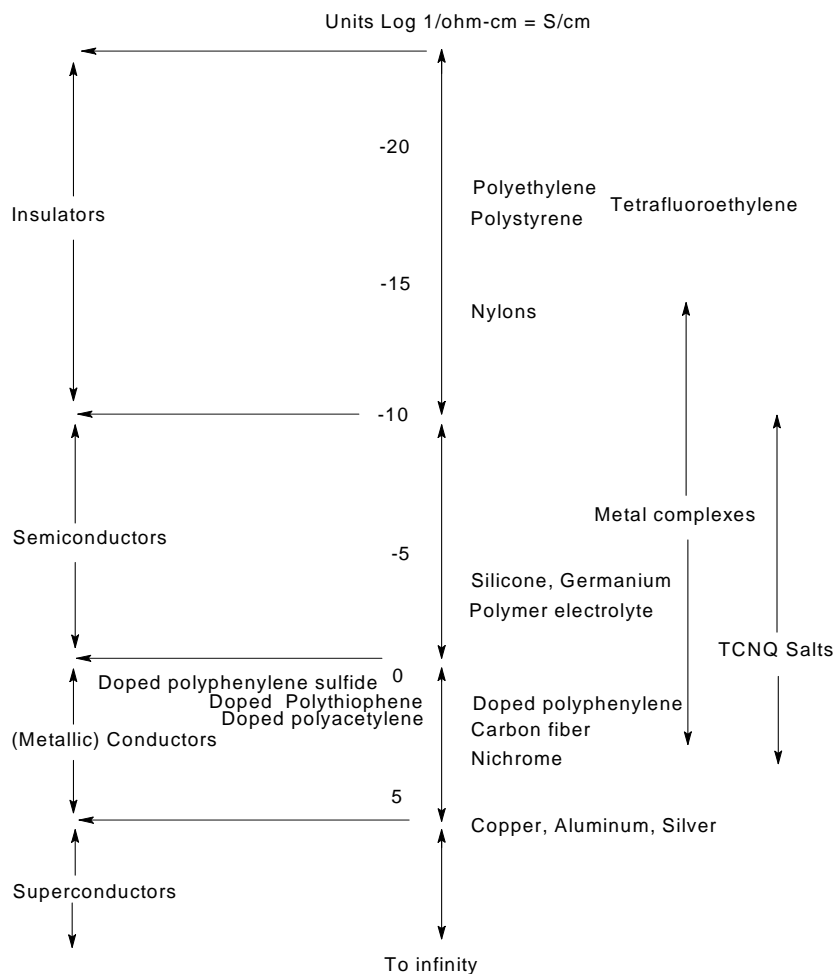


Figure 1.1.1(1) Conductivity values of conductive polymers in comparison with other materials ranging from quartz (insulator) to copper (conductor) where S = Sieman = 1/ohm [26].

An electrical conductor is defined as a material that has an ability to conduct electricity.

A material that has an electrical conductivity intermediate between a conductor and an insulator is termed a semiconductor. An insulator is defined as a material that does not possess any electrical conductivity. Some organic semiconductors can be transformed into conductive polymers by doping similar to inorganic semiconductors. Organic semiconductors are generally based on conductive polyacetylenes. Conductive polyacetylene, as well as polyaniline, polypyrrole, polythiophene and their derivatives are widely employed in most studies involving organic semiconductors [27]. Conductive polymers have structures that allow delocalization of electrons throughout their backbone. When charge carriers (electrons or holes) are introduced into the conduction or valence bands, increases in the electrical conductivity of the material are observed. Known conductive polymers are semiconductors in their non-doped state.

The band gap is the energy needed to excite an electron from a valence band to an empty conduction band. Metals have zero band gaps since they do not have localized valence electrons, i.e. the valence electrons are shared within the metal grouping. Insulators like polyethylene have a large band gap which means a lot of energy is needed for exciting an electron into an empty conduction band. Semiconductors have partially filled valence bands and a small band gap that can be overcome with the application of some electric current; hence their conductivity is intermediate between that of a conductor and an insulator.

Semiconductors play a vital role in technology and in today's society. Different combinations of semiconductors, usually silicon and germanium, allow the generation of devices with electrical properties which are helpful for controlling electrical signals.

Applications of semiconductors in industry include manufacturing of integrated circuits, diodes, transistors and silicon chips.

Semiconductors are classified into two types:

1) Intrinsic semiconductors: An intrinsic semiconductor is often referred to as an undoped semiconductor. In its pure form, an intrinsic material is a semiconductor without the presence of a significant amount of dopant concentration. The amount of charge carriers, either holes or electrons, is determined by the material's properties rather than the presence of impurities. In case of intrinsic semiconductors, the number of electrons and holes in the conduction and valence bands are equivalent. Thermal excitation or crystal defects can give rise to the conductivity in intrinsic semiconductors. Silicon and germanium are examples of intrinsic semiconductors [28]. Even so, the major material used in the construction of integrated circuits is doped silicon that changes it from a semiconductor to a conductor and as such silicon is also an extrinsic semiconductor.

2) Extrinsic semiconductors: An extrinsic semiconductor is a doped semiconductor. The process of doping involves addition of dopant atoms which changes the carrier concentrations of holes and electrons in a semiconductor. Doping increases the conductivity of the extrinsic semiconductor doped materials. Extrinsic semiconductors are further classified as n-type or p-type semiconductors [29].

The doping of a semiconductor is a process that changes an intrinsic or an undoped semiconductor to an extrinsic or doped semiconductor. In an intrinsic semiconductor, impurity atoms are added during the doping process. These impurity atoms are different than the atoms of an intrinsic semiconductor. The impurity atoms behave as donors or acceptors to the intrinsic or undoped semiconductor which changes

the concentrations of electrons and holes of the semiconductor. Depending on the effect on an intrinsic semiconductor, these impurity atoms can be classified as donor or acceptor atoms. For an n-type doped semiconductor, the doping agent adds additional electrons resulting in the material having an excess of electrons [29]. Examples of n-type semiconductor are doping pure silicon crystals with pentavalent impurity atoms like phosphorous, arsenic or antimony. Here, four covalent bonds are formed with one unbounded electron. This extra electron is easily excited into the conduction band as it is loosely held by the atom. In this case, the flow of the current is due to the excess electrons since they are the majority carriers. Because the doping atom has an extra electron these doping atoms are called donor atoms.

In p-type semiconductors, the number of valence electrons is less creating a material with “holes” [29]. Examples of p-type semiconductors are doping pure silicon crystals with trivalent impurity atoms like aluminum or boron. Of the usual four covalent bonds of the doped material, one electron is deficit in case of p-type materials. The movement of holes is the result of accepting an electron from the neighboring atom for the completion of fourth bond. The holes act as a positive charge quantity. In such p-type materials, since doping is carried out using a trivalent impurity, the dopant atoms accept an electron and hence are called acceptor atoms.

1.2 Polyacetylenes: charge transport mechanism

The concept of electron delocalization is a mechanism whereby polyacetylene types of polymers become conductive on doping creating an avenue for delocalization of electrons. [30-32]. In polyacetylene, every backbone carbon is connected by strong

localized “sigma” bond. They are further connected by a network of alternating less localized and weaker “pi” bonds. When dopants are introduced in these materials, an increase or deficiency of electrons is observed at those particular sites. When a deficiency of electrons or holes is created, electron flow occurs and fills this hole with the newly created hole which allows the charge to migrate within and between these polyacetylene chains. Hence, the concept of whole chain delocalization is used to describe how the charges might migrate from one chain to another [33].

Prior work has shown that compounds with whole chain delocalization are apt to act as extrinsic semiconductors whose conductivities can be increased through appropriate doping whereas other similar materials without whole chain delocalization are less conductive [34-36].

Today’s conversion of semiconductive polymers into near conductors or conductors is based on the addition of a doping agent. Iodine is widely used as a doping agent. It is experimentally easy to work with and does not induce degradation of the polymer which is a problem for many other doping agents [37]. Iodine doping can be carried out using two methods - an iodine chamber or in situ method. The iodine chamber method is the easiest method for surface doping of the materials [38]. In this method, the iodine crystals placed in a glass beaker are heated slowly and polymer films and disks are exposed to the iodine vapors [39]. This technique measures the surface behavior of the materials. In the in situ method [40] iodine is physically added to the sample and the measurements are carried out on samples containing varying amounts of added iodine. This technique involves the bulk behavior of the materials. Both techniques have been

employed in the present research but emphasis has been made using the in situ method because the iodine amounts can be more easily controlled.

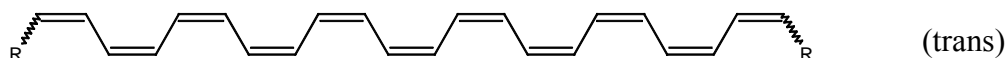
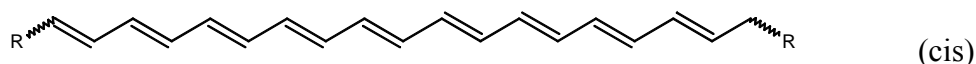
Our current project involves doping organometallic polymers with iodine and is referred to as “p-type” since iodine being an oxidizing agent, withdraws electrons from the polymer resulting in the formation of positive charges or holes. Since p-type doping gives rise to positive holes, holes are responsible for charge conduction in these materials.

1.3 History and discovery of polyacetylenes

Alan MacDiarmid, Alan Heeger and Hideki Shirakawa were awarded the Nobel Prize in Chemistry in 2000 for their innovative discovery and development of electrically conductive polymers. [41-44]. In 1975, Alan MacDiarmid and Alan Heeger began with the study of the metallic and stability properties of poly (sulfur nitride) (SN)_x to oxygen, air and water vapor [45] but moved their efforts to polyacetylene films after visiting with Hideki Shirakawa. Shirakawa and co-workers used a Ziegler Natta catalyst [46] for the preparation of polyacetylene silvery films in 1974. Despite the metallic appearance of the polyacetylene film, it was not electrically conductive. MacDiarmid, Heeger and Shirakawa found that the conductivity of the polyacetylene films could be increased through exposure of the films to oxidizing agents such as iodine. Initially the increases in conductivity were modest but eventually they achieved 10⁹ fold increases in the conductivity of polyacetylene films [47]. Treatment with agents such as iodine was termed “doping” similar to the addition of doping agents to silicon. Doped forms of polyacetylene exhibited a conductivity of 10⁵ S m⁻¹, which was found to be higher than the conductivity of any other polymer at that time. For comparison, the conductivity of

polytetrafluoroethylene (Teflon) is $10^{-16} \text{ S m}^{-1}$ and silver and copper have conductivities of 10^8 S m^{-1} .

A great deal of effort and learning occurred to understand the doping effects and limits. MacDiarmid carried out the doping of polyacetylene film by treatment with iodine. Shirakawa found that treatment of polyacetylene silvery films with chlorine or bromine altered the infrared transmission indicating that some degradation may have occurred. [48-50]. Polyacetylene has been produced by several methods, many utilizing the Zeigler-Natta polymerization systems. Both cis and trans isomers exist. The cis-polyacetylene is copper-colored with films having a conductivity of about 10^{-8} S/meter . By comparison, the trans-polyacetylene is silver-colored with films having a much greater conductivity on the order of 10^{-3} S/meter . Conductivity is dependent on the micro or fine structure of the fibrils, doping agent, extent and technique and aging of the sample. [51-53].



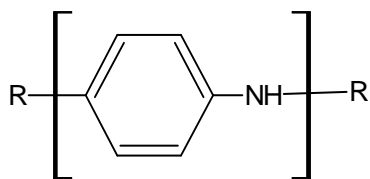
Conductive polyacetylene is largely crystalline [54] and is easily oxidized by the presence of oxygen in air and is sensitive to humidity. Polyacetylene films have limited flexibility and have a lustrous, silvery appearance. [55, 56].

Polyacetylene film is composed of small fibers or fibrils that are oriented in a random manner. As a result the conductivity of the film might be small because there are not enough contacts between these randomly oriented fibrils. Generally, two approaches

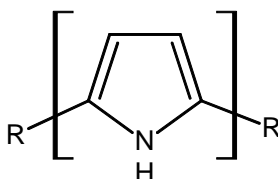
can be utilized to align polyacetylene fibrils. One approach is employing a liquid crystal solvent for the polymerization of acetylene and forming the film under agitation. Another approach is stretching the polyacetylene film mechanically which will help to orient the fibrils to align. Comparing the conductivities of the polyacetylene film, the conductivity is 100 times greater in the direction of the stretch compared to the measurements taken perpendicular to the stretching direction [57, 58]. The conductivity of the polyacetylene films is dependent on the precise structure of the fibrils, technique employed to make the measurement and doping agent.

1.4 Applications of conductive polymers

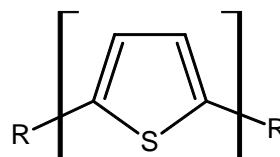
Today, the most widely used conductive polymers are polyaniline, polypyrrole, polythiophene and derivatives of these polymers.



Polyaniline



Polypyrrole



Polythiophene

Following are the application areas of conductive polymers grouped according to their classification. Thus far conductive organic polymers have been used in the following applications.

i) Electrostatic materials: Preventing accumulation of building up of static electricity is possible by coating an insulator with a thin layer of conducting polymer. The sudden discharge of static electricity in computer areas can cause damage to the microcircuits. At a low voltage, the integrated circuits which are more sensitive can be damaged by static

discharge. Hence, the thermoplastic material is modified by addition of a conducting plastic which can be used to protect against electrostatic discharge [59, 60].

ii) Conducting adhesives: Most electrical devices generate electromagnetic radiation generally within the microwave frequencies. This can result in the malfunctioning of the electrical devices. The plastic casing in many electrical devices is susceptible to such types of radiation. This radiation can be absorbed by coating the inner side of the plastic casing with a conductive surface. In this case, conducting plastics are often employed because they are inexpensive, easily applicable in the form of thin layers with a complex structure, and can be used with a wide range of resins. The conducting adhesive gives an appropriate coverage and good thermal expansion properties [61]. It is possible to stick the two surfaces together by placing monomer material between two conducting surfaces and allowing them to polymerize. This kind of conductive adhesive can be used to stick conducting surfaces together allowing an electric current to pass through them. The conducting adhesives find applications in electronic packaging with emphasis on mechanical and electrical performance of the materials [62, 63]. Today, the electrically conductive adhesives can be used as a solder replacement in the industry [64].

iii) Printed circuit boards: Printed circuit boards, which are copper coated epoxy resins, are used in many electrical appliances. The copper is etched producing conducting lines to connect electrical devices. They are put in the holes which are cut into the resin. For attaining a good connection, the holes are lined with a conductor. Copper is often used but the coating method encounters several problems namely it is an expensive process, the plating is not selective and the adhesion is poor. This process is being replaced by use of conducting polymers. This process is inexpensive, easily applicable, selective and has

good adhesion ability [65]. Conductive polymers are also being employed in lithography and in printed circuit board technology [66].

iv) Molecular electronics: Molecular electronics involves the use of conducting polymers which are assembled atom by atom. For example, polyacetylene can be treated to have an electron accepting group at one end and an electron withdrawing group at the other. A spacer or modifiable barrier is used to decouple the functional groups [67].

v) Sensors: Conducting polymers are finding many uses as sensors. This involves the material's ability to change their electrical properties with various doping agents or in the presence of varying heat or moisture content. The development of gas sensors is an example. Polypyrrole behaves as a quasi p-type material. Polypyrrole's resistance is found to increase in presence of ammonia which is a reducing gas and decrease in presence of nitrogen dioxide which is an oxidizing gas. The presence of these gases cause a change near surface charge carrier density by reacting with the oxygen ions adsorbed on the surface. Thus, the conductivity of polypyrrole is used to detect the presence of ammonia and nitrogen dioxide [68].

vi) Rechargeable batteries and solid electrolytes: Conductive polymers are being used in the construction of light weight rechargeable batteries. One such battery employs a polypyrrole – lithium combination that makes use of oxidation and reduction occurring along the polymer backbone. During the charge process, the polymer undergoes oxidation creating anions in the electrolyte which enters the porous polymer and balances the created charge. On the other hand, the lithium ions in the electrolyte are simultaneously electrodeposited on the lithium surface. During the discharge process, electrons are taken away from lithium which causes lithium ions again to enter the

electrolyte by passing through the load in the oxidized polymer. This results in the reduction of positive sites on the polymer which releases the charge balance anions again into the electrolyte. This process is similar to that found for a typical secondary battery cell [69]. Applications of this include the construction of microtweezers, microvalves and micropositioners for microscopic optical elements [70].

vii) Electromechanical actuators: Electromechanical actuators based on conducting polymers have attracted increasing interest because of their characteristic features like generation of large mechanical stress, high reversibility, maximum strain and precise control over small voltages [71]. Conducting polymers can also be used for conversion of electrical energy into mechanical energy. This makes use of significant size changes during doping and de-doping of conducting polymers. In electromechanical actuators, anodic and cathodic strips change sizes at different rates during charging and discharging processes [72].

viii) General applications: The main interest in using conductive polymers is the low manufacturing cost of the materials. Inkjet printer techniques can be employed in the manufacture of integrated circuits and light displays [73-77].

Following is a brief summary of some of the current applications of conductive organic polymers based on particular polymers.

1) Doped polyaniline has been employed as a conductor and to act as electromagnetic shielding for electronic circuits [78, 79].

2) Doped poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid is used as an antistatic coating material that prevents exposure of electrical discharge on photographic emulsions and it is used as a hole injecting electrode material in polymeric

light emitting devices. Doped PEDOT/ PSS find applications to optoelectronic devices such as patterning and inkjet printing [80]. Doped PEDOT/ PSS are used as chemical and biological sensors [81].

3) Derivatives of polythiophene find applications in the construction of field effect transistors [82].

4) Polypyrroles are used in sensing devices and also as microwave-absorbing “stealth” screen coating materials [83]. The conducting polypyrroles are employed as biosensors for biomolecules and in drug delivery systems [84].

1.5 Background and significance of organometallic polymers

Metal-containing polymers form some of the basis of life. They are at the heart of respiration (hemoglobin) and photosynthesis (chlorophyll) and thus are integral to animal and plant life.

The initial organometallic polymers of interest were based on silicon. In the 1920s Kipping first synthesized polysiloxanes [85]. Polysiloxane boots made the first footprints on the moon. They are employed as adhesives, lubricants, insulators, in cookware and medical applications, etc. The first organotin polymers were synthesized by Montermoso and co-workers in US [86] in 1958 and by Kochkin and Dothers [87] in Russia in the late 1950's based on organotin containing vinyl reactants. By the early 1970's these efforts were increased to organotin condensation polymers by Carraher and coworkers [88]. There are a large number of organotin compounds in commercial use than for any other metal. Essentially all of the organotin polymers have the dibutyltin moiety as the tin-containing unit. They are employed as thermal stabilizers for poly(vinyl chloride) fabrication and as antifouling and anti mildew agents in industry and agriculture and as

additives in paint formulations. During World War II, the US Air Force sponsored a large research program to find thermally stable polymers. Most of these efforts involved the synthesis and thermal characterization of transition-containing polymers. Unfortunately, the search did not provide useful materials with the polymers less thermally stable than the monomeric materials. Moreover, the materials were intractable and only oligomeric in nature. Further, these materials were not soluble. In the early 1950's two groups synthesized ferrocene [89, 242]. Ferrocene is a sandwich compound with iron resting between two cyclopentadiene groups which have a flat planar symmetry [90-95]. In 1955 Arimoto and Haven from DuPont reported the polymerization of vinylferrocene [96]. This did not attract much attention until the work of Hayes and George [97] and Pittman and coworkers in the 1970's [98] when they reported the synthesis of a variety of other ferrocene-containing polymers and copolymers. Many ferrocene-containing polymers have been investigated since then [99-102]. Unlike the true sandwich ferrocene structures, Group IV B metallocenes have distorted tetrahedral geometry with the cyclopentadiene groups facing the metal atom [103]. Cotton and Wilkinson described Group IV B metallocene compounds as 9-coordinate bonding hybrid orbitals which are derived from 1-s, 3-p and 5-d orbitals. The Group IV B metallocenes are important Ziegler-Natta catalysts and significant in the production of soluble catalysts [104]. In the early 1970's, Carraher and co-workers began synthesizing various condensation polymers based on the reaction of Group IVB metallocenes with various Lewis bases [105-108].

Carraher et al has reported the initial electrical measurement studies for some selected organometallic condensation polymers [109]. Abd-El-Aziz et al has recently reported the advances in organometallic polymers [110]. These efforts were based on the

idea that structures that allow delocalization of electrons along the polymer backbone would favor them being better conductors. None of the polymers initially studied were conductors but rather they were generally near semiconductors. There was no attempt to dope these materials.

The idea that delocalization of electrons over a polymer's backbone favored better conductivity was suggested by a number of individuals during the 1970's and today forms the basis for describing polymer conductivity.

1.6 Hypothesis

Essentially all of today's applications of doped conductive polymers involve vinyl-related polymers. While the application of conductive polymers is rapidly increasing there is need for additional materials with different electrical behaviors. The current research involves the study of condensation polymers that contain a metal atom and the possibility to undergo entire chain delocalization of electrons. These polymers are readily synthesized using the interfacial polycondensation technique that is employed in the industrial production of aramids and polycarbonates so that ready scale up is possible. Further, the polymers are made from industrially available materials again allowing for ready scale up. This research may set the stage for the study of not only metal-containing polymeric materials but also the ability to increase the conductivity of other condensation polymers such as nylons and polyesters through doping.

The **working hypothesis** of the current research is that metal-containing condensation polymers that allow delocalization of electrons are near semiconductors and can be successfully doped to increase their conductivity to within the near conductive region. There are two specific aims of the current research:

- i) Determine the electrical conductivity of a variety of metal-containing polymers that can exhibit whole chain electron delocalization.
- ii) Study the effects of doping selected metal-containing polymers with iodine to see if any increases in the conductivity are obtained.

CHAPTER 2. EXPERIMENTAL

2.1 Materials and Methodology

The following chemicals were used as received.

| Chemicals | CAS number | Manufacturer |
|--|-------------|----------------------------------|
| 4,6- diaminopyrimidine | 156-81-0 | Aldrich Chemical Co, WI |
| 4,6-diamino-5-nitropyrimidine | 2164-84-3 | Aldrich Chemical Co, WI |
| 4,6-diamino-2- methylmercaptopyrimidine | 1005-39-6 | Aldrich Chemical Co, WI |
| 4,6-diamino-2-methyl-5- nitrosopyrimidine | 56472-03-8 | Parish chemical Co, UT |
| 4,6-diamino-2-mercaptopyrimidine | 303136-89-2 | Aldrich Chemical Co, WI |
| 4-chloro-2,6-diaminopyrimidine | 156-83-2 | Acros Organics, NJ |
| 2,4-diamino-6-hydroxypyrimidine | 56-06-4 | Acros Organics, NJ |
| 2,4-diamino-6-hydroxy-5- nitrosopyrimidine | 2387-48-6 | Avocado Chemicals, Lancashire |
| 4,6-diamino-5-(4-chlorophenyl)-6- ethylpyrimidine | 58-14-0 | MP Biomedicals, OH |
| 2-nitro-1,4-phenylenediamine | 5307-14-2 | Aldrich Chemical Co, WI |
| N-methyl-1,4-phenylenediamine | 623-09-6 | Ivy Fine Chemicals, NJ |
| Dibutyltin dichloride | 683-18-1 | Acros Organics, NJ |

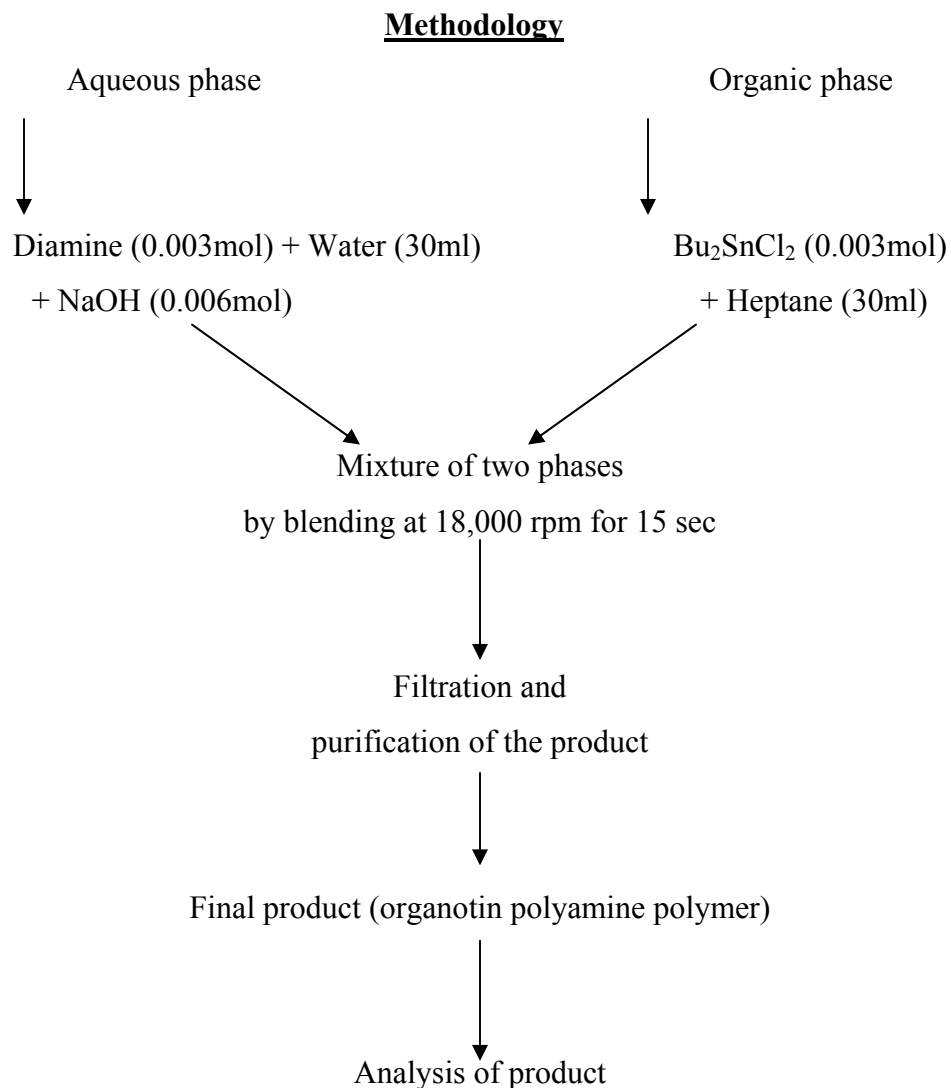
| | | |
|--|------------|-----------------------------|
| Bis(cyclopentadienyl)titanium(IV) dichloride | 1271-19-8 | Aldrich Chemical Co, WI |
| Bis(cyclopentadienyl)zirconium(IV) dichloride | 1291-32-3 | Alfa Inorganics, Inc, MA |
| Bis(cyclopentadienyl)hafnium(IV) dichloride | 12116-66-4 | Alfa Products, MA |
| Iodine | 7553-56-2 | Fisher Scientific, NJ |

2.2 Synthesis

2.2.1 Synthesis of organotin polymers from substituted 4, 6 - diaminopyrimidines

Syntheses were carried out employing an interfacial polycondensation technique. An aqueous solution 30 ml containing the diamine (0.00300 mol) and sodium hydroxide (0.00600 mol) was transferred to a one quart Kimax emulsifying jar fitted on the top of a Waring Blender (model 1120 with load speed of about 18,000 rpm and reactions carried out at 25 °C). Stirring was begun and then hexane solution 30 ml containing the dibutyltin dichloride (0.00300 mol) was added rapidly (about 3-4 seconds) through a hole in the jar lid using a powder funnel. The resulting solution was blended for 15 seconds. The precipitate was recovered using vacuum filtration. The product is recovered as a precipitate. It is washed several times with deionized water and hexane to get rid of the unreacted materials and unwanted by-products such as sodium chloride that is formed from the reaction between the sodium hydroxide and created hydrochloric acid. The solid was obtained using vacuum filtration, was washed onto a glass petri dish and allowed to dry at room temperature.

2.2.1(1) Flowchart for synthesis of organotin polymers



2.2.2 Synthesis of samples especially studied for doping

Syntheses of the doped samples were similar to that described in **2.2.1**.

The syntheses of these materials were carried out employing the reaction between 2-nitro-1,4-phenylenediamine and titanocene dichloride as the template. The 2-nitro-1,4-phenylenediamine (0.00300 mol) was dissolved in 30 ml of water. To this aqueous phase, sodium hydroxide (0.00600 mol) was added. Titanocene dichloride (0.00300 mol) was

dissolved in 30 ml chloroform. The aqueous phase was first added to the Kimex emulsifying jar. The resulting aqueous phase was stirred at about 18,000 rpm and the organic phase was quickly added (about 3-4 seconds addition time). Stirring was further continued for an additional 15 seconds. The dark brown precipitate was collected using vacuum filtration and repeatedly washed with water and chloroform to remove any unreacted materials and unwanted byproduct until the filtrate was colorless. The solid was then washed into a glass petri dish and allowed to dry.

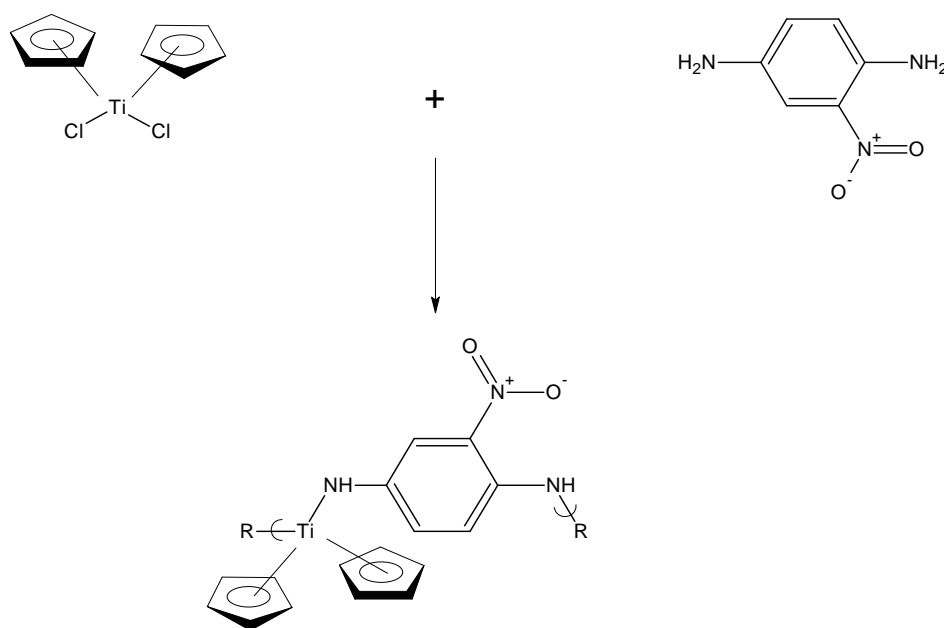


Figure 2.2.2(1) Synthesis of polymer from reaction of 2-nitro-1, 4 – phenylenediamine and titanocene dichloride where ‘R’ is simply the chain extension.

2.3 Physical Characterization

2.3.1 Solubility of polymers

Solubility tests were carried out by placing 5 to 15 mg of sample in approximately 3 ml of solvents like dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMA), hexamethylphosphoramide (HMPA), N,N-dimethyl formamide (DMF), water (H₂O),

acetone (CH₃COCH₃) and 1-methyl-2-pyrrolidinone (MP). The solid-liquid combinations were periodically shaken and observed over a period of 2 to 4 weeks. Disappearance of the solid indicated that solubility occurred.

2.3.2 Molecular weight determination using light scattering photometry

A Brice-Phoenix BP 3000 Universal Light Scattering Photometer was employed for carrying out the light scattering measurements. A Bausch & Lomb Abbe Model 3L Refractometer was employed for determining the refractive indices of the materials. The molecular weights for the samples were calculated based on the theory of light scattering phenomenon. The amount of light scattered is proportional to the product of the weight average molar mass and the solute concentration. The equation for the dilute polymer solution using Rayleigh-Debye-Gans light scattering model can be expressed as follows:

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc$$

where,

$$H = \frac{32\pi^3 n^2 \left(\frac{n - n_0}{c} \right)^2}{3\lambda^4 N}$$

The measurement was carried out at 436μm.

$$H = 15.2 \times 10^{-5} \times n^2 \left(\frac{n - n_0}{c} \right)^2$$

where,

c = concentration of the solution

n = refractive index of the solution and

n_0 = refractive index of the solvent

Also,

$$\tau = \left(\frac{16TD}{3 \times 1.049 \times h} \right) \left[n^2 \left(\frac{R_{IC}}{R_c} \right) \right] \left[a \times F \times \left(\frac{G_g}{G_{IV}} \right) \right]$$

where,

TD = diffuse transmittance of reference opal times diffuser correction factor, for $\lambda = 436\mu\text{m}$, $TD = 0.381$

h = width of primary beam, $h = 1.20$ cm in our measurements

n = refractive index of the solution

$\frac{R_{IC}}{R_c}$ = correction for incomplete compensation for refraction effects

a = working standard constant for $\lambda = 436\mu\text{m}$, $a = 0.0517$

F = product of transmittances of the neutral filters in determining the scattering ratio.

G_g = light scattering measurement at 90°

G_{IV} = light scattering measurement at 0°

Therefore we have,

$$\tau = 0.0835 \times n^2 \times \left(\frac{G_g}{G_{IV}} \right)$$

A standard made of polystyrene obtained from Waters Associates, Milford, Massachusetts with a reported molecular weight of 110,000 dalton was measured using light scattering photometry. The polystyrene standard was dissolved in toluene solvent. The concentration of the standard solution was 5×10^{-3} g/ml with $G_g = 196$ and $G_{IV} = 4640$. All the filters were pulled out during the measurements. The refractive index of

toluene was 1.4961 and the refractive index of the standard solution was 1.4971. These values were placed into the above equations and the following results were obtained:

$$\frac{Hc}{\tau} = \frac{15.2 \times 10^{-5} \times 1.4971^2 \left(\frac{1.4971 - 1.4961}{5 \times 10^{-3}} \right)^2 \times 5 \times 10^{-3}}{0.0835 \times 1.4971^2 \left(\frac{196}{4640} \right)}$$

$$= 8.6 \times 10^{-5}$$

And we get,

$$M = 120,000 \text{ dalton}$$

Some other standards like chitosan obtained from Fluka Biochemicals, Switzerland with reported molecular weight of 70,000 dalton was also measured on this instrument. The results are close to the reported molecular weight of 60,000 dalton.

Table 2.3.2(1) represents standards for light scattering photometer

| Standards | Actual Mw (Dalton) | Experimental Mw (Dalton) |
|-------------|--------------------|--------------------------|
| Polystyrene | 110,000 | 120,000 |
| Chitosan | 70,000 | 60,000 |
| Trypsin | 66,000 | 67,000 |

2.3.3 Fourier transform infrared spectroscopy (FTIR)

Mattson Instruments Galaxy Series 4020 Fourier Transform Infrared Spectroscopy (FTIR) was employed for obtaining the infrared spectra of these compounds using 32 scans and an instrumental resolution of 4 cm⁻¹ employing KBr pellets.

2.3.4 Nuclear magnetic resonance spectroscopy (^1H and ^{13}C NMR)

^1H NMR spectra were recorded on Varian Mercury 400 (400MHz) and reported in ppm utilizing solvent as the internal standard (TMS at 0.00 ppm and d_6 DMSO at 2.50 ppm) Data are reported as (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet; coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) spectrometer. Chemical shifts are reported in ppm trimethylsilane and solvent resonance employed as the internal standard (d_6 DMSO at 40.0 ppm) using 4 mm NMR tube. Sample was prepared 5 to 20 mg/ml in d_6 DMSO.

2.3.5 Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI TOF MS)

HR MALDI-TOF (High resolution electron impact positive ion matrix assisted laser desorption ionization time of flight mass spectrometry) was carried out using a Voyager-DE STR Biospectrometer, Applied Biosystems, Foster City, CA. The standard settings were set with a linear mode of operation and an accelerating voltage of about 25,000 volts; grid voltage 90% and an acquisition mass range of 150 to 2,000. Each spectrum was subjected to two hundred shots. Several matrix materials were employed but only results employing 2,5-dihydroxybenzoic acid (DHB) and α -cyano-hydroxycinnamic acid (CHCA) are included in the dissertation.

2.4 Determination of particle size

The N-methyl-1,4-phenylene diamine and titanocene dichloride polymer was finely ground to a powder employing a mortar and pestle in the usual fashion and viewed under an optical microscope to determine an average size of the particles. The particles

were irregular spheres with an average diameter of 1.02×10^{-7} (± 0.04) for ($n = 20$) meters.

2.5 Measurement of electrical properties

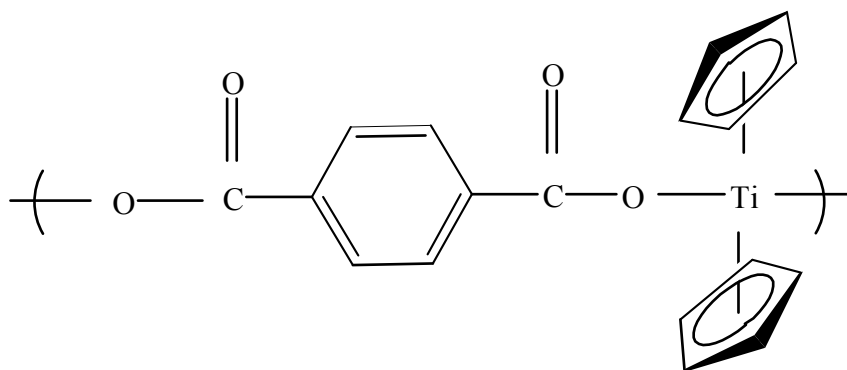
The electrical measurements were obtained employing a standard process [111]. A known amount of sample was pressed into pellets using a Carver laboratory press. These pellets were then utilized for the measurement of the conductivity of materials. The thickness and diameter of the sample pellet were measured using a micrometer screw gauge. The pellet thickness of about 0.59 mm and diameter of about 13 mm were held constant for the current studies. A GenRad 1650-B Impedance Spectroscopy Bridge was used for the measurement of electrical properties of these materials. The sample holder consists of an enclosed cage which houses the copper electrodes. The pellets were then placed between the copper electrodes and an alternating current was applied. The sample holder was connected to the impedance bridge which measures the various electrical properties. The impedance bridge was also connected to a 1311-A audio oscillator which allowed the frequency to be varied. The conductivity measurements were done for the following frequencies: 0.4 KHz, 1 KHz, 2 KHz, 5 KHz and 10 KHz respectively. The measurements and calculations were done in the usual manner [112, 113].

Surface doping was carried out in the usual manner [38]. Initially, the pellets were exposed to the iodine vapors for known amounts of time. They were then removed from the iodine vapor and inserted between the copper electrodes and electrical measurements were carried out. A blanket of nitrogen was present during the doping and the measurement procedures to maintain an oxygen and moisture free surroundings. Bulk doping was carried out by mixing together a known weight of ground polymer with

different weights of iodine. The solid mixture was ground together and a pellet was made from the mixture.

2.5.1 Equations for calculation of dielectric constant, dielectric loss and dissipation factor for the materials

Following is a sample calculation employed to calculate the dielectric constant, dielectric loss and dissipation factor for each sample using data gathered for the product of terephthalic acid and titanocene dichloride



Terephthalic acid derivative

General product dimensions

Thickness of sample pellet (t) = 0.36 mm = 0.036 cm

Diameter of sample pellet (d) = 12 mm = 1.2 cm

Radius of sample pellet (r) = 12/2 = 6 mm = 0.6 cm

Surface area (a) of the sample pellet in cm² will be

$$a = (\pi/4) (d/2)^2 = (\pi/4) (r)^2$$

$$a = (3.142/4) (0.6)^2 = 0.28278$$

Capacitance calculation

C_a = Direct inter-electrode capacitance in vacuum derived from the surface area (a), thickness (t) and diameter (d) of the pelletized material

$$C_a = \text{assembly constant} \times (a/t) = 0.088542 \times (a/t) = 0.088542 \times (0.28278/0.036)$$

$$C_a = 0.6955$$

$$\text{Also, } (a/t) = (0.28278/0.036) = 7.855$$

From this C_a is measured that is entered in the table for calculation of the dielectric constant. C_s , C_p , D_s and D_p values are directly read from the instrument. For the sample polymer these results are given in the following table.

Table 2.5.1(1) Table showing parameters involved in calculation of bulk conductivity

| Frequency | C_s | C_p | D_s | D_p | ΔC | D_{sample} | $C_s/\Delta C$ | $K=C_s-C_p/C_a$ |
|-----------|-------|-------|-------|-------|------------|---------------------|----------------|-----------------|
| 0.4KHz | 0.90 | 0.69 | 0.12 | 0.55 | 0.21 | 0.34 | 4.29 | 0.30 |
| 1KHz | 0.58 | 0.41 | 0.80 | 0.42 | 0.17 | 1.09 | 3.41 | 0.24 |
| 2KHz | 0.36 | 0.28 | 1.40 | 0.25 | 0.08 | 2.15 | 4.50 | 0.12 |
| 5KHz | 0.26 | 0.18 | 0.13 | 0.26 | 0.08 | 0.12 | 3.25 | 0.12 |
| 10KHz | 0.20 | 0.14 | 0.16 | 0.14 | 0.06 | 0.01 | 3.34 | 0.09 |

where,

f = frequency in Hertz

C_s = total capacitance of the sample

C_p = residual capacitance of the sample

D_s = total dissipation factor

D_p = residual dissipation factor

ΔC = difference between total and residual capacitance of the material

D_{sample} = dissipation loss of the material

K = dielectric constant of the material

The dielectric constant of the material is calculated using the equation,

$$K = (C_{\text{total}} - C_{\text{residual}}) / C_a$$

Dielectric loss of the material is calculated employing the following equation,

$$D = C_s / C_s - C_p \times (D_s - D_p) \times f / 10^3$$

Dissipation loss is calculated using the following equation,

$$D_{\text{sample}} = D_{\text{measured}} + (C_{\text{residual}} / C_{\text{total}}) \times \Delta D$$

The bulk resistivity, P_f , is the reciprocal of the bulk conductivity and can be calculated, at different frequencies, from the capacitance and the dissipation loss employing the following equation,

$$P_f = [1 / (2\pi f C_{\text{sample}} D_{\text{sample}})] (a/t)$$

where,

C_{sample} = difference in the total and residual capacitance

D_{sample} = dissipation loss of the material

f = set frequency

a = surface area of the sample pellet

t = thickness of the sample pellet

CHAPTER 3. RESULTS

Most synthetic polymers employed in the industry are insulators. Within the electronic industry they are employed as coatings of wires and as non-conductive materials for electric switches. Materials like polyethylene, polypropylene and polystyrene tend to have low conductivities and low dielectric constants. The dielectric properties of polymers are determined by the polymer structures which are related to the polar or non-polar nature of the materials.

Materials are often characterized by three electrical values. These electrical parameters are dielectric constant, dissipation factor and conductivity (or its inverse resistivity). The electrical polarization is determined by the dielectric constant and is related to the dissipation of electrical energy. The dielectric constant is referred as the property of the material which is related to the charge displacement of the material under the influence of electric field. Generally, the dielectric constant for a vacuum is 1 [114] with values for other materials greater than 1. In most cases, the dielectric constants vary with the polarity of the materials and are relatively large for polar materials with values of approximately 100 for water [115] and 5000 or more for barium titanate [116]. One important factor considered in polar polymers is the alternating current frequency because it is related to the time taken to align polar dipoles. Polar polymers at lower frequencies generally have dielectric constants in the range of 3 to 9 whereas at higher frequencies they exhibit dielectric constants between 3 and 5. Non-polar polymers

generally exhibit dielectric constant values of less than 3. For comparison, dielectric constants (60 Hz) for typical polymers vary from about 2 for polytetrafluoroethylene to 8.4 for poly (vinylidene fluoride) with values for nylons, polycarbonates and polyesters in the range of 3 to 5. Values of dielectric constants for the highly polar Group IVB polyoximes [117] vary from 2 to 10 and 5 to 120 for a series of palladium polyamines [118] that can exhibit whole-chain delocalization in their backbones.

The dissipation factor of the material can be defined as the ability of the dielectric materials to absorb some electrical energy on application of the AC signal frequency. Dissipation factors, D , vary from near zero to 100. Values of the dissipation factor for Group IVB polyoximes [117] vary from 2.6 to 10 and for the palladium polyamines [118] from 0.2 to 28. Values for commercial polymers are nylon 66 - 0.02; polyethylene - 0.0002; polypropylene - 0.0003; Teflon - 0.0003; and poly (vinyl chloride) - 0.01. In general, more polar molecules have higher D values.

For most electrical applications, particularly when dealing with potentially conductive polymers, the most significant parameter is the electrical conductivity. The results of this measurement indicate whether the material is an electrical conductor, semiconductor or an insulator. The surface conductivity, as the name suggests, is the measure of the conductance to the electrical flow of the current over the surface. Bulk conductivity is similar except the conductivity is measured through the material. Both surface and bulk conductivity is expressed in $S\text{ cm}^{-1}$ where “S” represents Siemens. Due to the high conductivity of metals, the surface conductivity of metals is generally never measured but rather bulk conductivity is reported.

The variance of electrical properties as a function of applied frequency is complex with the most common relationships taking on convex, concave and sinusoidal shapes. This variance is essentially universal and is dependent on a number of variables. It is the interplay between these various factors that results in the complex behavior of the electrical properties with applied current for materials. The most often cited structural variables are described briefly. Several of these are related to polarizability and the ability of various units within the compound to respond to the applied current. Instantaneous polarization occurs when rapid transitions occur. Electric polarizations are related to the displacement of charges within the atoms. At low frequencies the material has time to allow for both fast dipole polarizations to occur as well as slower segmental polarizations to occur. At high frequencies only the fast dipole polarizations occur and influence the electronic behavior of the material. For polymers, such electric polarizations are dependent on the nature of the particular units and also on their ability to respond to the applied current. This ability to respond is in turn dependent on many factors including the crystalline/amorphous mixture of the structure, steric hindrance and segmental chain mobility. Also, the ability for the structural units to carry an electrical charge is dependent on the crystalline/amorphous mixture, steric hindrance and segmental chain mobility. Atomic polarization contributions are dependent on perturbations caused by the applied field and these are, in turn, related to various absorptions in the infrared region. Other contributions include absorptive types related to relaxation times corresponding to the ability of various dipole moments to align with the applied current including chain alignment as well as unit alignment [119-123]. It is the interplay between these various factors that result in the complex behavior of the electrical properties with applied current

for materials [124-135]. The frequencies employed in the current study are those typically employed in the evaluation of electrical properties of the materials. The lowest frequency employed in the current study is often used as representative for the application of direct current.

There were two major areas of the research. The first area involved determining the electrical conductivity of a number of different series of compounds. The second area involved doping some of these compounds to determine if doping had an effect on their electrical conductivity.

The initial area of the project involved surveying a number of different compounds. The compounds were chosen using the following criteria. First, the chain structure was to offer potential whole chain delocalization of electrons. Second, there should be sufficient material that would allow the electrical properties to be measured without an additional synthesis. Third, some materials were chosen where the conductivity could be measured as a function of the electron density on the Lewis base. Fourth, other materials were chosen that would offer a variety of metal and structures.

There are several objectives for this area of the research project. First, to determine if any of these materials were themselves conductive without doping. Second, to allow the selection of several materials for further doping experiments. Third, to evaluate the effect of structure, such as dependence of electron density of the Lewis base, on the electrical conductivity.

Initially, the results for the various polymers will be given with an emphasis on grouping similar products together as the results are presented. The focus will be on

presentation of the conductivity results since this is the primary focus of the electrical measurements.

3.1 Surveying of undoped Group IVB metallocene - containing polymers

3.1.1 Group IVB metallocene - containing polymers

The initial major groupings of compounds studied were all derived from reaction of Group IVB metallocenes with various Lewis bases. A wide variety of Group IVB metal-containing polymers have been synthesized. The synthesis and characterization of Group IVB containing polymers has been recently reviewed.

The initial synthesis of metallocene compounds started during the 1950's when two different groups synthesized ferrocene by reacting iron II chloride with cyclopentadienyl magnesium bromide and also by carrying out the reaction of reduced iron with cyclopentadiene in presence of bases such as potassium oxide [136, 137]. Ferrocene is considered to be a true sandwich compound with the iron metal lying between two flat plain cyclopentadiene groups [138-143]. A number of ferrocene containing polymers have been synthesized [140-143]. This topic has been recently reviewed.

In comparison, the Group IV B metallocenes have cyclopentadiene groups present in a distorted tetrahedral fashion facing the metal atom [144] as shown in **Figure 3.1.1**

(1)

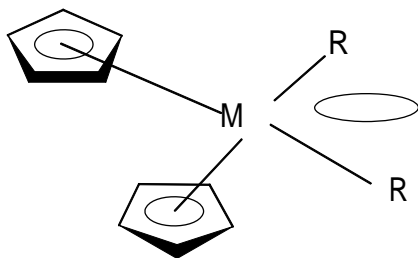
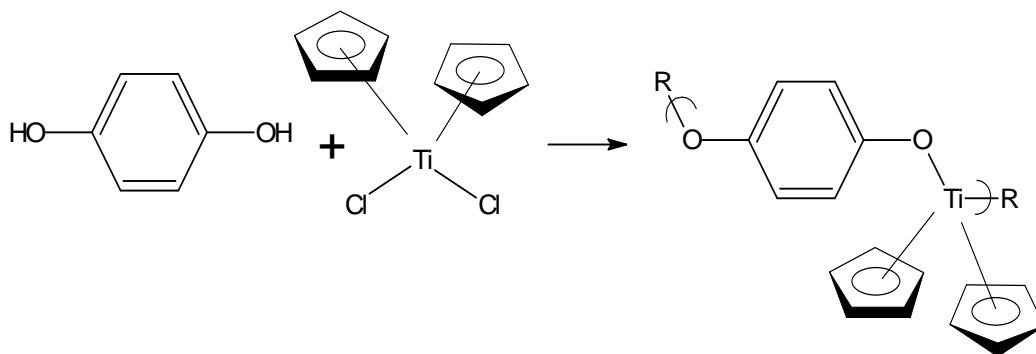


Figure 3.1.1(1)

The bonding in Group IVB metallocene compounds is described by Cotton and Wilkinson [145] as being derived from one s, three p and five d orbitals which contain nine coordinate bonds with the hybrid orbitals. Each π cyclopentadienyl ring contains three hybrid orbitals. The other three orbitals consist of two equivalent sp_{x-y}^2 , d_z^2 orbitals which overlap the oxygen, nitrogen and halides. There is one vacant sp orbital which is shown in the above **Figure 3.1.1(1)**. It is believed that conductivity may occur because of the ability of this vacant orbital to exchange electrons.

3.1.2 Group IV B metallocene polyethers

The titanocene polyethers were synthesized from the reaction of hydroquinone and its derivatives with titanocene dichloride as described in **3.1.2(1)** [146-162].



3.1.2(1)

The electrical properties for a series of titanocene polyethers are reported in this section along with the electrical properties for some related structures. The results for the product of hydroquinone and titanocene dichloride are reported in detail to illustrate the magnitude of the dielectric constant, dissipation factor and electrical conductivity.

3.1.2(2) Electrical properties of titanocene polyethers derived from reaction with hydroquinone and hydroquinone derivatives with titanocene dichloride

The electrical properties for the product of hydroquinone and titanocene dichloride are given in Table 3.1.2(3) and Figure 3.1.2(4). The structure for this product is given in Figure 3.1.2(5)

Table 3.1.2(3) Electrical properties for the product of hydroquinone and titanocene dichloride as a function of applied frequency.

| Frequency in KHz | C _s | C _p | ΔC | D _{sample} | (D _s) | K = ΔC/C _A | Bulk conductivity in S cm ⁻¹ | Log bulk conductivity in S cm ⁻¹ |
|---------------------|----------------|----------------|------|---------------------|-------------------|--------------------------|---|---|
| 0.4KHz | 1.07 | 0.89 | 0.18 | 0.25 | 0.32 | 0.30 | 1.65 x 10 ⁻¹¹ | -10.78 |
| 1KHz | 0.91 | 0.67 | 0.24 | 0.94 | 0.83 | 0.40 | 2.10 x 10 ⁻¹⁰ | -9.68 |
| 2KHz | 0.73 | 0.46 | 0.27 | 1.96 | 1.35 | 0.45 | 9.90 x 10 ⁻¹⁰ | -9.00 |
| 5KHz | 0.44 | 0.29 | 0.15 | 0.67 | 0.65 | 0.25 | 4.69 x 10 ⁻¹⁰ | -9.33 |
| 10KHz | 0.29 | 0.20 | 0.09 | 0.41 | 0.44 | 0.15 | 3.41 x 10 ⁻¹⁰ | -9.47 |

All units are in nano farads (10⁻⁹)

Figure 3.1.2(4) Conductivity plot for the product of hydroquinone and titanocene dichloride as a function of applied frequency.

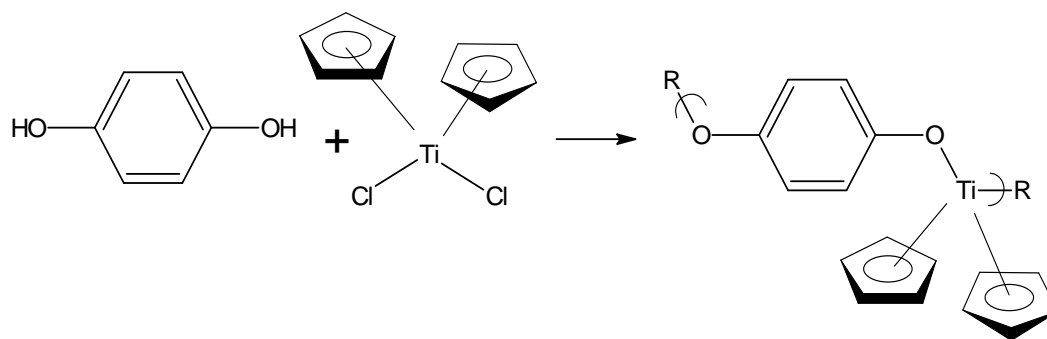
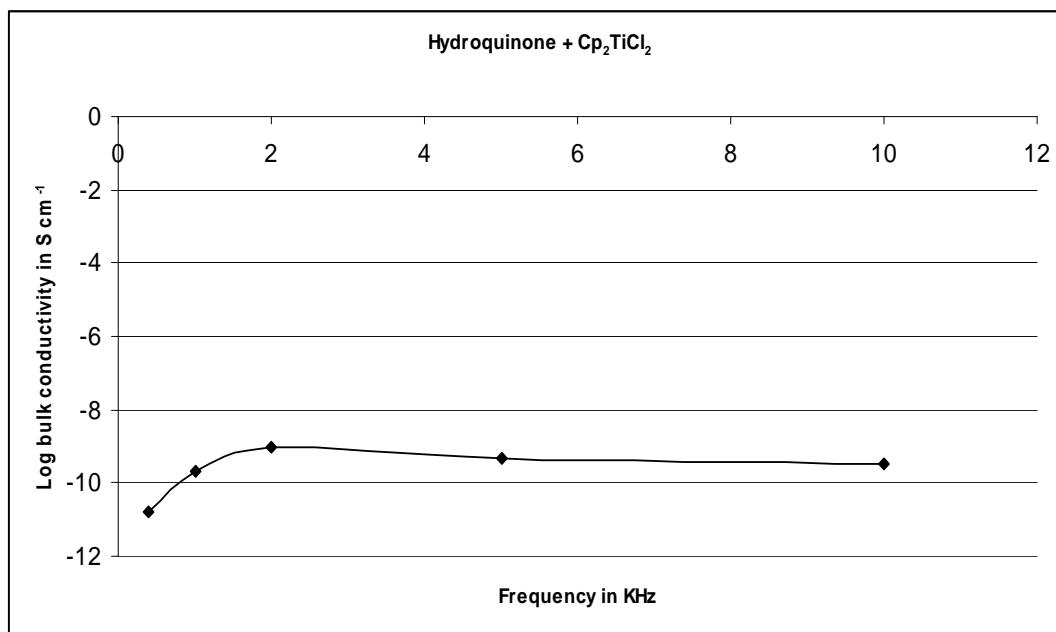
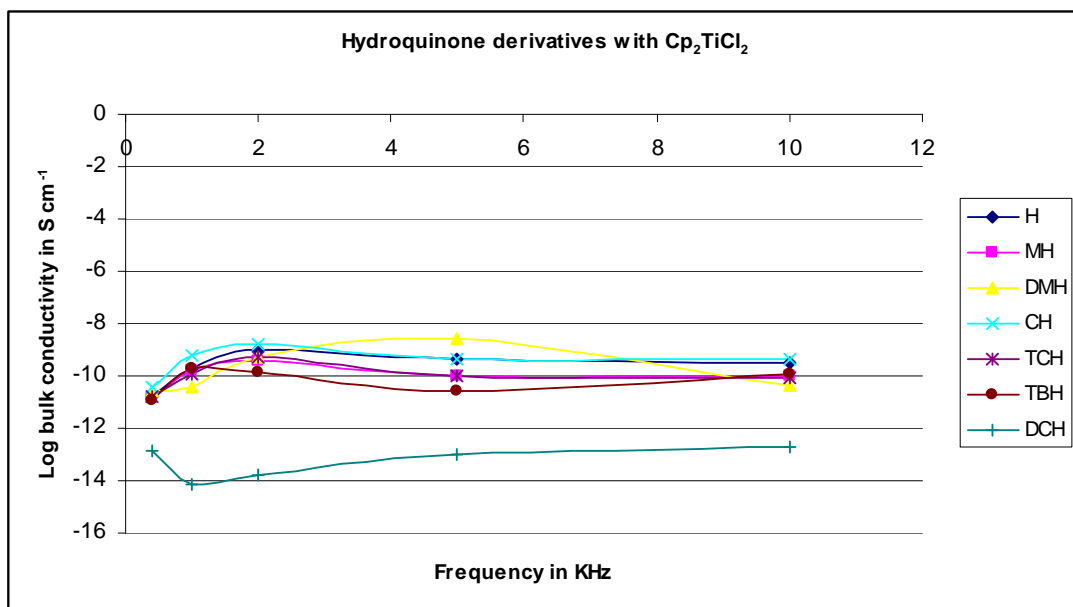


Figure 3.1.2(5) Structure of the product of hydroquinone and titanocene dichloride.

Similarly, data represented in **Table 3.1.2(3)** was obtained for other compounds in the hydroquinone series. From this, conductivity plots were made (Figure 3.1.2(6))

Figure 3.1.2(6) Conductivity plots for the products derived from hydroquinone and its derivatives as a product of applied frequency.



where; H = hydroquinone; MH = methyl hydroquinone; DMH = dimethylhydroquinone; CH = chlorohydroquinone; TCH = tetrachlorohydroquinone; TBH = t-butyl hydroquinone; and DCH = dicyano hydroquinone

All of the plots of log conductivity are slightly concave with the exception again of the dicyanohydroquinone polymer. The relationship between frequency and the particular structural contributions is complex. Thus, little should be currently made of the concave shape other than the observation that it appears to be common for all but one of the samples tested.

Table 3.1.2(7) contains the conductivity values for various titanocene polyethers where the hydroquinone moieties are arranged in increasing order of electron deficiency to see if there is some discernable relationship between the structure and the conductivity

Table 3.1.2(7) Conductivity for titanocene polyether products as a function of electron density on the phenylene moiety. (All values are minus log bulk conductivity)

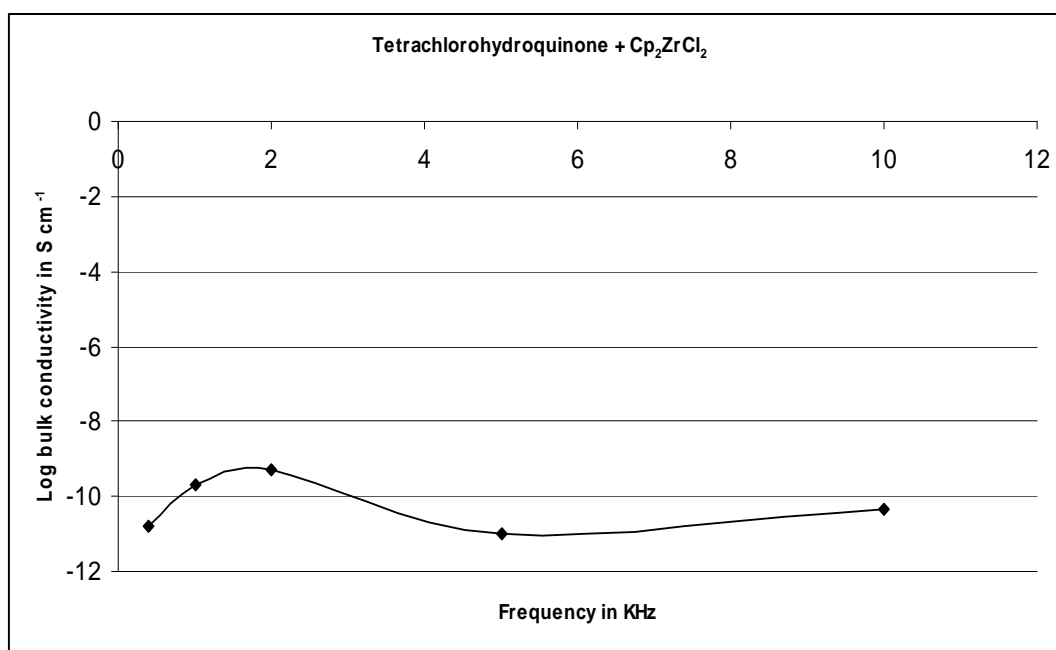
| Diol | Applied Frequency | | |
|---------------|--------------------------|--------------|---------------|
| | 0.4 KHz | 2 KHz | 10 KHz |
| DimethylHQ | -10.6 | -9.3 | -10.3 |
| t-butylHQ | -10.9 | -9.9 | -10.0 |
| HQ | -10.8 | -9.4 | -10.0 |
| 2,3-dicyanoHQ | -12.8 | -13.8 | -12.7 |
| ChloroHQ | -10.4 | -8.8 | -9.3 |
| TetrachloroHQ | -10.8 | -9.3 | -10.1 |

All of the values are similar with the exception of those for the 2,3-dicyanohydroquinone product which are much lower pushing the material into the non-conductive range. Thus there does not appear to be a major relationship between the electron density on the phenylene and the bulk conductivity for these materials.

The dielectric constants for this series varied from 0.04 to 2.29 [163] with the dissipation factors ranging from 0.001 to 4 [164]. The dielectric constant and dissipation factor values for the hydroquinone series polymers are consistent with the materials being polar.

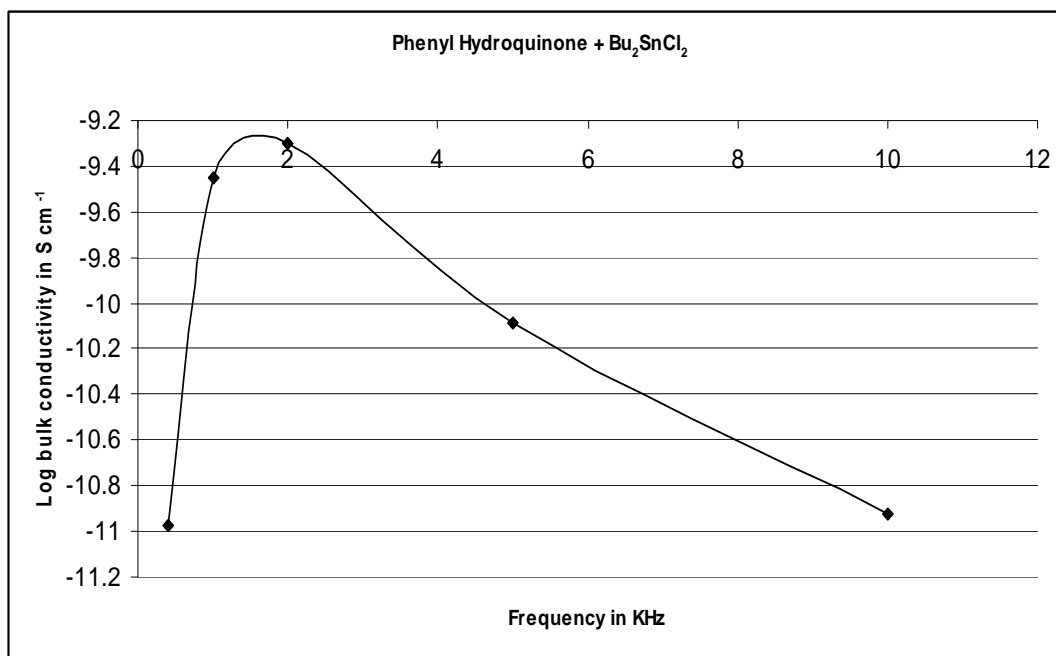
In addition to employing titanocene; zirconocene and dibutyltin dichloride polyethers were also studied. Results for the zirconocene product are given in Figure 3.1.2(8). The magnitude of the conductivity and behaviour as a function of frequency for the zirconocene product is similar to that observed for the titanocene polyethers. This is consistent with the nature of the Group IVB not affecting the electrical properties for these polyethers.

Figure 3.1.2(8) Conductivity plot for the product of tetrachlorohydroquinone and zirconocene dichloride as a function of applied frequency



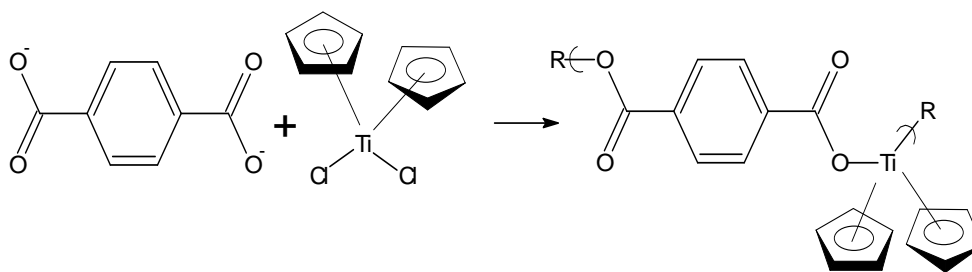
The conductivity for the product of dibutyltin dichloride and phenylhydroquinone is given in Figure 3.1.2(9). The magnitude of conductivity is similar to those obtained for the titanocene and zirconocene products consistent with the idea that for such metal-containing polyethers, the general magnitude of conductivity is not significantly tied to the nature of the metal atom.

Figure 3.1.2(9) Conductivity plot for the product of phenylhydroquinone and dibutyltin dichloride as a function of applied frequency



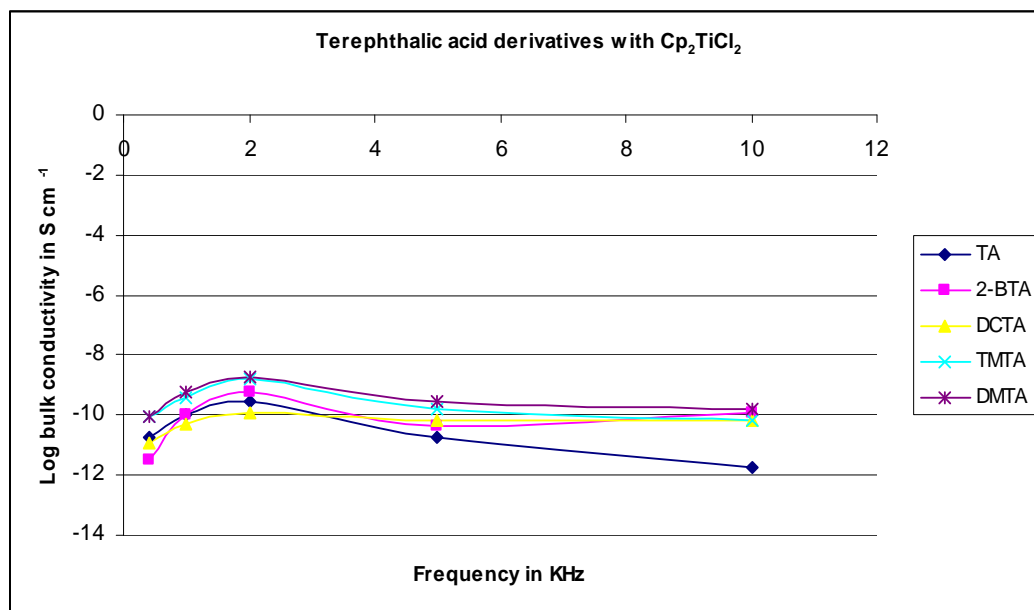
3.1.3 Group IVB metallocene polyesters

The next grouping studied was the Group IVB metallocene polyesters. The Group IV B containing polyesters were synthesized by using dicarboxylic acid salts employing the interfacial solution system as shown in Figure 3.1.3(1) [165-183].



3.1.3(1)

Figure 3.1.3(2) Conductivity plot for the titanocene polyesters derived from terephthalic acid and its derivatives as a function of applied frequency



where; TA = terephthalic acid; 2-BTA = 2-bromoterephthalic acid; DCTA = dichloro- terephthalic acid; TMTA = tetramethyl terephthalic acid; and DMTA = dimethyl- terephthalic acid

Table 3.1.3(3) contains the conductivity values for the various titanocene polyesters where the terephthalic moieties are arranged in increasing order of electron deficiency to see if there is some discernable relationship between the structure and the conductivity

Table 3.1.3(3) Conductivity for terephthalic acid products as a function of electron density on the phenylene moiety. (All values are minus log bulk conductivity)

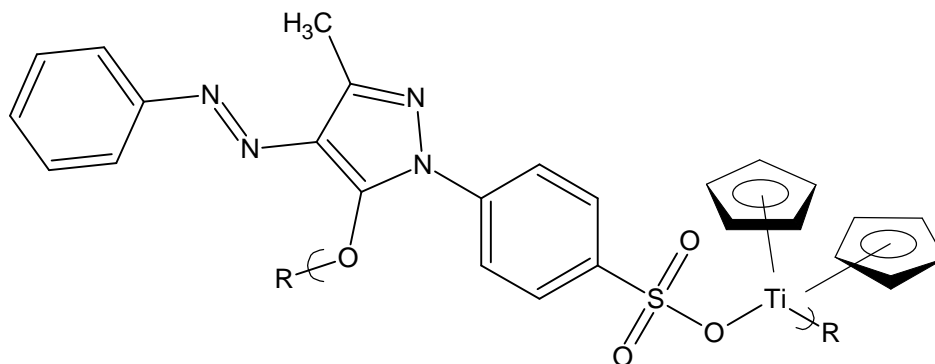
| Diacid | Applied Frequency | | |
|------------------------------|--------------------------|--------------|---------------|
| | 0.4 KHz | 2 KHz | 10 KHz |
| Tetramethylterephthalic acid | -12.4 | -13.1 | -11.5 |
| Dimethylterephthalic acid | -13.4 | -11.3 | -11.6 |
| Terephthalic acid | -10.5 | -9.8 | -11.0 |
| 2-Bromoterephthalic acid | -10.8 | -9.8 | -10.4 |
| Dibromoterephthalic acid | -11.0 | -10.1 | -10.4 |

The log of bulk conductivity values for terephthalic acid derivatives range from -9 to -13 suggesting the materials lie in the region of semiconductor to non-conductor (Figure 3.1.3(2)). While the magnitude and behavior is similar for the titanocene polyesters, a mild difference is found between those containing electron donating substituents with log bulk conductivity values clearly within the near semiconductor to non-conductor range while those containing electron withdrawing groups being a little higher, being within the semiconductor region. The difference is on the order of 10^2 to 10^3 fold, so may be significant.

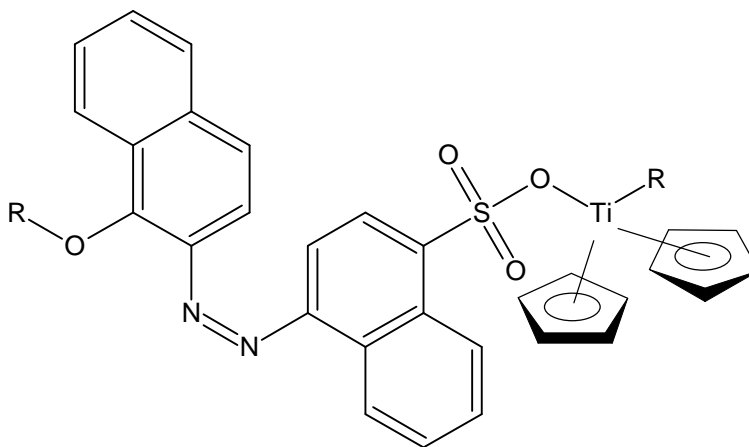
The dielectric constants are moderate ranging from 0.04 to 1.02 [184] with dissipation factors varying from 0.124 to 2 [185]. Both the dielectric constants and dissipation factors are similar to those found for the titanocene polyesters described in the previous section.

3.1.4 Group IVB metallocene phenylsulfonephthalein polydyes

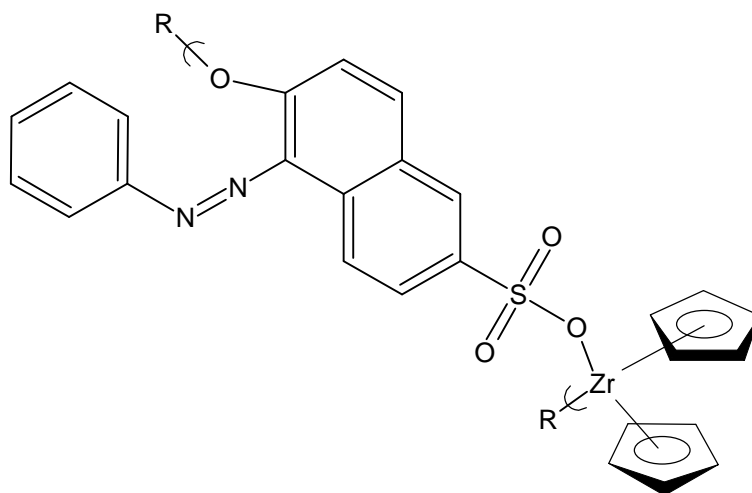
A number of reactions have been carried out employing the metallocene dichlorides by reacting with various dyes. As a group, these products are referred to as polydyes. This particular section contains results from selected polydye products derived from phenylsulfonephthalein dyes. These products were made in an attempt to increase the color lifetime of materials containing them. The synthesis and description of these materials has been recently reviewed [186-195]. The structures of phenylsulfonephthalein dyes are presented as 3.1.4(1) through 3.1.4(5)



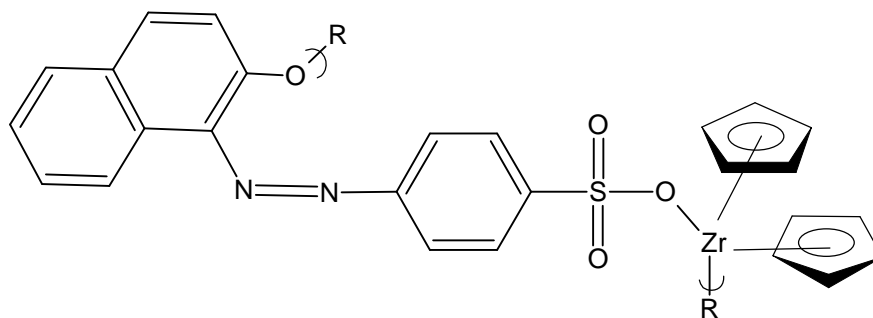
3.1.4(1) Flavazin L and Cp_2TiCl_2 product



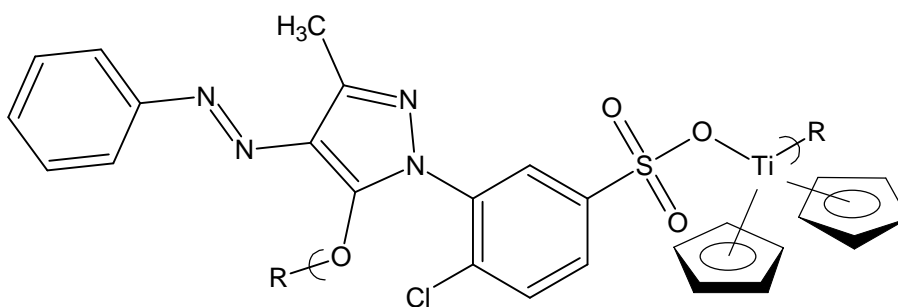
3.1.4(2) Acid Red 88 and Cp_2TiCl_2 product



3.1.4(3) Crocein Orange G and Cp_2ZrCl_2 product



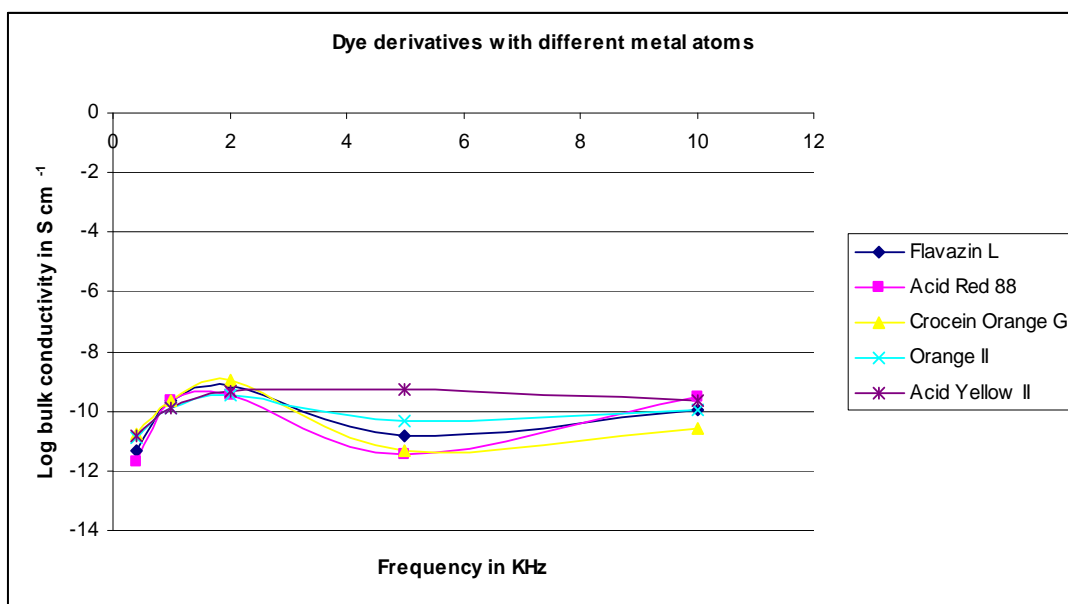
3.1.4(4) Orange II and Cp_2ZrCl_2 product



3.1.4(5) Acid Yellow II and Cp_2HfCl_2 product (except where the metal is hafnium)

The plot of conductivity for the products of phenylsulfonephthalein dyes and various organometallic dihalides as a function of applied frequency is given in Figure 3.1.4(6)

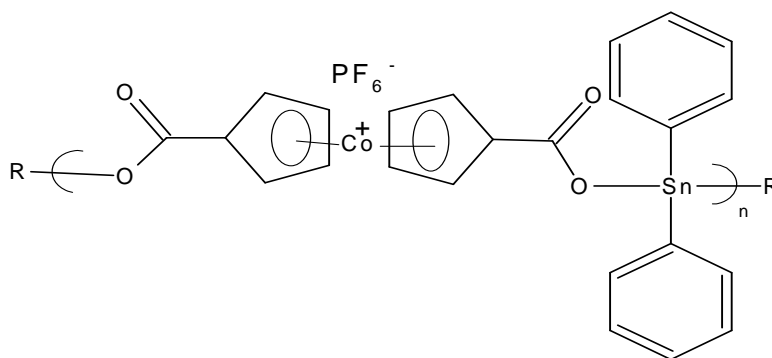
Figure 3.1.4(6) Conductivity plot for the products of selected phenylsulfonephthalein dyes and various organometallic dihalides as a function of applied frequency



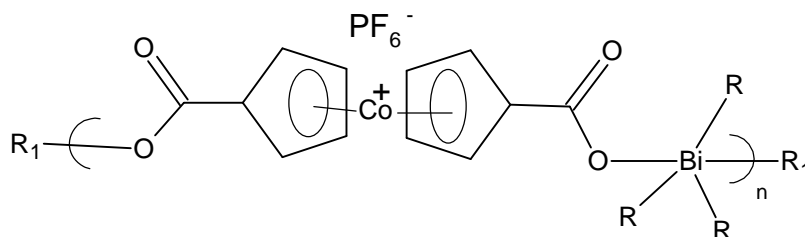
The phenylsulfonephthalein dye products with a variety of metal atoms exhibit log conductivity values ranging from about -9 to -11 within the near semiconductor to semiconductor region. Here, the conductivity plots are slightly sigmoid or linear. The dielectric constants for these dyes vary from 0.04 to 4.43 with dissipation factors in the range of 0.08 to 2. These values are consistent with the materials being polar as expected. This may be expected because the polymer is composed of polar portions with somewhat polar metallocene moiety connected to the polar dye moiety.

3.1.5 Cobalticene-containing products

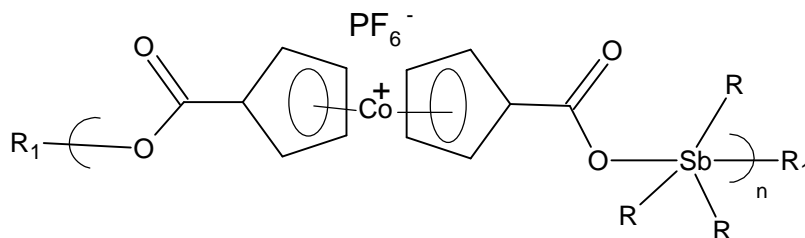
The next series of compounds presented are Group VA products of cobalticene hexafluorophosphate and various organometallic dihalides. The syntheses of the cobalticene hexafluorophosphate with organometallic dihalides have been reported. [196]. The topic of antimony-containing polymers has been recently reviewed [197]. In all cases, the products formed are the same except the metal atom is varied (Sn, Bi and Sb)



3.1.5(1) Cobalticene hexafluorophosphate and Ph_2SnCl_2 product



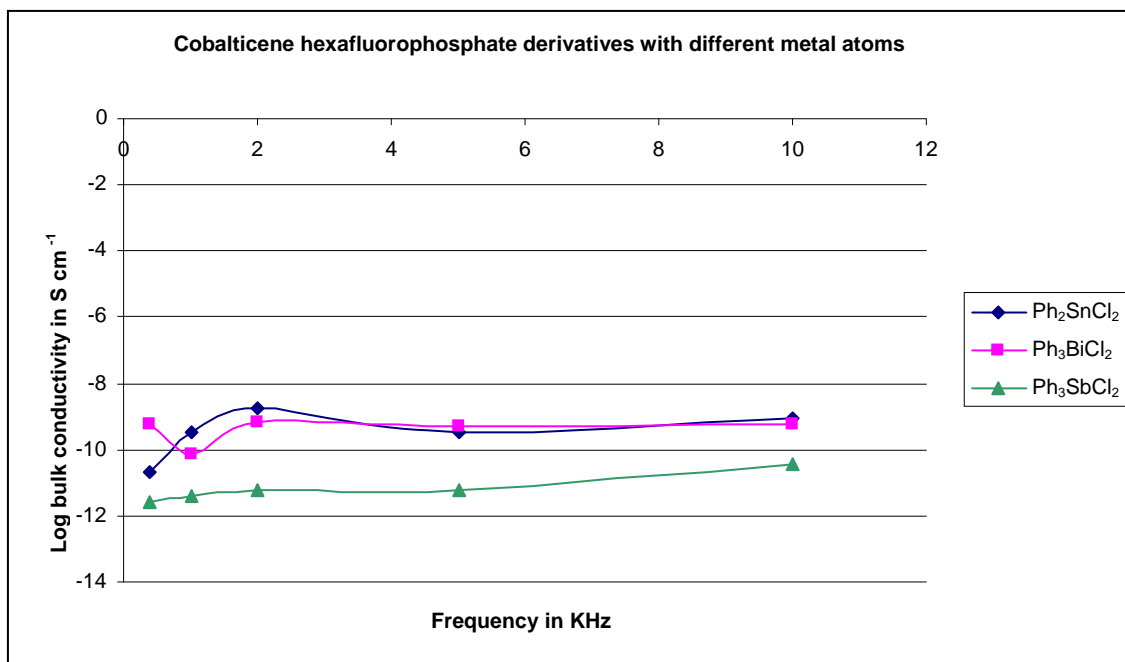
3.1.5(2) Cobalticene hexafluorophosphate and Ph_3BiCl_2 product



3.1.5(3) Cobalticene hexafluorophosphate and Ph_3SbCl_2 product

The conductivity results appear in Figure 3.1.5(4)

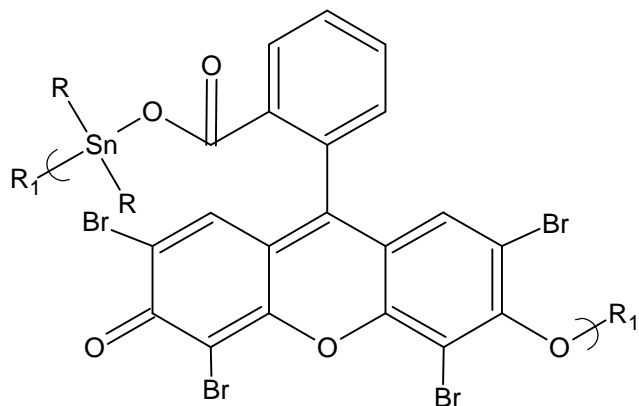
Figure 3.1.5(4) Conductivity plot for cobalticene hexafluorophosphate polyesters with various organometallic dihalides as a function of applied frequency



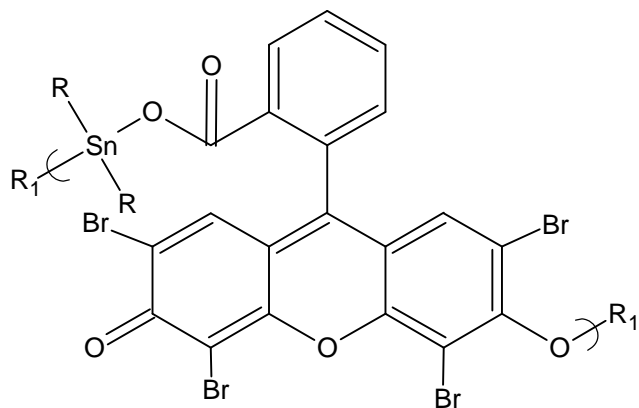
The three products are non-conductors to near-conductors. While there is a variance in the conductivity as the applied frequency is varied, this variance is generally on the order of 10 fold and less. The dielectric constants for these polymers vary from 0.28 to 32.93 and dissipation factors in the range of 0.10 to 1.55 at higher frequency. These values are consistent with the materials being polar as expected.

3.1.6 Organotin polydyes

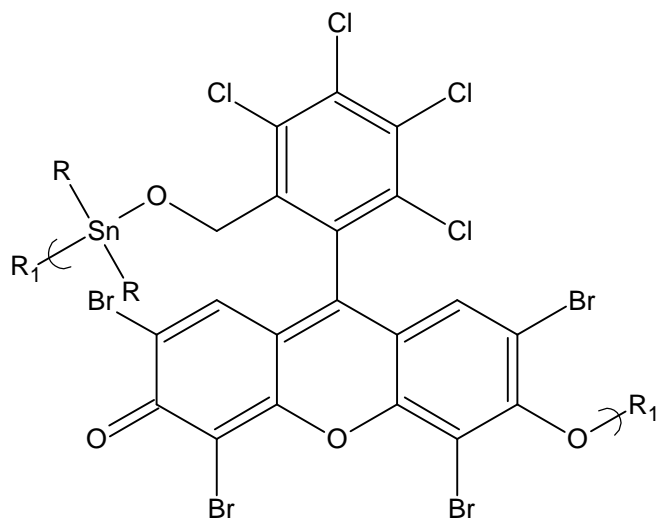
The next series of compounds are the products of various organotin dichlorides and fluorescein polydyes. Structures for these materials are given below



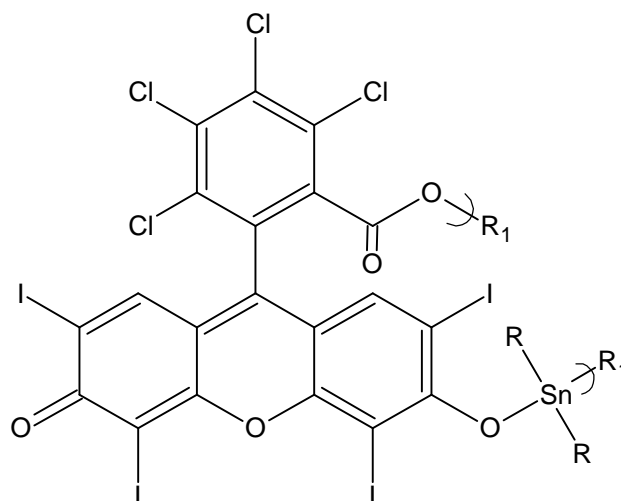
3.1.6(1) Organotin polymer from Eosin Y where R = Phenyl



3.1.6(2) Organotin polymer from Eosin Y where R = Methyl



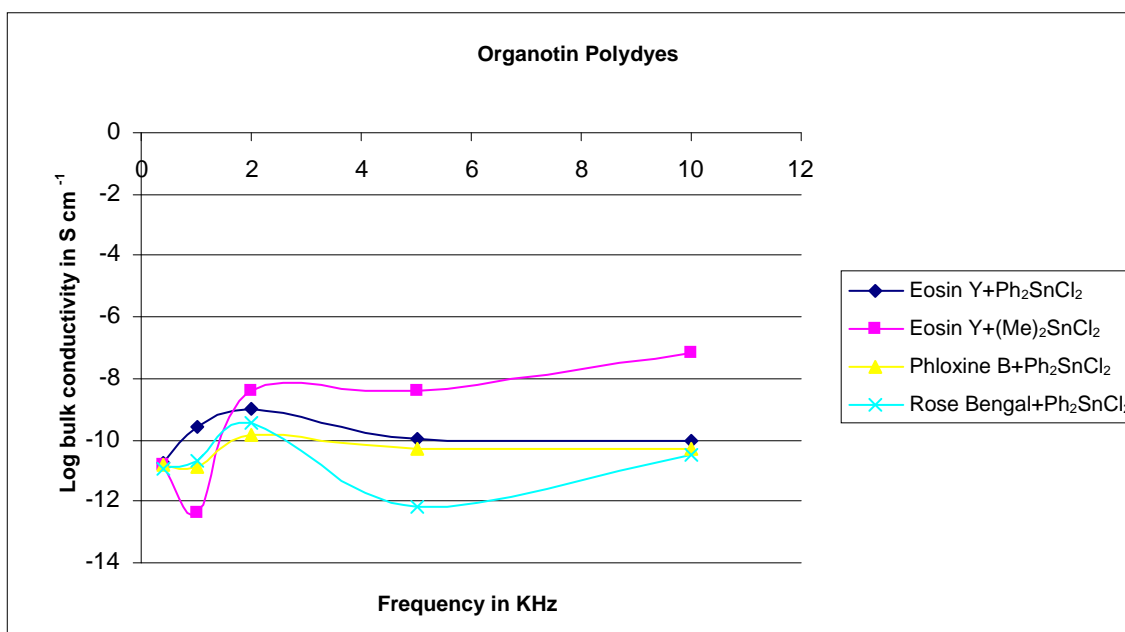
3.1.6(3) Phloxine B and Ph_2SnCl_2 product



3.1.6(4) Rose Bengal and Ph_2SnCl_2 product

Figure 3.1.6(5) contains conductivity results as a function of applied frequency

Figure 3.1.6(5) Conductivity plot for the series of organotin polydyes as a function of applied frequency



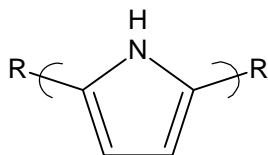
The organotin polydyes behave in a fashion similar to sigmoidal behavior as the frequency varies with the conductivity. The organotin polydyes range from the products

being near semiconductors to semiconductors with the Eosin Y-dimethyltin product showing log bulk conductivity value of -7 being near the conductor region. We expect the presence of phenyl groups on tin might assist in delocalization of electron flow. The dielectric constants for the present products vary from 0.04 to 9.92 whereas the dissipation factors for these polymers were in the range of 0.024 to 1.75 respectively. In all cases, the dielectric constants and dissipation factors are consistent with the materials being polar.

3.2 Dibutyltin pyrimidine compounds

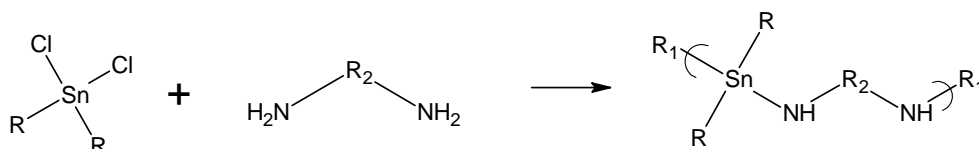
3.2.1 Structural characterization of dibutyltin pyrimidine compounds

A number of products were synthesized from the reaction of dibutyltin dichloride and 4, 6-diaminopyrimidines. These products were synthesized because of the similarity in ring structure to polypyrrole, a widely employed polymer that becomes electrically conductive after doping with iodine. There are a number of different 4,6-diaminopyrimidines commercially available to allow the products to offer a variety of structurally similar materials where the electronic and steric nature of the core pyrimidines varies. Following is a description of the synthesis, structural characterization and finally electrical characterization of these materials



3.2.1(1) Polypyrrole

Carraher and co-workers reported the synthesis of organotin polyamines over 30 years ago, [198-200] focusing on the synthesis of organotin polyamines as antibacterial agents and emphasized relatively simple aliphatic and aromatic amines.



3.2.1(2)

Reaction between the diaminopyrimidines and dibutyltin dichloride occurred for all of the diamines tried. Table 3.2.1(3) contains product yield, molecular weights and chain lengths.

Table 3.2.1(3) Product yields, molecular weights and chain lengths for the dibutyltin polyamines

| Diamines | Product ID | Product yield (%) | Molecular weight (Mw) | DP |
|--|------------|-------------------|-----------------------|--------|
| 4,6-diaminopyrimidine | AB1 | 54 | 3.7×10^6 | 10,800 |
| 4,6-diamino-5-nitropyrimidine | AB2 | 63 | 1.3×10^5 | 725 |
| 4,6-diamino-2-methyl mercaptopyrimidine | AB3 | 83 | 1.8×10^5 | 490 |
| 4,6-diamino-2-methyl-5-nitrosopyrimidine | AB4 | 49 | 5.5×10^5 | 1400 |
| 4,6-diamino-2-mercaptopyrimidine | AB5 | 47 | 1.8×10^6 | 5300 |
| 4-chloro-2,6-diaminopyrimidine | AB6 | 60 | 1.4×10^5 | 375 |
| 2,4-diamino-6-hydroxypyrimidine | AB7 | 71 | 2.1×10^5 | 600 |

| | | | | |
|--|-----|----|----------------------|-----|
| 2,4-diamino-6-hydroxy-5-nitrosopyrimidine | AB8 | 88 | 2.8×10^{-5} | 725 |
| 2,4-diamino-5-(p-chlorophenyl)-6-ethylpyrimidine | AB9 | 53 | 3.5×10^{-4} | 75 |

***Reaction conditions:** Dibutyltin dichloride (0.003 mol) in heptane (30 ml) was added to stirred (18,000 rpm) solutions of diamine (0.003 mol) and sodium hydroxide (0.006 mol) dissolved in water (30 ml).

Polymer solubility was studied using a variety of solvents that other metal-containing polymers have been found to be soluble in. These solvents are dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMA), hexamethylphosphoramide (HMPA), N,N-dimethylformamide (DMF), water (H₂O) and 1-methyl-2-pyrrolidinone (MP). Table 3.2.1(4) gives the solubility results for the products.

Table 3.2.1(4) Results for solubility tests for the series of dibutyltin pyrimidines in various attempted polar liquids

| Product | DMSO | DMA | HMPA | DMF | Water | MP |
|---------|------|-----|------|-----|-------|----|
| AB1 | - | 0 | + | - | - | + |
| AB2 | - | + | + | - | - | + |
| AB3 | 0 | 0 | + | - | - | + |
| AB4 | 0 | 0 | + | - | - | + |
| AB5 | - | 0 | 0 | - | - | + |
| AB6 | - | + | + | - | - | + |
| AB7 | - | + | + | - | - | + |
| AB8 | - | - | + | - | - | + |
| AB9 | + | + | + | 0 | - | + |

where,

(-) = not soluble; (0) = partially soluble and (+) = soluble

There does not appear to be a clear trend between the electronegativity or steric requirements of the diaminopyrimidines and the yields of the products. With respect to the steric hindrance, AB1 offers the least steric hindrance, yet is in the middle of the percentage yield range. AB2 and AB6 represent the most electron deficient rings yet the yields are in the middle range for the series. AB5 and AB7 represent the most electron rich rings yet yield for AB5 is in the lower range while the yield for AB7 is in the higher range.

Light Scattering Photometer was employed to determine molecular weights for diaminopyrimidines in 1-methyl-2-pyrrolidinone (MP) solvent. While these compounds are soluble to a large extent in a variety of solvents; they are all completely soluble in one solvent, 1-methyl-2-pyrrolidinone, MP. The products were found in the range of moderate polymers to high polymers with chain lengths ranging from 75 to 10,800. Chain lengths were found to be of the general order $AB1 > AB5 > AB4 > AB2 \cong AB8 \cong AB7 > AB3 \cong AB6 > AB9$. The longest chain length was found for the least sterically hindered diamine, 4,6-diaminopyrimidine (AB1) and the shortest chain length for the most sterically hindered diamine, 2,4-diamino-5-(p-chlorophenyl)-6-ethylpyrimidine (AB9) but no clear trend was found to exist for the other pyrimidines.

Lack of solubility of metal-containing condensation polymers is a common problem. The solubility of such type of polymers can be increased by “clothing” the rigid portion of the backbone with groups that encourage solubility. Such attachments also encourage amorphous structures, further encouraging the solubility of polymers. The product which offers the greatest range of solubility is derived from 2,4-diamino-5-(p-chlorophenyl)-6-ethylpyrimidine which has two “solubilizing” arms, the ethyl arm and the p-chlorophenyl arm, which is consistent with this idea.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR) for determination of functional groups in organotin polyamines

Infrared spectra were obtained for the monomers as well as polymers employing the KBr pellets. Assignments are made from looking at literature values and from studying the infrared spectra of the monomers and polymers. [201-207]. Assignments derived from dibutyltin dichloride moiety are given in Table 3.2.2(1). An in-depth study

of the infrared absorption of 4-chloro-2,6-diaminopyrimidine has been reported [208]. IR spectrum for the dibutyltin dichloride monomer (Figure 3.2.2(2)), 4-chloro-2,6-diaminopyrimidine monomer (Figure 3.2.2(3)) and the product from the condensation of 4-chloro-2,6-diaminopyrimidine (Figure 3.2.2(5)) are given. Assignments derived from the dibutyltin moiety are given in Table 3.2.2(1)

Table 3.2.2(1) IR assignments derived from dibutyltin dichloride and the Sn-N moiety

| Assignments | Bu ₂ SnCl ₂ | AB1 | AB2 | AB3 | AB4 | AB5 | AB6 | AB7 | AB8 | AB9 |
|-------------------------------|-----------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| CH ₃ asym. st. | 2959, 2872 | 2953, 2870 | 2951, 2870 | 2954, 2870 | 2956, 2869 | 2957, 2867 | 2954, 2870 | 2954, 2870 | 2955, 2869 | 2954, 2869 |
| CH ₂ sym. st. | 2927, 2858 | 2928, 2858 | 2921, 2853 | 2928, 2850 | 2926, 2850 | 2926 | 2928, 2854 | 2931, 2856 | 2928, 2850 | 2928, 2850 |
| CH ₂ asym. bending | 1463 | 1463 | 1457 | 1460 | 1446 | 1455 | 1463 | 1465 | 1484 | 1462 |
| CH ₂ sym. bending | 1380 | 1375 | 1372 | 1375 | 1380 | 1380 | 1370 | 1376 | 1375 | 1375 |
| C-C st. | 1178, 1152 | 1141 | 1182, 1148 | 1192, 1150 | 1190 | 1178 | 1178, 1150 | 1178, 1151 | 1178 | 1190, 1151 |
| CH ₃ rocking | 878 | 878 | 878 | 880 | 879 | 880 | 880 | 882 | 880 | 880 |
| Sn-N | - | 420 | 420 | 420 | 420 | 420 | 420 | 420 | 420 | 420 |
| Sn-Cl | 630 | - | - | - | - | - | - | - | - | - |
| Sn-C asym. st. | 592 | 595 | 591 | 595 | 593 | 591 | 595 | 596 | 595 | 595 |
| Sn-C sym. st. | 509 | 509 | 509 | 516 | 506 | 506 | - | - | - | - |

Figure 3.2.2(2) IR spectrum for dibutyltin dichloride monomer

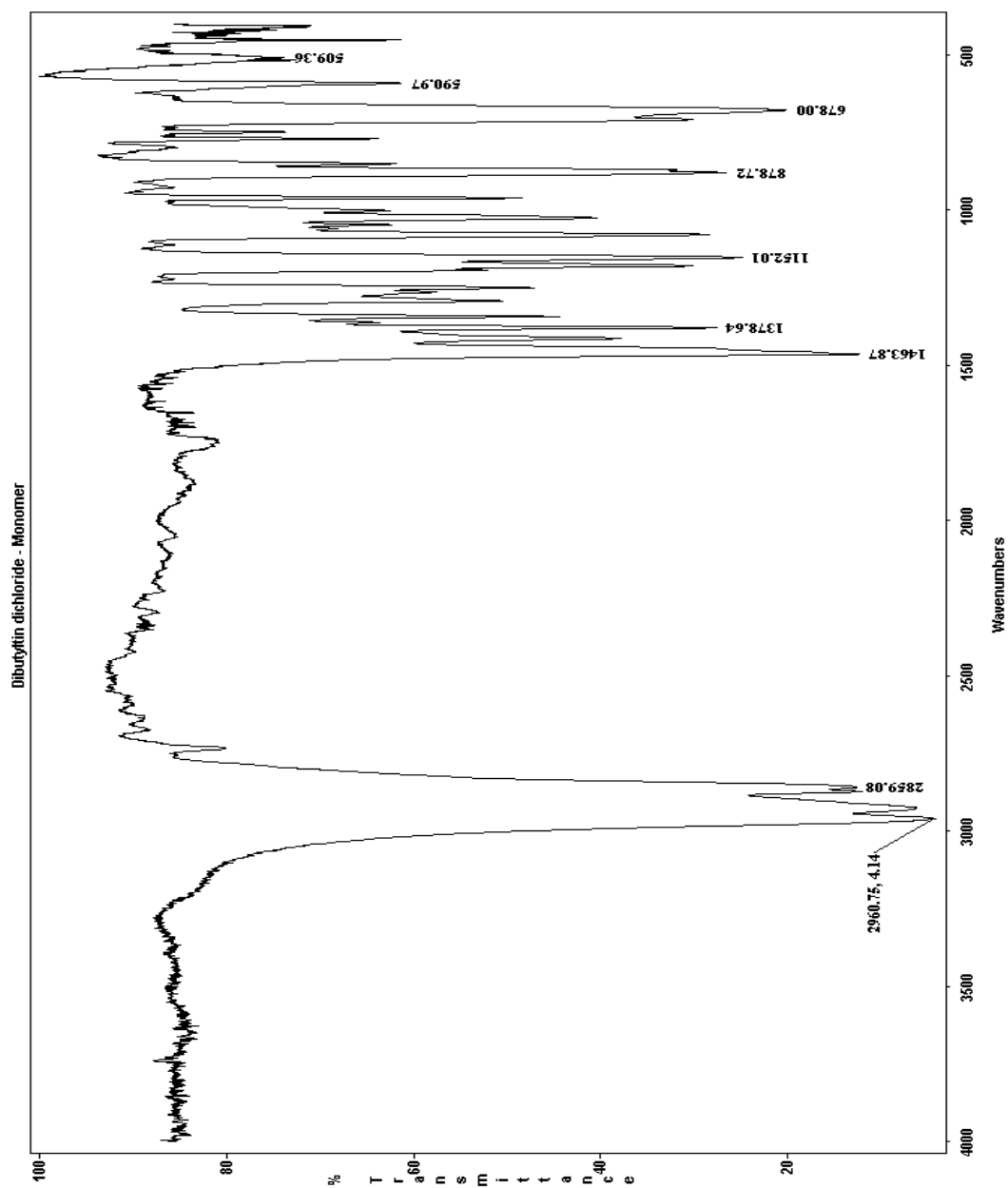
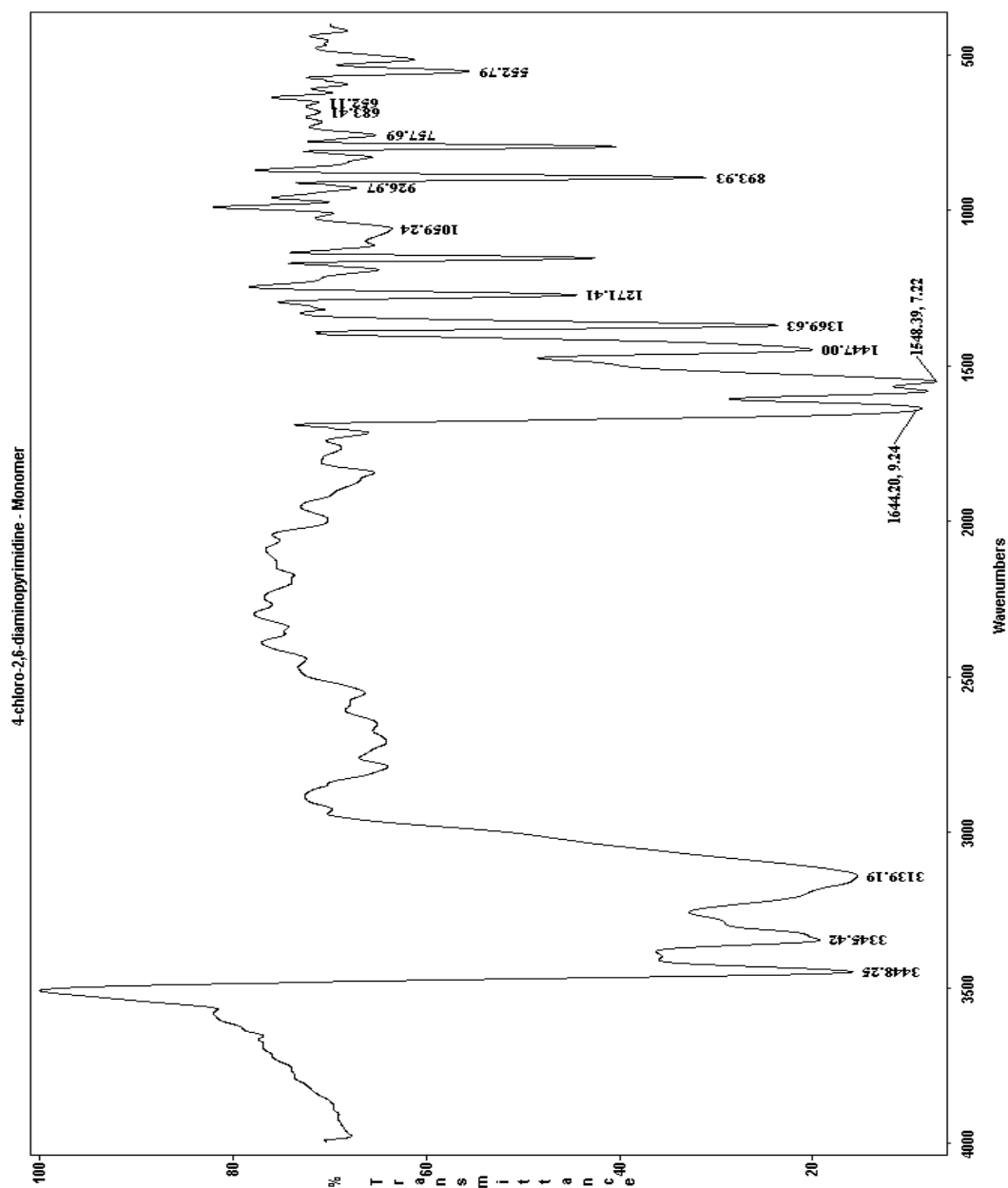


Figure 3.2.2(3) IR spectrum of 4-chloro-2,6-diaminopyrimidine monomer



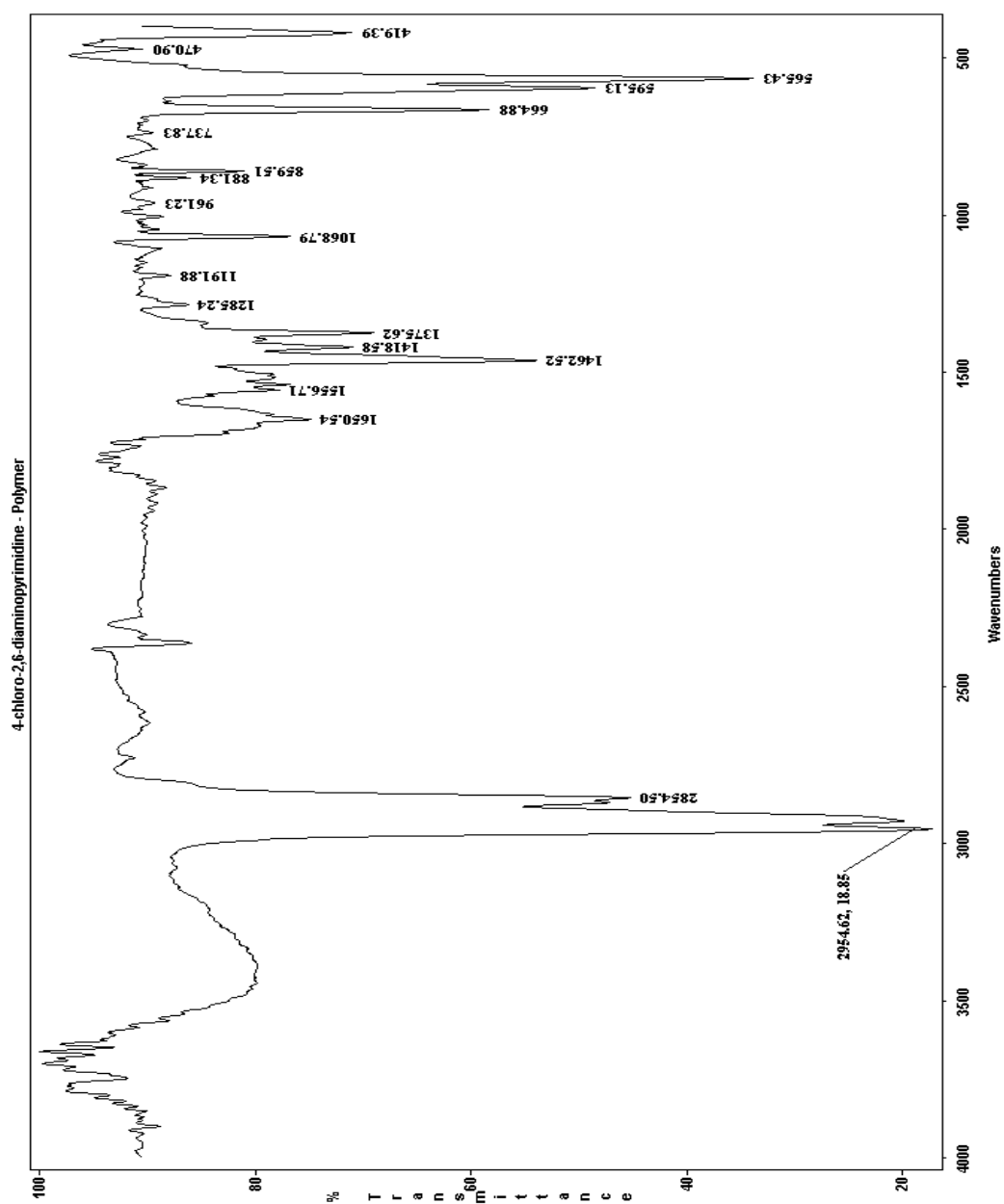
As noted before, an in-depth study of the infrared absorption spectra of 4-chloro-2,6-diaminopyrimidine has been reported [209]. Table 3.2.2(4) gives assignments and band locations from this article along with the corresponding bands obtained by us for the monomer and dibutyltin polymer. These bands are found to be in good agreement which

is consistent with the presence of the pyrimidine moiety in the polymer sample. As expected, there are some shifts in the bands associated with the amine moiety that is now connected to the dibutyltin moiety.

Table 3.2.2(4) IR bands derived from 4-chloro-2,6-diaminopyrimidine and dibutyltin dichloride polymer

| Assignments | 4-chloro-2,6-diaminopyrimidine | | AB 6 polymer |
|-------------------------------|--------------------------------|----------------------|------------------------|
| | Literature | Present study | |
| NH ₂ asym. st. | 3550, 3450 | 3449 | 3426 |
| NH ₂ sym. st. | 3410, 3340 | 3346 | 3340 |
| N-H st. | 3280, 3160 | 3201, 3140 | 3200 |
| N-H sym deform | 1650 | 1638 | 1650 |
| Ring stretching | 1590, 1545, 1480, 1390 | 1581, 1551, --, 1371 | 1600, 1558, 1462, 1395 |
| C-NH st. | 1265 | 1272 | 1285 |
| NH rock | 1080 | 1057 | 1068 |
| C-H in plane ring bend | 940 | 930 | 930 |
| C-H oop bend | 850 | 852 | 859 |
| C-Cl | 765 | 758 | 758 |
| NH wag | 690, 675 | 682, 652 | 690, 665 |
| In plane pyrimidine ring bend | 545 | 553 | 565 |

Figure 3.2.2(5) IR spectra for 4-chloro-2,6-diaminopyrimidine/dibutyltin dichloride polymer



All assignments are reported in wave numbers (cm^{-1})

The product of 4-chloro-2,6-diaminopyrimidine (AB6) and dibutyltin dichloride bands associated with various N-H stretching modes are present at 3426 cm^{-1}

(asymmetric stretching), 3340 cm^{-1} (symmetric stretching), a broad band centered at 3200 cm^{-1} (symmetric stretching) and 1650 cm^{-1} (symmetrical deformation). The bands associated with the C-H stretching are present at 2954 cm^{-1} derived from the C-H stretch in the butyl groups of the dibutyltin moiety. The bands at 2928 cm^{-1} , 2870 cm^{-1} and 2854 cm^{-1} are assigned to various C-H aliphatic stretching modes derived largely from the organotin butyl group. The bands associated with the pyrimidine ring stretching or breathing are found at 1600 cm^{-1} , 1558 cm^{-1} , 1462 cm^{-1} and 1395 cm^{-1} . A band at 595 cm^{-1} is assigned to the asymmetric stretch for the Sn-C moiety and the band at 506 cm^{-1} is assigned to the symmetric stretch for this moiety. The Sn-N stretching is assigned to the region about 420 cm^{-1} . The presence of a band at 420 cm^{-1} is assigned to the Sn-N moiety and is found to be consistent with the formation of the organotin polyamine linkage.

The product of dibutyltin dichloride and 4,6-diaminopyrimidine (AB1) bands associated with various N-H stretching modes are present at 3447 cm^{-1} (asymmetric stretching), 3306 cm^{-1} (symmetric stretching), a broad band centered at 3107 cm^{-1} (symmetric stretching) and 1636 cm^{-1} (symmetrical deformation). The bands associated with the C-H stretching are present at 2953 cm^{-1} derived from the C-H stretch in the butyl groups of the dibutyltin moiety. The bands at 2927 cm^{-1} , 2870 cm^{-1} and 2858 cm^{-1} are assigned to various C-H aliphatic stretching modes derived largely from the organotin butyl group. The bands associated with the pyrimidine ring stretching or breathing are found at 1600 cm^{-1} , 1556 cm^{-1} , 1482 cm^{-1} and 1390 cm^{-1} . A band at 595 cm^{-1} is assigned to the asymmetric stretch for the Sn-C moiety and the band at 509 cm^{-1} is assigned to the symmetric stretch for this moiety. The Sn-N stretching is assigned to the

region about 420 cm^{-1} . The presence of a band at 420 cm^{-1} is assigned to the Sn-N moiety and is found to be consistent with the formation of the organotin polyamine linkage.

The product from dibutyltin dichloride and 2,4-diamino-6-hydroxypyrimidine (AB7) shows bands characteristic of various N-H stretching modes at 3390 cm^{-1} (asymmetric stretching), 3301 cm^{-1} (symmetric stretching), 3138 cm^{-1} and 3107 cm^{-1} (symmetric stretching) and 1624 cm^{-1} (symmetrical deformation). The bands associated with the C-H stretching are present at 2954 cm^{-1} derived from the C-H stretch in the butyl groups of the dibutyltin moiety. The bands at 2931 cm^{-1} , 2870 cm^{-1} and 2856 cm^{-1} are assigned to various C-H aliphatic stretching modes derived largely from the organotin butyl group. The bands associated with the pyrimidine ring stretching or breathing are found at 1590 cm^{-1} , 1560 cm^{-1} , 1480 cm^{-1} and 1360 cm^{-1} . A band at 596 cm^{-1} is assigned to the asymmetric stretch for the Sn-C moiety. The presence of the band at 420 cm^{-1} is assigned to the Sn-N moiety and is found to be consistent with the formation of the organotin polyamine linkage. A strong band at 1648 cm^{-1} is present in the 2, 4-diamino-6-hydroxypyrimidine monomer (AB7) and is assigned the amide carbonyl emphasizing that while the compound is named as a hydroxyl, the oxygen actually exists in the keto rather than in the enol form. This band is present at 1654 cm^{-1} in the polymer.

Thus, the IR vibrational results are found to be consistent with the proposed structure.

3.2.3 Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI TOF MS) for determination of ion fragments

The metal-containing condensation polymers are found to be poorly soluble. Thus, alternative methods are needed to assist in the structural analysis of these important

materials. Mass spectrometry is one analysis technique that does not require the polymer sample soluble in the solution. Here we employed matrix assisted laser desorption ionization time of flight mass spectrometry, MALDI TOF MS, to assist in the structural characterization of the present dibutyltin polyamines.

Tin has 10 isotopes with seven of them present in abundances that allow for compounds containing tin atoms to be identified employing their isotopic abundance ratios. Table 3.2.3(1) contains these abundant tin isotopes. Isotope abundance ratios have been employed in the current research to identify the presence of one, two and three tin-containing ion fragment clusters.

Table 3.2.3(1) Isotopic abundances of tin

| m/e | Natural abundance (%) |
|------------|------------------------------|
| 116 | 15 |
| 117 | 8 |
| 118 | 24 |
| 119 | 9 |
| 120 | 33 |
| 122 | 5 |
| 124 | 6 |

While MALDI MS were obtained and analyzed for all of the 4, 6-diaminopyrimidine products, results for only several will be described here. The ion fragments cited in the tables in section 3.2.3 are at least five times the background.

The first product described is from 2, 4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride polymer. It is interpreted in detail along with the modeling results.

Table 3.2.3(2) contains the major ions found in the range of 100 to 1,000 Da. Throughout this presentation; ions associated with the matrix are omitted.

Table 3.2.3(2) Major (greater than three times the background) ions found for the product of 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride

| m/e | Tentative assignments |
|-----|-----------------------------|
| 177 | BuSn |
| 387 | 1U |
| 565 | 1U + BuSn |
| 636 | 1U + Bu ₂ Sn, NH |
| 795 | 2U + Na |

* U = unit

There are four major ions, all ion fragment clusters, in the mass range of 500 to 1,000 Da. A portion of the MALDI MS for the polymer is given in Figure 3.2.3(3) that displays these major ions.

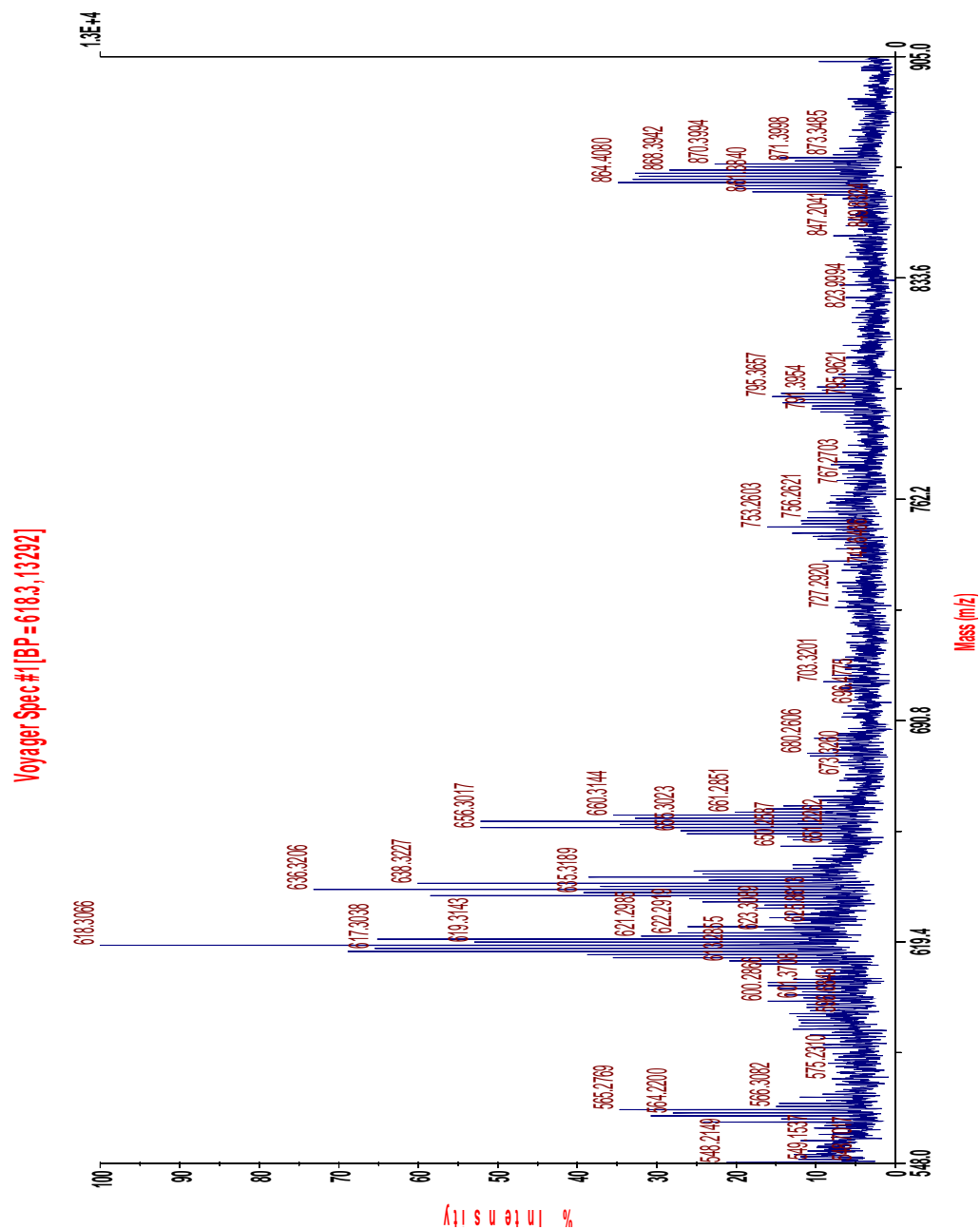


Figure 3.2.3(3) MALDI MS for the product of 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride.

Here we will identify each of the major ion fragment clusters over the mass range of about 500 to 800 daltons. The initial significant ion fragment cluster occur about 565 daltons. An expanded view of this ion fragment cluster is given in Figure 3.2.3(4)

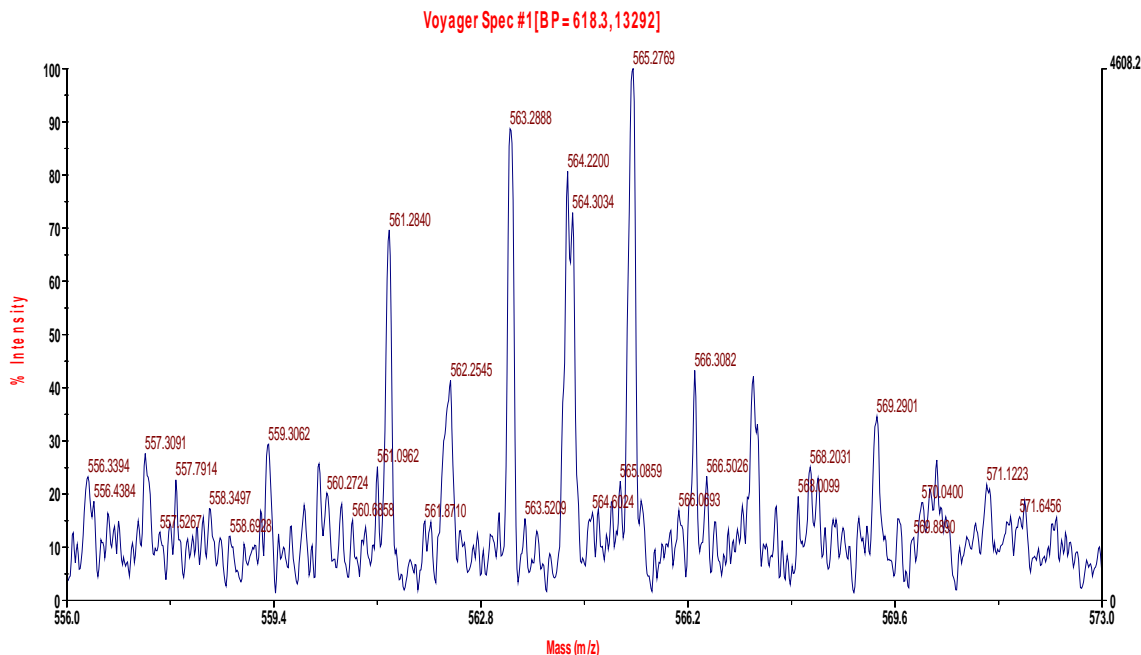


Figure 3.2.3(4) Expanded view of the ion fragment cluster appearing at about 565 daltons for the product of 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and dibutyltin dichloride.

This ion fragment cluster is tentatively assigned as being associated with the structure given below; i.e. two organotin moieties connected to one 2,4-diamino-6-hydroxy-5-nitrosopyrimidine. Its suggested structure is given below in Figure 3.2.3(5)

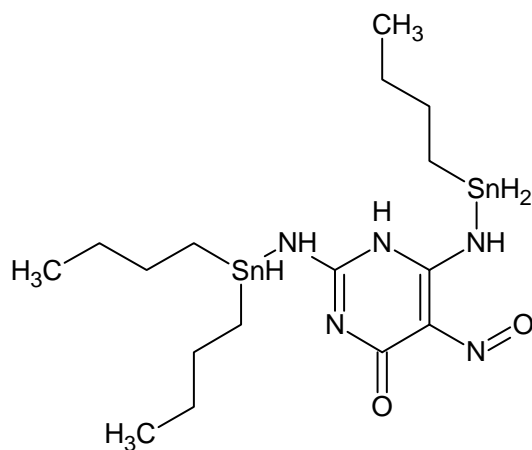


Figure 3.2.3(5) Structural assignment for the ion fragment cluster found about 565 Da

This structure is modeled (Figure 3.2.3(6)) using a modeling program that allows the relative ion fragment intensities to be calculated from the assigned structure [210]. The calculated figure is given below and is in reasonable agreement with the ion fragment cluster about 565 daltons consistent with the assignment being reasonable.

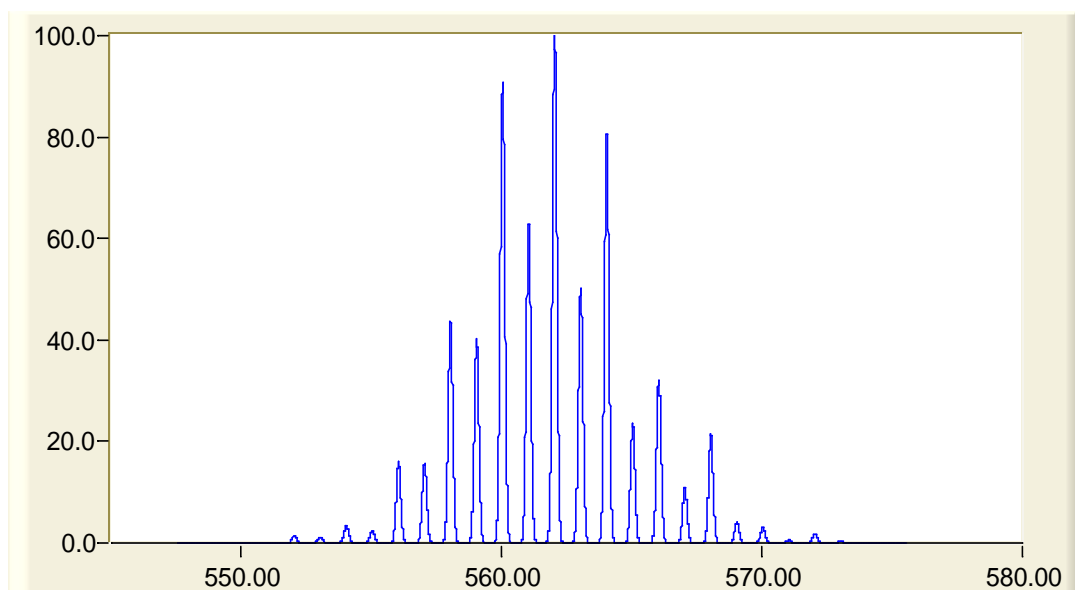


Figure 3.2.3(6) Calculated ion fragment cluster from the proposed structure containing one 2,4-diamino-6-hydroxy-5-nitrosopyrimidine unit and two dibutyltin units as pictured above.

The next major ion fragment cluster occurs at about 618 daltons. An expanded view of this cluster is given in Figure 3.2.3(7).

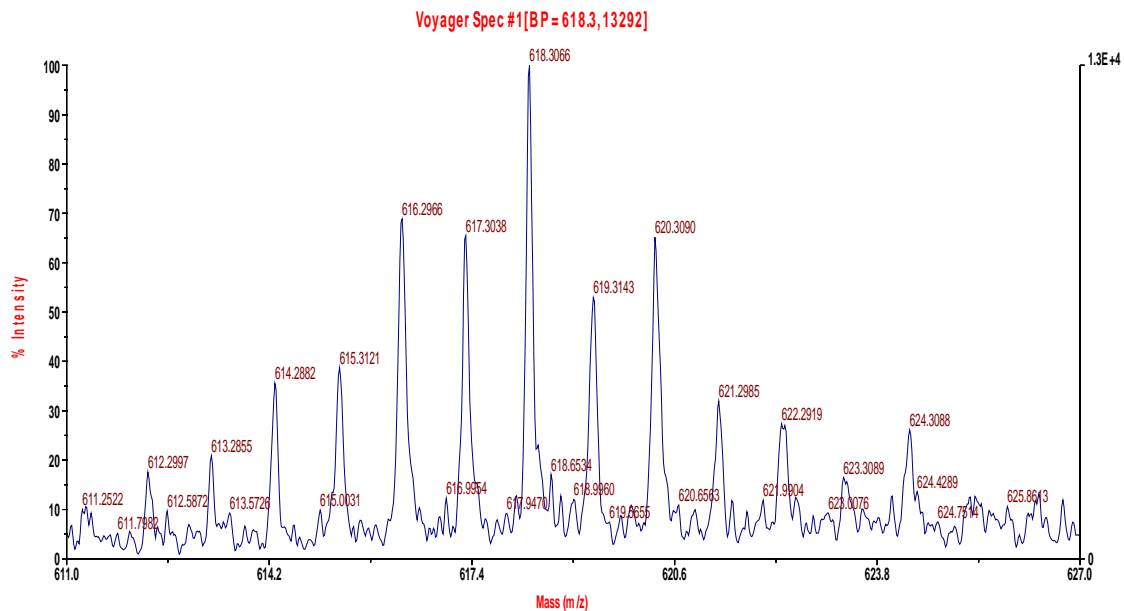


Figure 3.2.3(7) Expanded MALDI MS for the ion fragment cluster occurring about 618 daltons.

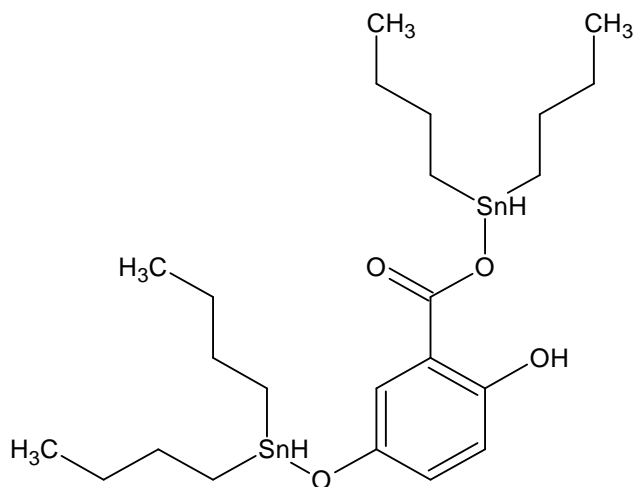


Figure 3.2.3(8) Suggested tentative assignment centered at 618 Da

Tentative structural assignment for the ion fragment cluster found about 618 Da

The corresponding model calculation is shown in Figure 3.2.3(9).

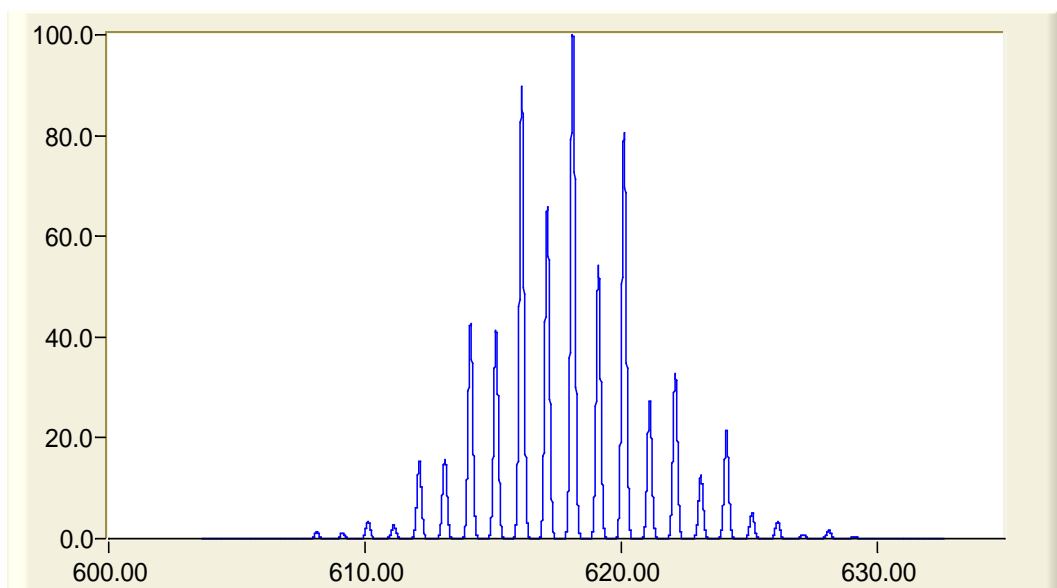


Figure 3.2.3(9) Model of the structure tentatively assigned for the ion fragment about 618 Da

There is reasonable agreement between the model and the suggested structure.

As with other organotin polymers, there is a tendency at low masses (below 1,000 daltons) where the organotin moiety is broken free from the chain reacting with the matrix. This tendency is found for 2,5-dihydroxybenzoic acid, the matrix material employed in the current study. [211, 212]. The ion fragment cluster centering about 618 daltons is then tentatively assigned the structure of two dibutyltin moieties with one unit derived from the matrix material 2,5-dihydroxybenzoic acid as pictured above.

Other ion fragments are also associated with the matrix material. These will be omitted since they only show the presence of the organotin moiety. It is not surprising that such ion fragments are formed since the organotin moiety is reported to be particularly sensitive to degradation in the presence of UV radiation and the particular MALDI MS employs a UV source as the laser light source [213]. Further, 2,5-dihydroxybenzoic acid contains the acid group that is known to be active in condensation

with organotin units as well as the presence of two alcohol groups that can also react with the organotin unit.

The next major ion fragment cluster occurs at about 636 daltons. The tentative structure assigned to this ion fragment cluster is given below and consists of two dibutyltin moieties connected to one 2,4-diamino-6-hydroxy-5-nitrosopyrimidine unit with an additional NH group connected to one of the tin atoms. The expanded MALDI MS for this is given in Figure 3.2.3(10).

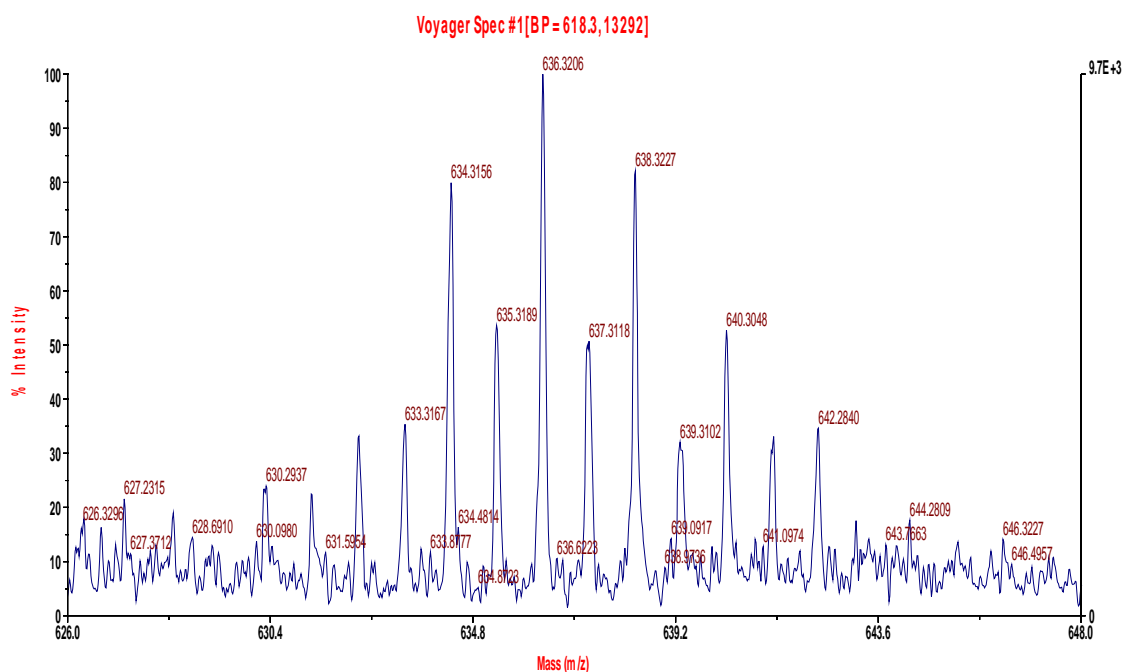


Figure 3.2.3(10) Expanded MALDI MS spectrum for the ion fragment cluster occurring about 636 daltons.

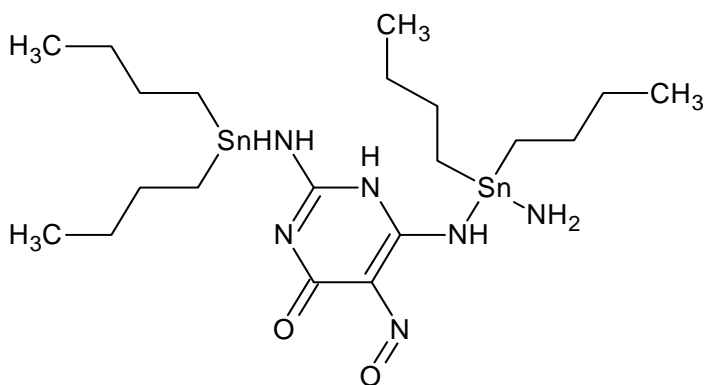


Figure 3.2.3(11) Structural assignment for the ion fragment cluster centered about 636 Da

The calculated model for the tentative assigned ion fragment cluster at 636 Da is given in Figure 3.2.3(12).

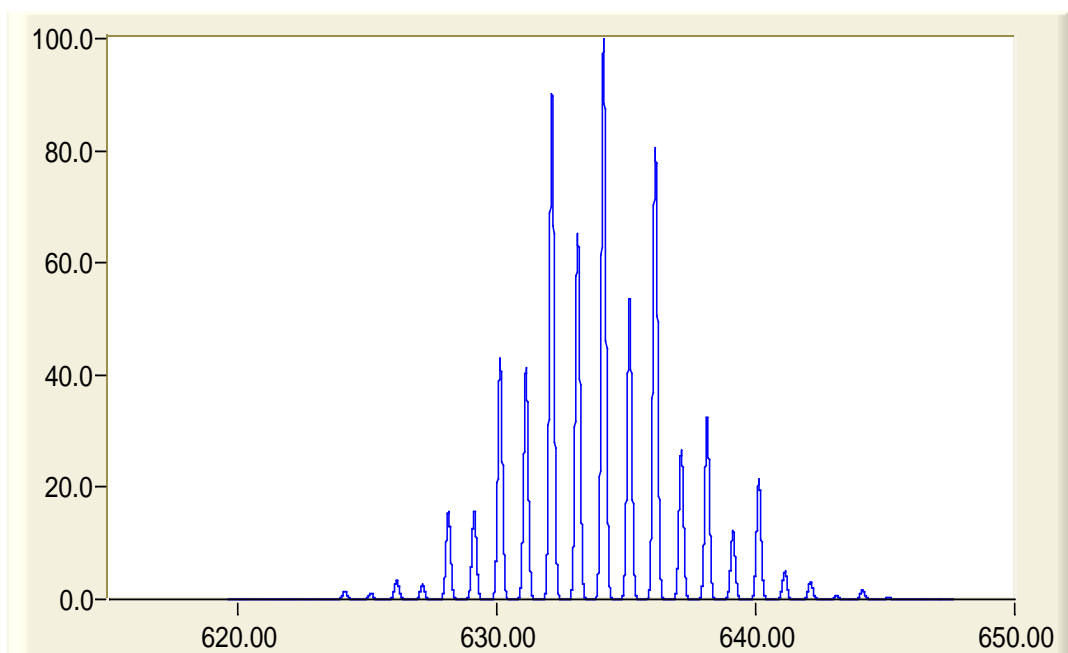


Figure 3.2.3(12) Calculated ion fragment cluster created from the tentatively assigned structure containing two dibutyltin moieties connected to 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and NH moiety.

The next major ion fragment cluster occurs at about 795 daltons. The tentative structure assigned to this ion fragment cluster is given below and consists of two dibutyltin moieties connected to two 2,4-diamino-6-hydroxy-5-nitrosopyrimidine moieties corresponding to two units plus one sodium ion. The expanded MALDI MS for this is given in Figure 3.2.3(13).

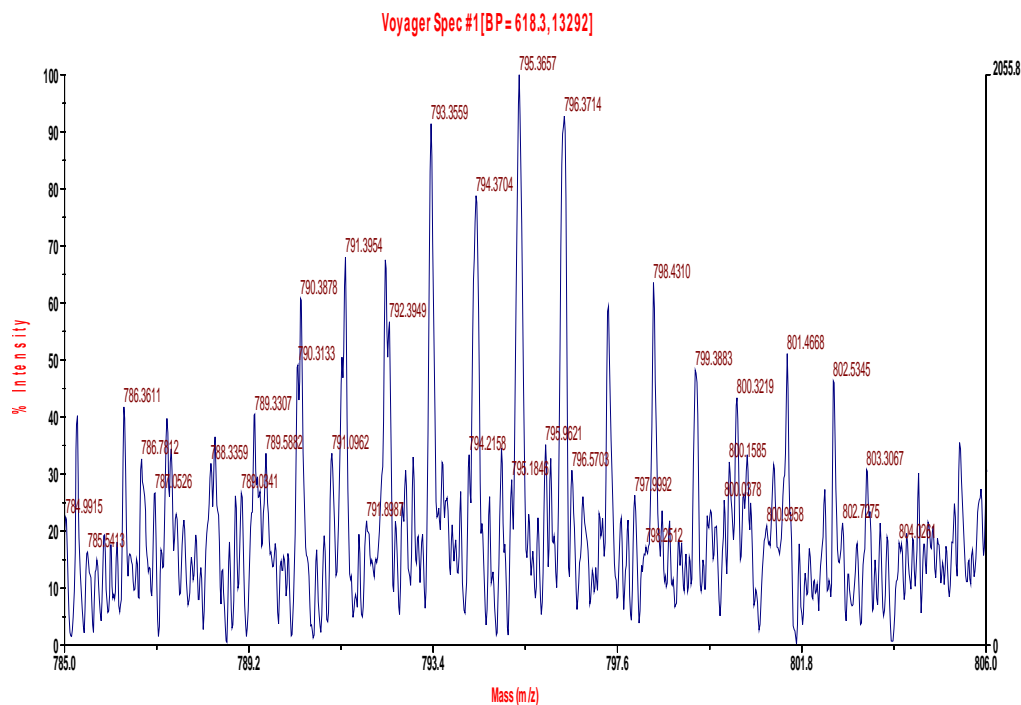


Figure 3.2.3(13) Expanded MALDI MS spectrum for the ion fragment cluster occurring about 795 daltons.

Figure 3.2.3(14) Calculated ion fragment cluster created from the tentatively assigned structure containing two dibutyltin moieties connected to two 2,4-diamino-6-hydroxy-5-nitrosopyrimidine moieties corresponding to two units plus one sodium ion.

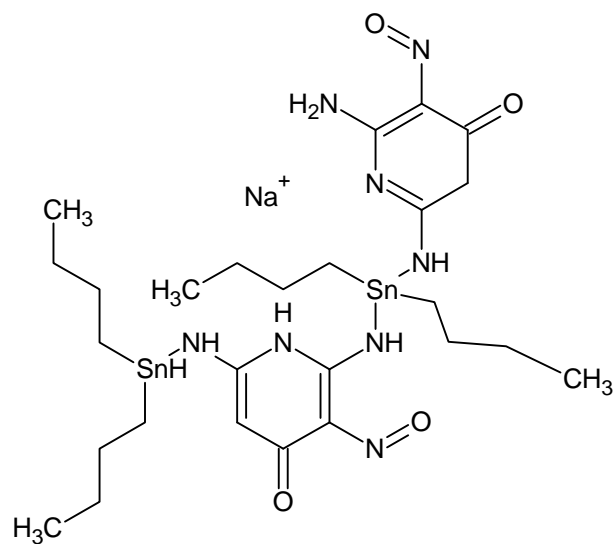


Figure 3.2.3(14) Structural assignment for the ion fragment cluster centered about 795 Da.

The calculated model for the tentative assigned ion fragment cluster at 795 Da is given in Figure 3.2.3(15)

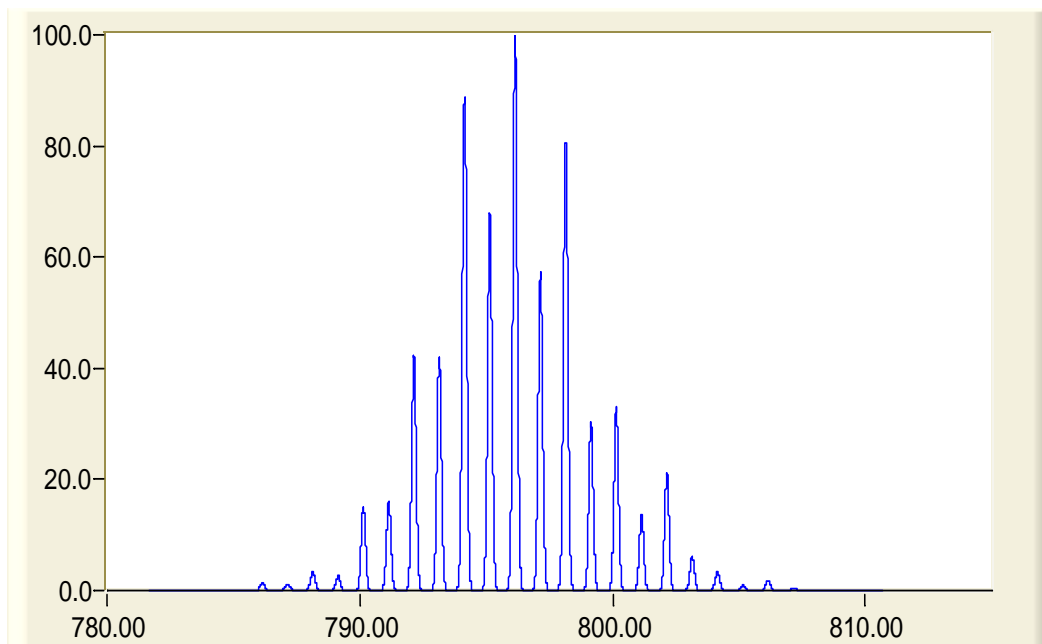


Figure 3.2.3(15) Calculated ion fragment cluster created from the tentatively assigned structure containing two dibutyltin moieties connected to two 2,4-diamino-6-hydroxy-5-nitrosopyrimidine plus one sodium ion.

MALDI MS assists in the structural analysis of the organotin polyamines. Units containing one and two units are easily identified and the proposed structures are consistent with results based on modeling. Such modeling is particularly useful for polymers that contain one or more atoms where there are several isotopes that are present in a reasonable amount.

The description of the MALDI MS results for two additional compounds is given below. Table 3.2.3(16) contains the major ions derived from the product of 2,4-diamino-6-hydroxypyrimidine and dibutyltin dichloride.

Table 3.2.3(16) Significant ion fragments derived from the product of 2, 4-diamino-6-hydroxypyrimidine and dibutyltin dichloride employing 2,5-dihydroxybenzoic acid as the matrix below $m/e = 2,000$ Daltons.

| m/e | Proposed assignment | m/e | Proposed assignment |
|------------|----------------------------|------------|-------------------------------------|
| 177 | BuSn | 193 | BuSnNH |
| 246 | Bu ₂ SnNH | 264 | Bu ₂ Sn(NH) ₂ |
| 303 | U-Bu | 358 | U |
| 464 | U+Py-NH | 479 | U+Py |
| 655 | 2U-Bu | 889 | 2U+BuSn |
| 907 | 2U+BuSnO | 947 | 2U+Bu ₂ Sn |
| 1004 | 3U-Bu | 1117 | 3U+Cl |
| 1293 | 4U-Py | 1465 | 4U+Cl |
| 1659 | 5U-Py | 1850 | 5U+Cl |
| 1863 | 5U+Py-Bu | 1966 | 5U+BuSnNH |

Those ion fragments that contain Cl must be end groups containing at least one end of the chain. Their loss of no more than a single butyl group is consistent with other studies of similar organotin polymers where loss of butyl groups and other non-chain groups occurring only at the sites of bond scission.

Table 3.2.3(17) and **Table 3.2.3(18)** contains selected **two** and **three** tin containing ion fragment clusters

Table 3.2.3(17) Isotopic abundance matches for the ion fragment 2U-Bu containing **two** tin atoms derived from the product of 2,4,-diamino-6-hydroxypyrimidine and dibutyltin dichloride

| m/e | % Natural Abundance | m/e | % Abundance Found |
|------------|--------------------------------|------------|------------------------------|
| 232 | 17 | 649 | 20 |
| 233 | 14 | 650 | 14 |
| 234 | 46 | 651 | 50 |
| 235 | 36 | 652 | 36 |
| 236 | 94 | 653 | 80 |
| 237 | 51 | 654 | 60 |
| 238 | 100 | 655 | 100 |
| 239 | 35 | 656 | 45 |
| 240 | 81 | 657 | 80 |
| 242 | 32 | 659 | 40 |
| 249 | 22 | 661 | 22 |

Table 3.2.3(18) Isotopic abundance matches for ion fragment 3U-Bu containing **three** tin atoms derived from the product of 2,4,-diamino-6-hydroxypyrimidine and dibutyltin dichloride

| | | 2U+BuSn | | 3U-Bu | |
|------------|--------------------------------|----------------|------------------------------|--------------|------------------------------|
| m/e | % Natural Abundance | m/e | % Abundance Found | m/e | % Abundance Found |
| 350 | 20 | 883 | 25 | 997 | 20 |
| 351 | 20 | 884 | 20 | 998 | 20 |
| 352 | 47 | 885 | 47 | 999 | 60 |
| 353 | 42 | 886 | 45 | 1000 | 60 |
| 354 | 79 | 887 | 85 | 1001 | 84 |
| 355 | 60 | 888 | 60 | 1002 | 50 |
| 356 | 100 | 889 | 100 | 1003 | 100 |
| 357 | 57 | 890 | 55 | 1004 | 57 |
| 358 | 88 | 891 | 82 | 1005 | 75 |
| 359 | 37 | 892 | 35 | 1006 | 34 |
| 360 | 63 | 893 | 61 | 1007 | 50 |
| 361 | 17 | 894 | 20 | 1008 | 22 |
| 362 | 34 | 895 | 34 | 1009 | 34 |
| 364 | 19 | 897 | 18 | 1010 | 19 |

The ion abundance agreements are consistent with the ion fragments containing two and three tin atoms.

Tables 3.2.3(19) - 3.2.3(21) contain ion fragments derived from the product of 4, 6-diaminopyrimidine and dibutyltin dichloride. Again, isotopic abundance studies for selected ion fragment clusters are consistent with these clusters containing **two** and **three** tin atoms.

Table 3.2.3(19) Ion fragments derived from the product of 4,6-diaminopyrimidine and dibutyltin dichloride employing 2,5-dihydroxybenzoic acid as the matrix between 500 to 5000 daltons.

| m/e | (Proposed) Assignment | m/e | (Proposed) Assignment |
|------------|----------------------------------|------------|----------------------------------|
| 537 | U+Bu ₂ Sn,Na-Bu | 575 | U+Bu ₂ Sn |
| 585 | 2U-Py | 631 | 2U,Na-2NH |
| 722 | 2U+Cl | 753 | 2U+Py-2NH |
| 922 | 3U-Py | 1024 | 3U |
| 1116 | 3U+Py-NH | 1140 | 3U+Py |
| 1351 | 4U-NH | 1690 | 5U-NH |
| 1975 | 6U-Py+2NH | 3020 | 9U-Bu |
| 3352 | 10U-Bu+Py | 3676 | 11U-Bu,NH |
| 4119 | 12U+NH | 4679 | 14U-Py+NH |

Table 3.2.3(20) Isotopic abundance matches for selected ion fragments containing **two** tin atoms derived from the product of 4,6-diaminopyrimidine and dibutyltin dichloride (>5%)

| | | U+Bu(NH)₂ - Bu | | 2U,Na+Py - NH | |
|------------|----------------------------|----------------------------------|--------------------------|----------------------|--------------------------|
| m/e | % Natural Abundance | m/e | % Abundance Found | m/e | % Abundance Found |
| 232 | 17 | 487 | 20 | 747 | 20 |
| 233 | 14 | 488 | 20 | 748 | 20 |
| 234 | 46 | 489 | 50 | 749 | 60 |
| 235 | 36 | 490 | 40 | 750 | 50 |
| 236 | 94 | 491 | 80 | 751 | 90 |
| 237 | 51 | 492 | 51 | 752 | 60 |
| 238 | 100 | 493 | 100 | 753 | 100 |
| 239 | 35 | 494 | 35 | 754 | 40 |
| 240 | 81 | 495 | 70 | 755 | 70 |
| 241 | 9 | 496 | 10 | 756 | 25 |
| 242 | 32 | 497 | 35 | 757 | 30 |
| 243 | 6 | 498 | 8 | 758 | 10 |
| 244 | 22 | 499 | 25 | 759 | 25 |

Table 3.2.3(21) Isotopic abundance matches for selected ion fragments containing **three** tin atoms derived from the product of 4,6-diaminopyrimidine and dibutyltin dichloride (>5%)

| m/e | % Natural Abundance | m/e | % Abundance Found | m/e | % Abundance Found |
|------------|--------------------------------|------------|------------------------------|------------|------------------------------|
| 348 | 7 | 1016 | 8 | 1108 | 10 |
| 349 | 7 | 1017 | 8 | 1109 | 10 |
| 350 | 20 | 1018 | 19 | 1110 | 25 |
| 351 | 20 | 1019 | 17 | 1111 | 17 |
| 352 | 47 | 1020 | 36 | 1112 | 50 |
| 353 | 42 | 1021 | 41 | 1113 | 55 |
| 354 | 79 | 1022 | 60 | 1114 | 60 |
| 355 | 60 | 1023 | 65 | 1115 | 60 |
| 356 | 100 | 1024 | 100 | 1116 | 100 |
| 357 | 57 | 1025 | 60 | 1117 | 50 |
| 358 | 88 | 1026 | 70 | 1118 | 70 |
| 359 | 37 | 1027 | 35 | 1119 | 40 |
| 360 | 63 | 1028 | 45 | 1120 | 61 |
| 361 | 17 | 1029 | 20 | 1121 | 17 |
| 362 | 34 | 1030 | 28 | 1122 | 40 |
| 363 | 8 | 1031 | 8 | 1123 | 10 |
| 364 | 19 | 1032 | 15 | 1124 | 19 |

MALDI MS results are consistent with the proposed repeat unit. Further, chain scission is consistent with other studies occurring between the Sn-N bond with some loss of the organotin butyl tin moiety, presumably only at the location for bond scission. [214, 215].

3.2.4 Structure elucidation of 4,6-diaminopyrimidine and dibutyltin dichloride polymer by ^1H and ^{13}C NMR spectroscopy

3.2.4(1) Proton (^1H NMR)

^1H NMR spectra were obtained for both the monomers (4,6-diaminopyrimidine hemisulfate and dibutyltin dichloride) as well as for the polymer (4,6-diaminopyrimidine and dibutyltin dichloride) as shown in **Figures 3.2.4(2) – 3.2.4(4)** respectively.

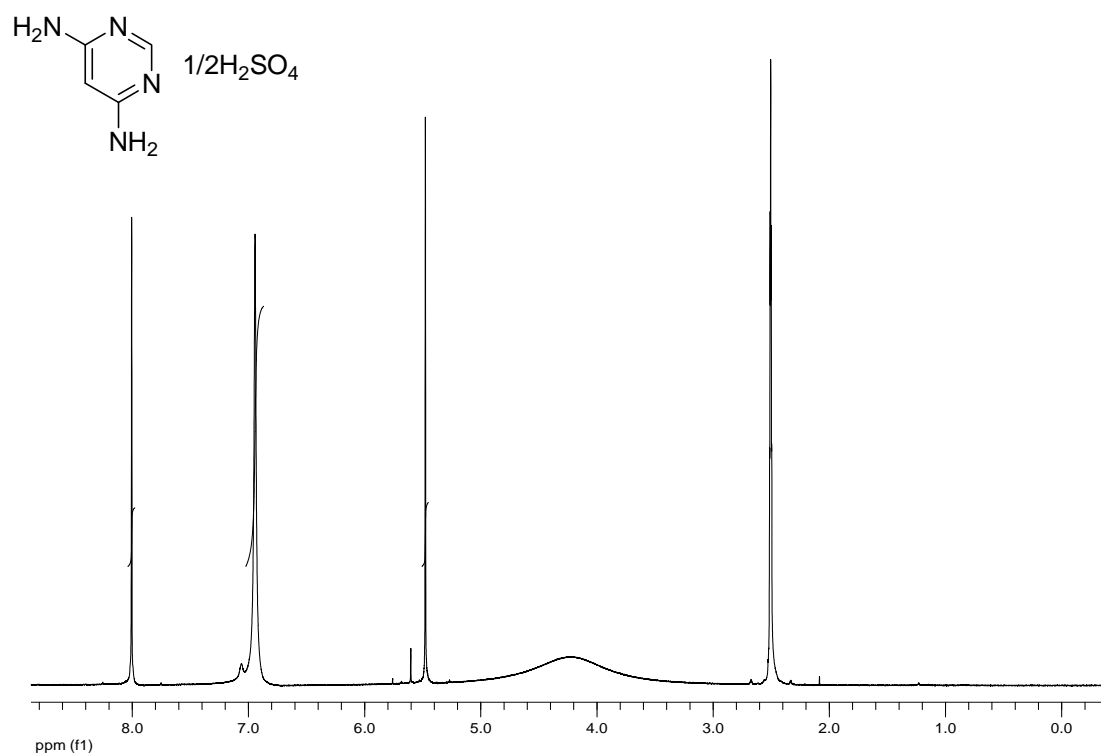


Figure 3.2.4(2) ^1H NMR spectrum for 4,6-diaminopyrimidine

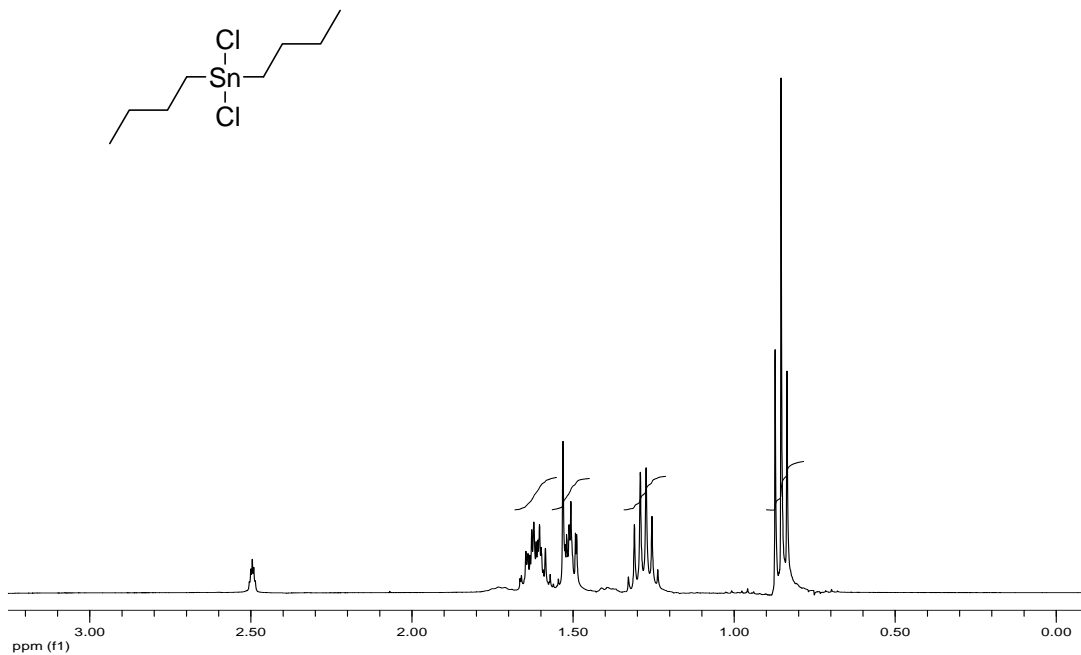


Figure 3.2.4(3) ^1H NMR spectrum for dibutyltin dichloride

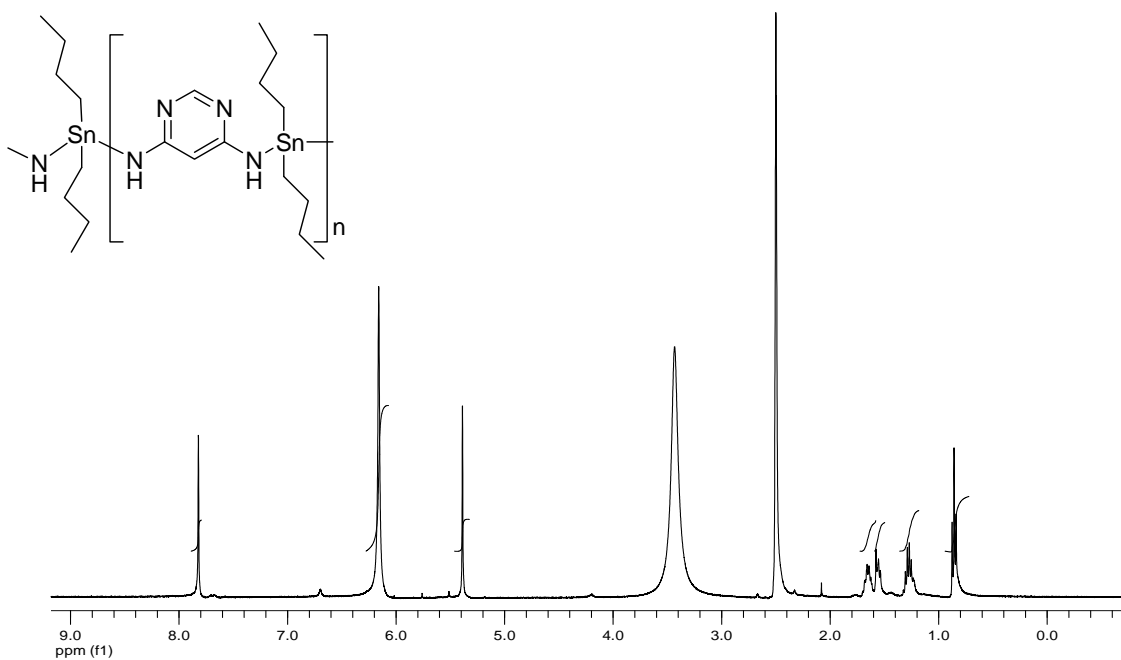


Figure 3.2.4(4) ^1H NMR spectrum for the product of 4,6-diaminopyrimidine and dibutyltin dichloride

The proton assignments for 4,6-diaminopyrimidine monomer are 5.472, 6.938 and 8.001 ppm respectively. These give rise to three unique proton signals in ^1H NMR spectrum of 4,6-diaminopyrimidine molecule. The proton 8.001 (s,1H) is the one lying between two heteroatoms (nitrogen) which is far downfield due to the electronegative effect. The proton assigned at 6.938 (s,1H) is slightly downfield as it is close to one heteroatom (nitrogen) whereas the proton at 5.472 (s,1H) is upfield as it does not have any heteroatom (nitrogen) in the nearby environment and arising from the NH moiety.

The proton assignments for the dibutyltin dichloride are 0.859 (t,1H) from the methyl (CH_3) grouping and other bands associated with various methylene (CH_2) groupings ranging from 1.241 (m,1H), 1.493 (m,1H) and 1.575 (t,1H) respectively which are upfield. These methylene (CH_2) groups from dibutyltin dichloride monomer range from 1.241 to 1.665 ppm respectively.

For the 4,6-diaminopyrimidine and dibutyltin dichloride polymer, the methyl (CH_3) grouping appears at 0.858 (t,1H) and other methylene (CH_2) groupings range from 1.252 to 1.683 ppm respectively which are upfield. Again in case of ^1H NMR for 4,6-diaminopyrimidine and dibutyltin dichloride polymer, three unique proton bands are noticed at 7.821 (s,1H), 6.160 (s,1H) arising from the aromatic ring and 5.388 (s,1H) arising from the NH moiety. The assignments in the polymer are moved slightly upfield due to the coupling of the dibutyltin moiety with the aromatic ring resulting in the formation of polymer. These results are consistent with the proposed structure and validate the polymeric nature of the molecule.

3.2.4(5) Carbon (^{13}C NMR)

^{13}C NMR spectra were obtained for both the monomers (4,6-diaminopyrimidine hemisulfate and dibutyltin dichloride) as well as for the polymer (4,6-diaminopyrimidine and dibutyltin dichloride) as shown in **Figures 3.2.4(6) – 3.2.4(8)** respectively.

Bands from ^{13}C NMR spectra for 4,6-diaminopyrimidine hemisulfate (monomer) are found at δ 81.290, 153.295 and 160.896 ppm respectively arising from the aromatic ring. The carbon atom at 160.896 is far downfield because of the influence of two heteroatoms (nitrogen). The assignment at 153.295 is slightly downfield whereas the carbon at 81.290 ppm is upfield which suggests this carbon is not close to heteroatom (nitrogen).

For dibutyltin dichloride, bands are found at δ 25.608, 27.723 and 38.047 ppm respectively arising from three methylene (CH_2) groups next to tin metal whereas δ 13.804 is associated with methyl (CH_3) group from butyl moiety.

Again in case of ^{13}C NMR for 4,6-diaminopyrimidine and dibutyltin dichloride polymer, similar bands arising from both the monomers are obtained. The ^{13}C NMR spectra for polymer displays bands at 13.812 arising from the methyl (CH_3) group from the butyl moiety. The assignments at 25.653 and 27.693 ppm respectively are assigned to two methylene (CH_2) groups but in this spectrum we are deficit of one carbon appearing at around 38.000 ppm which overlaps with the solvent peak. The carbon assignments appear at 163.267, 157.472 and 82.465 ppm respectively which arise from the 4,6-diaminopyrimidine monomer are downfield in comparison to the assignments obtained from the monomer itself. Again we notice, the similar bands arising in the ^{13}C NMR for

product is consistent with the proposed repeat unit and determines the polymeric nature of the molecule.

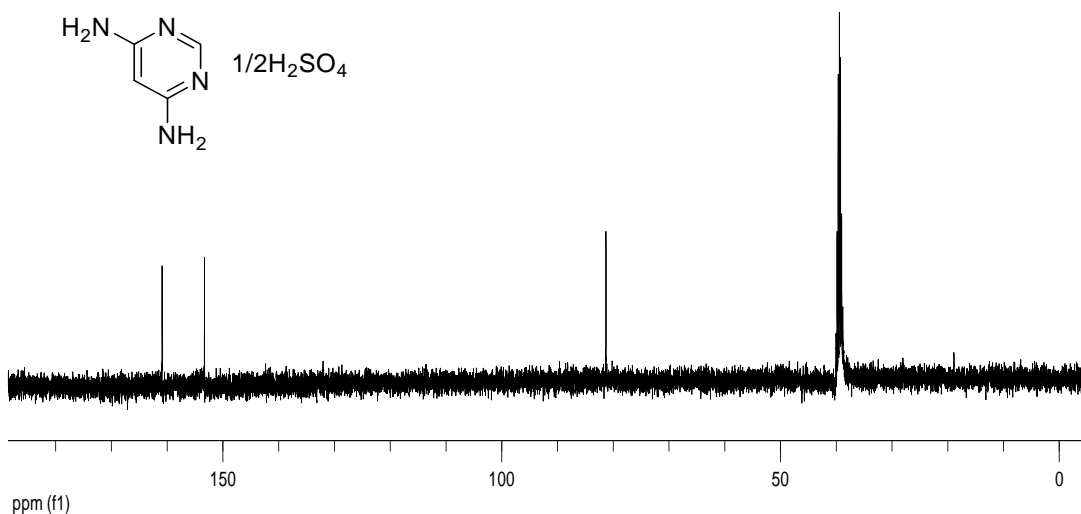


Figure 3.2.4(6) ^{13}C NMR spectrum for 4,6-diaminopyrimidine hemisulfate

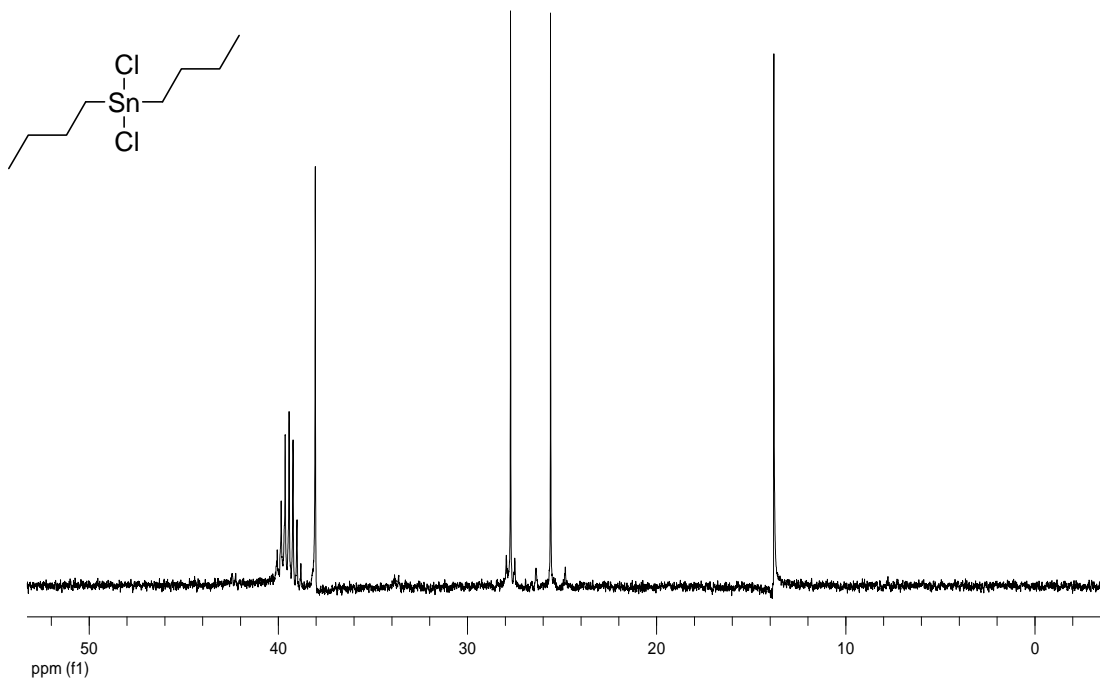


Figure 3.2.4(7) ^{13}C NMR spectrum for dibutyltin dichloride

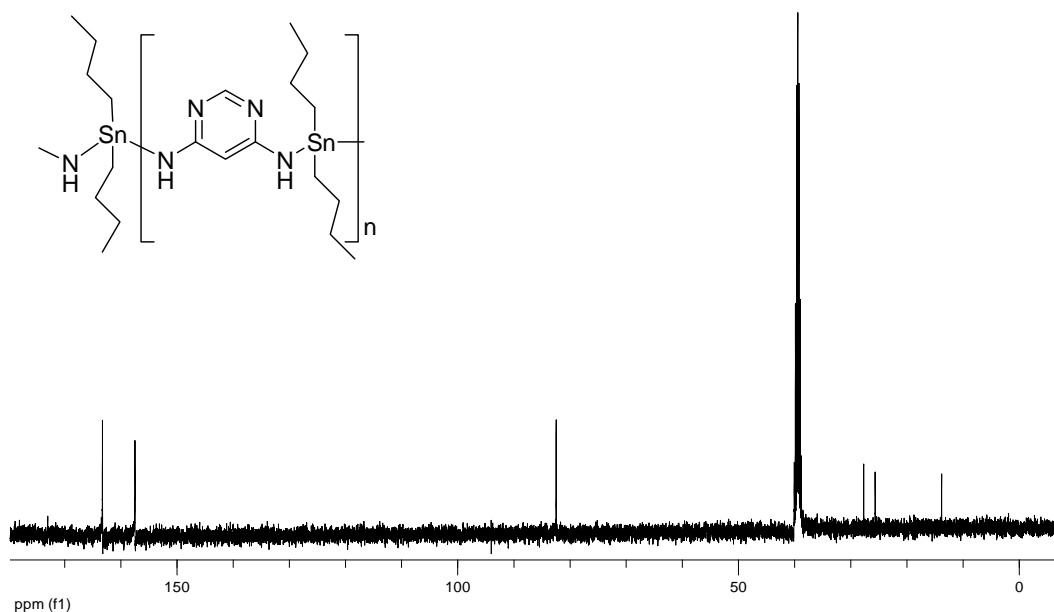


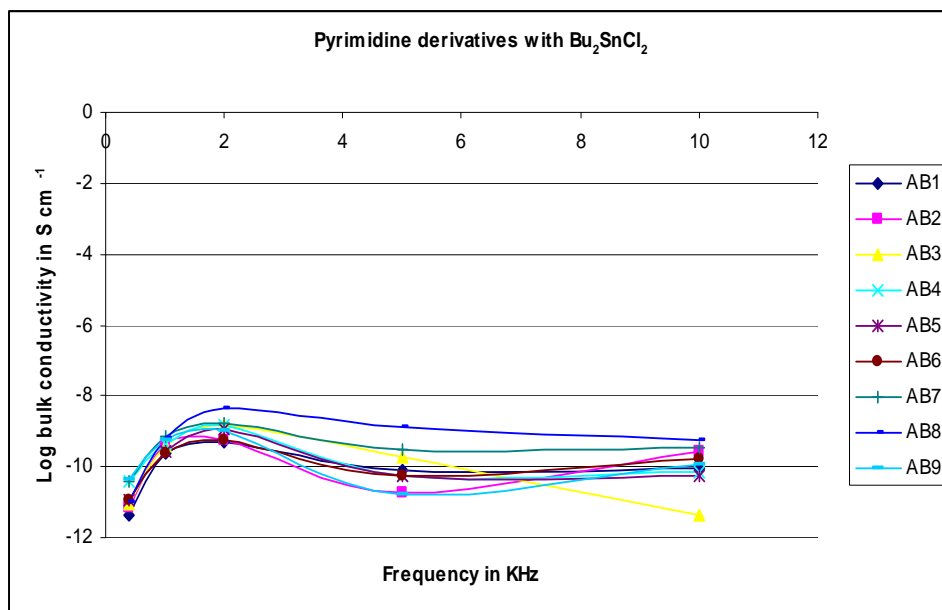
Figure 3.2.4(8) ^{13}C NMR spectrum for the product of 4,6-diaminopyrimidine and dibutyltin dichloride

Thus ^1H and ^{13}C NMR results are consistent with the proposed repeat unit for the polymer derived from 4,6-diaminopyrimidine and dibutyltin dichloride.

3.2.5 Electrical properties of dibutyltin pyrimidines

The electrical conductivity results for the dibutyltin pyrimidines appear in Figure 3.2.5(1).

Figure 3.2.5(1) Conductivity plot for the products derived from 4,6-diaminopyrimidine derivatives and dibutyltin dichloride as a function of applied frequency



where the various designations are for the 4,6-diamino derivatives reacted with dibutyltin dichloride; AB1 = 4,6-diaminopyrimidine hemisulfate; AB2 = 4,6-diamino-5-nitropyrimidine; AB3 = 4,6-diamino-2-methyl mercaptopyrimidine; AB4 = 4,6-diamino-2-methyl-5-nitrosopyrimidine; AB5 = 4,6-diamino-2-mercaptopyrimidine; AB6 = 4-chloro-2,6-diaminopyrimidine; AB7 = 2, 4-diamino-6-hydroxypyrimidine; AB8 = 2,4-diamino-6-hydroxy-5-nitrosopyrimidine and AB9 = pyrimethamine

The log conductivity values are generally within less than a tenfold difference throughout the series. The conductivity is found to be independent of the chain length and electronic nature of the pyrimidine ring. The conductivity values are in the range of non-conductor to near semiconductor region. The conductivity plots for this series as a function of applied frequency are linear or slightly sigmoid. The dielectric constants for pyrimidine polyamines vary from 0.07 to 1.63 [216] whereas the dissipation factors range from 0.13 to 1.85 [217] respectively. These values are consistent with the polar nature of the materials as expected.

Table 3.2.5(2) contains average values for the samples surveyed in this part of the study.

Table 3.2.5(2) Electrical conductivity results for the entire series of undoped samples shown below

| Samples | Log Conductivity (General range) | Classification range |
|--|---|-----------------------------|
| HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Methyl-HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Dimethyl-HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Chloro-HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Tetrachloro-HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| t-butyl-HQ + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Dicyano-HQ + Cp ₂ TiCl ₂ | -14 | Insulator |
| Tetrachloro-HQ + Cp ₂ ZrCl ₂ | -11 | Near semiconductor |
| Phenyl-HQ + Bu ₂ SnCl ₂ | -11 | Near semiconductor |
| TA + Cp ₂ TiCl ₂ | -11 | Near semiconductor |
| 2-Bromo-TA + Cp ₂ TiCl ₂ | -11 | Near semiconductor |
| Dichloro-TA + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Tetramethyl-TA + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| Dimethyl-TA + Cp ₂ TiCl ₂ | -10 | Semiconductor |
| TA + Cp ₂ ZrCl ₂ | -11 | Near semiconductor |
| Flavazin L + Cp ₂ TiCl ₂ | -11 | Near semiconductor |

| | | |
|---|-----|--------------------|
| Acid Red 88 + Cp_2TiCl_2 | -11 | Near semiconductor |
| COG + Cp_2ZrCl_2 | -11 | Near semiconductor |
| Orange II + Cp_2ZrCl_2 | -10 | Semiconductor |
| Acid Yellow II + Cp_2HfCl_2 | -10 | Semiconductor |
| CHFP + Ph_2SnCl_2 | -10 | Semiconductor |
| CHFP + Ph_3BiCl_2 | -10 | Semiconductor |
| CHFP + Ph_3SbCl_2 | -11 | Near semiconductor |
| TDP + Ph_3SbCl_2 | -11 | Near semiconductor |
| 2, 6-DP + Ph_3SbCl_2 | -12 | Near semiconductor |
| Eosin Y + Ph_2SnCl_2 | -10 | Semiconductor |
| Eosin Y + $(\text{Me})_2\text{SnCl}_2$ | -12 | Near semiconductor |
| Phloxine B + Ph_2SnCl_2 | -11 | Near semiconductor |
| Rose Bengal + Ph_2SnCl_2 | -11 | Near semiconductor |
| Cp_2ZnCl_2 Ferrocinium complex | -10 | Semiconductor |
| 4, 6 – DAP + Bu_2SnCl_2 | -11 | Near semiconductor |
| 4, 6-DA-5-NP + Bu_2SnCl_2 | -11 | Near semiconductor |
| 4,6-DA-2-MMP+ Bu_2SnCl_2 | -11 | Near semiconductor |
| 4,6-DA-2-M-5-NP + Bu_2SnCl_2 | -10 | Semiconductor |
| 4, 6 – DA-2-MP + Bu_2SnCl_2 | -10 | Semiconductor |
| 4-Chloro - 2, 6 -DAP + | -10 | Semiconductor |

| | | |
|---|-----|---------------|
| Bu ₂ SnCl ₂ | | |
| 2, 4 - DA-6-HP + Bu ₂ SnCl ₂ | -10 | Semiconductor |
| 2, 4 -DA-6H-5-NP + Bu ₂ SnCl ₂ | -10 | Semiconductor |
| Pyrimethamine + Bu ₂ SnCl ₂ | -10 | Semiconductor |

where,

HQ = hydroquinone; TA = terephthalic acid; COG = Crocein Orange G; CHFP = cobalticene hexafluorophosphate; TDP = Thio diaminopyrimidine; DAP = diaminopyrimidine; DA = diamino; NP = nitropyrimidine; MMP = methyl mercaptopyrimidine; M = methyl; MP = mercaptopyrimidine; HP = hydroxypyrimidine; H = hydroxy

In the present survey, the majority of the compounds are found to lie in the range of semiconductor to near conductor region.

3.3 Doping Experiments

3.3.1 Surface and bulk doping studies for 2-nitro-1, 4-phenylenediamine titanocene dichloride polymer

In the previous section we described the results for the undoped samples. Most of these materials were non-conductors to near semiconductors. Here we describe the doping results for samples that gave higher conductivities, generally close to being semiconductors. Iodine is the most widely used doping agent because of the ease of application. It is experimentally easy to work with iodine as it does not induce degradation of the polymer. [37]. The iodine chamber method is employed for carrying

surface doping in polymers [38]. In the iodine chamber method, the iodine crystals are heated slowly which are placed in a glass beaker and polymer films or disks are exposed to the iodine vapors. **Table 3.3.1(1)** contains results for some of these doping experiments and the results. Almost all of the samples showed little or no change in the conductivity between the doped and the undoped samples. Even so, one compound was found to give significant, 100 fold and greater, increases in conductivity when doped. This was the product formed from the reaction of 2-nitro-1,4-phenylenediamine and titanocene dichloride as shown in **Figure 3.3.1(2)**

Because of the positive response to doping, this product underwent extensive study of its electrical behavior as a function of a number of variables. Two types of doping were employed. Initially, surface conductivity was studied by simply exposing the polymer pellets to iodine vapors. Because of the difficulty of controlling the amounts of iodine deposited on the pellet surface, bulk studies were carried out. Here, iodine is mixed with the polymer sample and measurements were then made on the mixtures.

Table 3.3.1(1) Results for samples exposed to iodine vapors

| Samples | Log conductivity results | | Classification range |
|--|--------------------------|-------|----------------------|
| | Undoped | Doped | |
| 1,4- phenylenediamine | -6.9 | -6.7 | Semiconductor |
| Chloro-HQ + Cp ₂ TiCl ₂ | -9.8 | -10.1 | Semiconductor |
| Methyl-HQ + Cp ₂ TiCl ₂ | -10.3 | -11.0 | Near semiconductor |
| Eosin Y + (Me) ₂ SnCl ₂ | -11.7 | -10.2 | Semiconductor |
| Eosin Y + Ph ₂ SnCl ₂ | -10.2 | -10.6 | Near semiconductor |
| 4,6-DA-2-M-5-NP + Bu ₂ SnCl ₂ | -10.1 | -10.0 | Semiconductor |
| CHFP + Ph ₂ SnCl ₂ | -10.0 | -10.4 | Semiconductor |
| Cp ₂ ZnCl ₂ Ferrocinium complex | -10.2 | -10.1 | Semiconductor |
| Terephthalic acid + Cp ₂ ZrCl ₂ | -10.7 | -10.3 | Near semiconductor |

where,

HQ = hydroquinone; DA = diamino; M = methyl; NP = nitropyrimidine; CHFP = cobalticene hexafluorophosphate

Figure 3.3.1(2) represents the product formed from the reaction of 2-nitro-1,4-phenylenediamine with titanocene dichloride

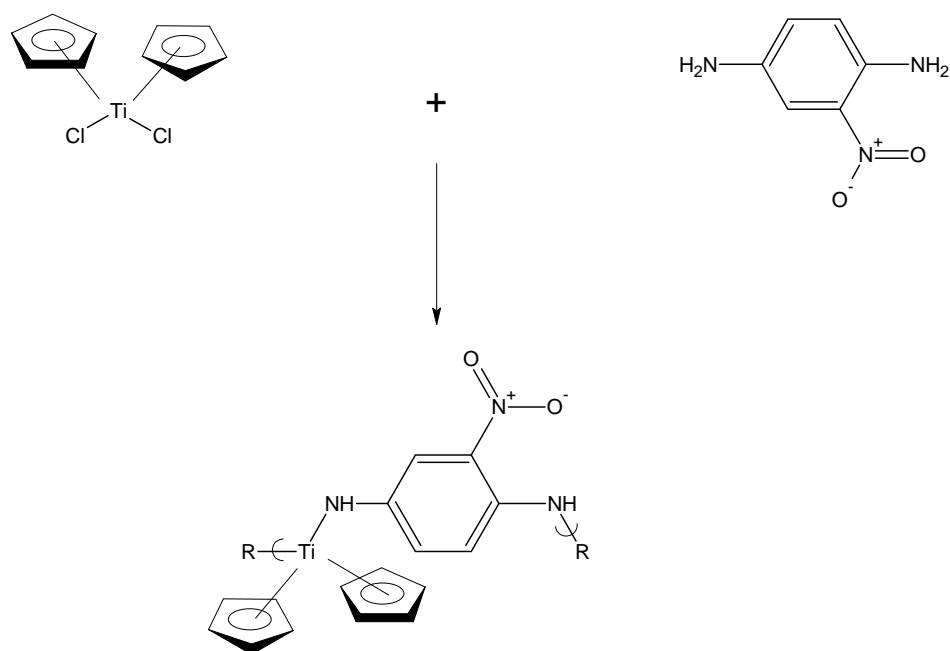


Figure 3.3.1(2) Reaction between 2-nitro-1,4-phenylenediamine and titanocene dichloride forming the test polymer, where “**R**” is simple chain extension.

The results for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer employing both surface and bulk doping with iodine are given below

3.3.2 Surface conductivity studies for 2-nitro-1, 4-phenylenediamine titanocene dichloride polymer

Several factors were important to establish. These factors were the effect of amount of iodine added to the surface described below as “cumulative doping” when iodine is added in stages (section 3.3.3) and “individual doping” when the sample is exposed to iodine for different times (section 3.3.4). Another important factor was to see if the doping was reversible. This is addressed in section 3.3.5 under the title “Recycling Tests.

3.3.3 Cumulative doping

A number of experiments were carried out on the test polymer. Two individual sets of experiments were performed and the results are reported. Here, the electrical properties were studied as a function of the amount of doping to determine the optimal doping time. In the first set of experiments, the sample was initially exposed to iodine vapor for five seconds and measurements were made on the sample. The same sample was again exposed for an additional five seconds for a total exposure to iodine vapor for 10 seconds and again measurements were made. This same sample was again exposed to iodine vapor for an additional five seconds giving a cumulative or total exposure time of 15 seconds. This was continued until the total exposure time was 60 seconds. Table 3.3.3(1) contains results for the undoped sample and Table 3.3.3(2) contains results for the exposure of the same sample to iodine for five seconds. On exposure to iodine for 5 seconds, the surface became shiny which is consistent with reports for other studies involving vinyl polymers [218].

Table 3.3.3(1) Electrical properties for undoped 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer as a function of applied frequency

| Frequency in KHz | C_s | C_p | ΔC | D_{sample} | D_s | K | Bulk conductivity in S cm^{-1} | Log bulk conductivity in S cm^{-1} |
|---------------------|-------|-------|------------|---------------------|-------|------|---|---|
| 0.4KHz | 1.35 | 1.08 | 0.27 | 0.18 | 0.29 | 0.54 | 2.20×10^{-11} | -10.66 |
| 1KHz | 1.02 | 0.68 | 0.34 | 1.32 | 0.95 | 0.68 | 5.03×10^{-10} | -9.30 |
| 2KHz | 0.85 | 0.48 | 0.37 | 2.78 | 1.85 | 0.74 | 2.30×10^{-9} | -8.64 |
| 5KHz | 0.43 | 0.31 | 0.12 | 1.56 | 0.98 | 0.24 | 1.05×10^{-9} | -8.98 |
| 10KHz | 0.26 | 0.20 | 0.06 | 0.68 | 0.58 | 0.12 | 4.55×10^{-10} | -9.34 |

where,

ΔC = sample capacitance

D_s = dissipation factor

K= dielectric constant and

C_A = surface area of the pellet

The dielectric constants for the undoped sample varied from 0.12 to 0.74 and the dissipation factors are in the range of 0.29 to 1.85 as shown in **Table 3.3.3(1)**. The bulk conductivity values were about $10^{-10} \text{ S cm}^{-1}$ consistent with the material being a semiconductor.

Table 3.3.3(2) Electrical properties for 2-nitro-1,4-phenylenediamine/ titanocene dichloride polymer exposed to iodine vapors for **5 seconds** as a function of applied frequency.

| Frequency in KHz | C _s | C _p | Δ C | D _{sample} | D _s | K | Bulk conductivity in S cm ⁻¹ | Log bulk conductivity in S cm ⁻¹ |
|---------------------|----------------|----------------|------|---------------------|----------------|-------|---|---|
| 0.4KHz | 7.00 | 3.35 | 3.65 | 1.05 | 0.06 | 13.67 | 3.21 x 10 ⁻⁹ | -8.49 |
| 1KHz | 5.25 | 1.99 | 3.26 | 0.89 | 1.00 | 12.21 | 6.02 x 10 ⁻⁹ | -8.22 |
| 2KHz | 4.25 | 1.08 | 3.17 | 1.74 | 1.70 | 11.87 | 2.29 x 10 ⁻⁸ | -7.64 |
| 5KHz | 3.70 | 0.62 | 3.08 | 4.03 | 3.63 | 11.53 | 1.29 x 10 ⁻⁷ | -6.89 |
| 10KHz | 2.35 | 0.56 | 1.79 | 5.75 | 4.80 | 6.70 | 2.14 x 10 ⁻⁷ | -6.67 |

Again here,

Δ C = sample capacitance

D_s = dissipation factor

K= dielectric constant and

C_A = surface area of the pellet

Figure 3.3.3(3) shows the comparison of undoped vs. sample exposed to iodine vapors for 5 seconds for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer

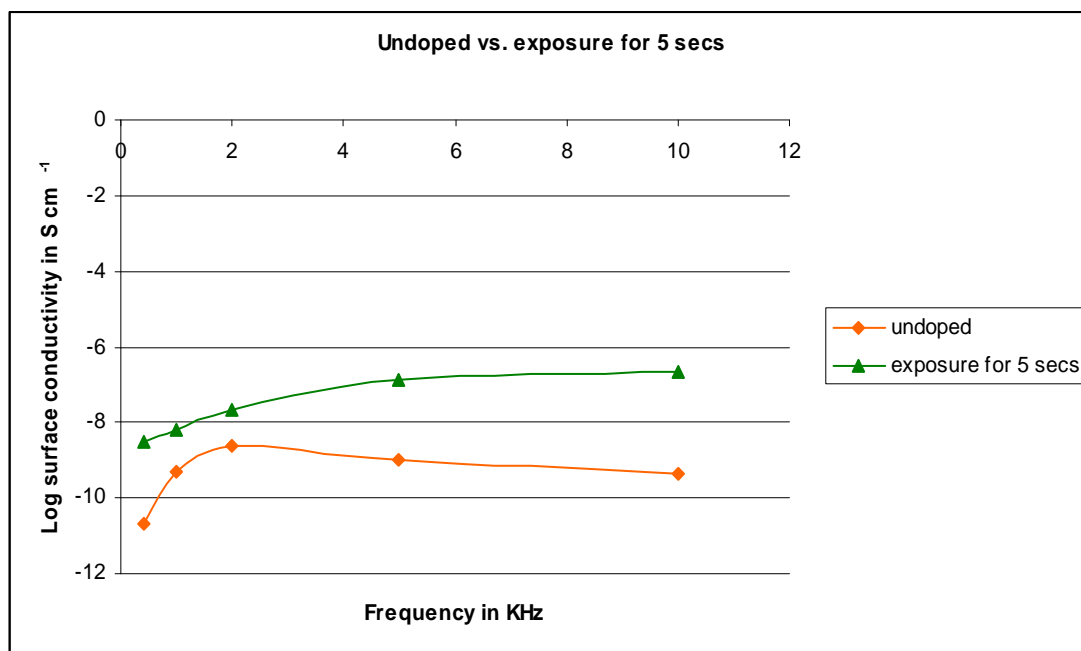


Figure 3.3.3(3) Comparison of undoped vs. sample exposed to iodine vapors for 5 seconds for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer as a function of applied frequency

For ready comparison, each of the following figures includes the results for the undoped sample.

Figure 3.3.3(4) gives the results for **single experiment** (n=1) illustrating the effect on surface conductivity by cumulative doping with iodine vapors for different doping intervals.

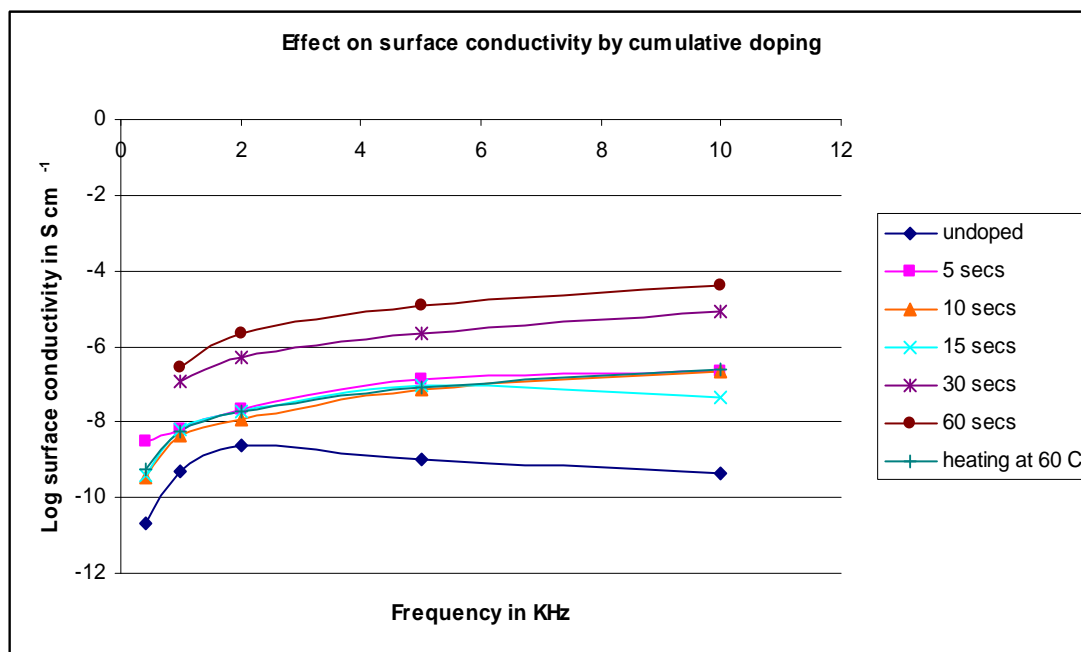


Figure 3.3.3(4) Results for **single experiment** (n=1) for surface conductivity as a function of cumulative doping with iodine vapors for different doping intervals

In case of cumulative surface doping with iodine vapors on 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer, there was a marked increase in both the dielectric constant and dissipation factor values with corresponding increases in the conductivity. Conductivity generally increased as the cumulative exposure time increased to 60 seconds. The conductivity increase was significant beginning in the range of 10^{-11} to $10^{-10}\ S\ cm^{-1}$ within the near conductor range for the undoped material and ending up with a cumulative exposure time of 60 seconds within the range of 10^{-6} to $10^{-4}\ S\ cm^{-1}$

which is in the near conductor range. The increase was then about 10^6 or one million fold.

The initial conductivity of KBr pellet was $10^{-10} \text{ S cm}^{-1}$. For comparison, a KBr pellet was exposed to iodine vapors for about 20 seconds and it showed the same conductivity after doping on the order of $10^{-10} \text{ S cm}^{-1}$, within the non-conductor range as expected. Thus, the doping effect was not simply related to the conductivity of the iodine layer.

We also measured the amount of iodine deposited on the polymer pellet. This is presented in Table 3.3.3(5) as both an absolute weight and as a percentage increase in weight. As expected, there was a small gradual increase in the amount of iodine deposited on the pellet as the cumulative exposure time increased. The amount of deposited iodine was less than 1%. For comparison, the amounts of iodine vapor employed in the doping of polyacetylene generally ranged from about 4% to 40% so that amounts of iodine vapor needed to achieve the conductivity increased in the present experiments were smaller and approached the levels employed to dope silicon producing silicon semiconductors [219]. The amount of doping agent added to silicon semiconductors was well below 1%. It must be remembered that the doping of silicon wafers employed different doping agents and was intended to move the silicon wafer from being a non-conductor to a semiconductor. Further, work with organic conductor focuses on the surface conductivity while the silicon semiconductor wafer focuses on the bulk conductivity.

Table 3.3.3(5) Weight increases of the test polymer disk exposed to iodine vapors as a function of doping time. The initial weight of the sample pellet was 0.1986g

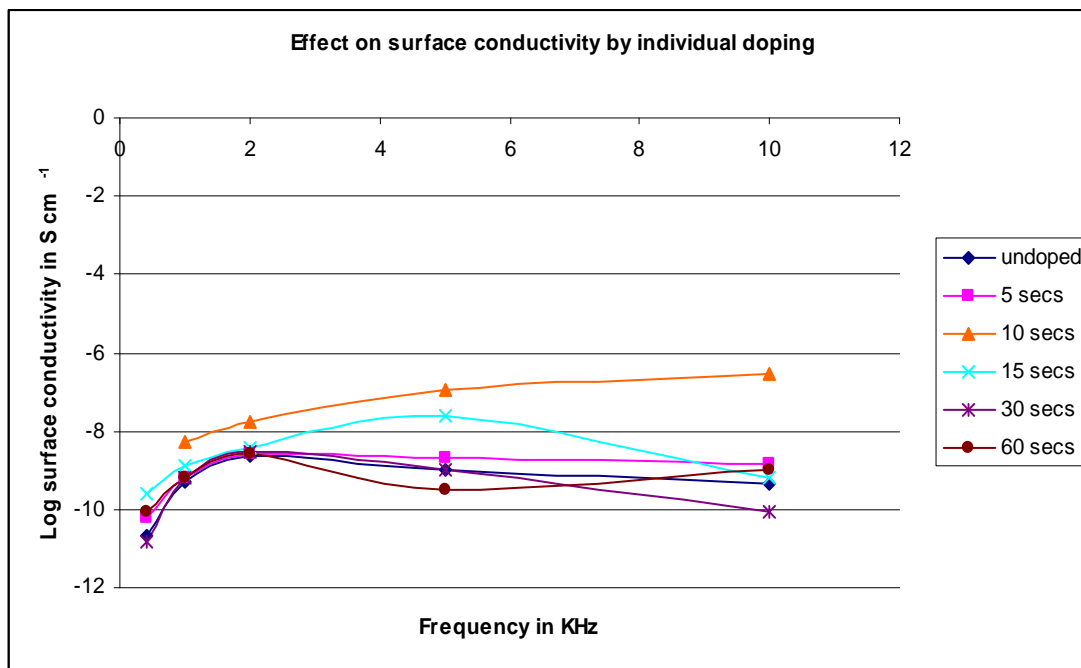
| Cumulative exposure time (seconds) | Increased weight (g) | % increased weight |
|---|-----------------------------|---------------------------|
| 5 seconds | 0.0004 g | 0.16 % |
| 10 seconds | 0.0006 g | 0.30 % |
| 15 seconds | 0.0007 g | 0.35 % |
| 30 seconds | 0.0014 g | 0.70 % |

3.3.4 Individual doping

The second set of experiments was constructed to get some measures of several variables at the same time. These variables were intended to get some measure of the effect of the extent of exposure time of iodine on the conductivity and second, to measure the ability to regenerate the decreased conductivity after repeated exposure to iodine. The second set of experiments i.e. individual doping was carried out by again exposing the sample pellet to iodine vapors for different specific, not cumulative time intervals. In this case, initially the polymer sample was exposed to iodine vapor for 5 seconds and the resulting conductivity was determined. The sample pellet was then placed in the oven at 60 °C to remove the iodine vapors on the pellet. The sample pellet was further exposed for a period of 10 seconds and again in a similar manner this process was carried out over a period of time and resulting conductivities were determined.

The results obtained for the second set of experiments are given in Figure 3.3.4(1)

Figure 3.3.4(1) Data for **single experiment** (n=1) showing the effect on surface conductivity by individual doping with iodine vapors for different doping intervals



The largest increase in the conductivity occurred after 10 seconds heating time with the increase being on the order of 10^3 to 10^4 fold in magnitude. At longer exposure times, the increases were more modest being on the order of 10^2 fold. Even so, all of the exposure cases showed an increase in the conductivity, there appears to be some ability for the sample to be regenerated with respect to its conductivity behavior.

3.3.5 Recycling tests

The surface conductivity was measured for the test polymer at varying frequencies and different doping intervals. Again these are all **single experiments** conducted to determine whether this process is reversible or cyclic. For clarity, we will look at the results for each of the applied frequencies. These results are shown in Figures 3.3.5(1) to 3.3.5(5).

The behavior for the test polymer was similar for each of the applied frequencies.

Figure 3.3.5(1) Surface conductivity measurements at different doping intervals at 0.4 KHz

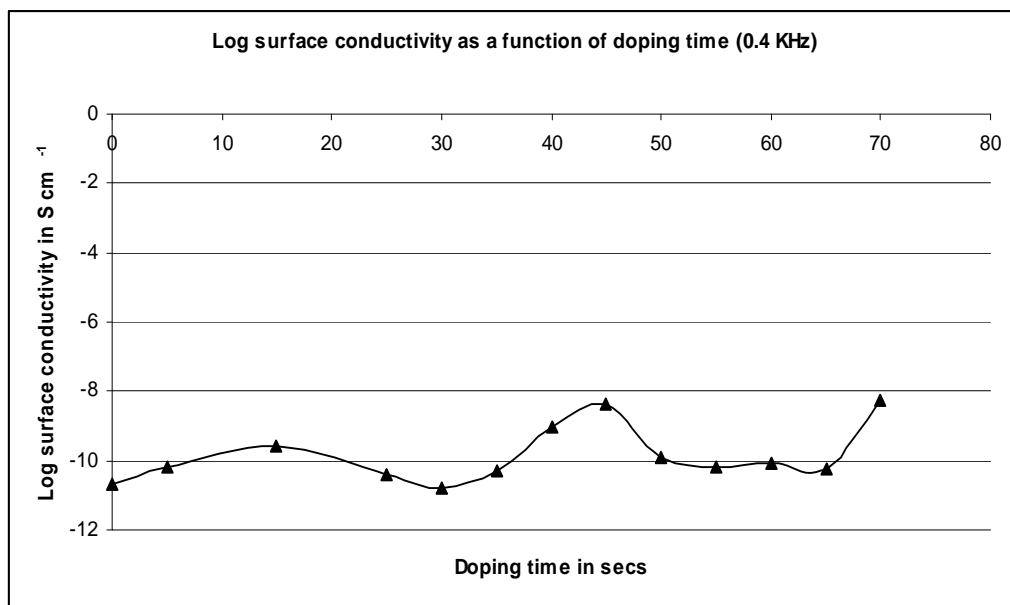


Figure 3.3.5(2) Surface conductivity measurements at different doping intervals at 1 KHz

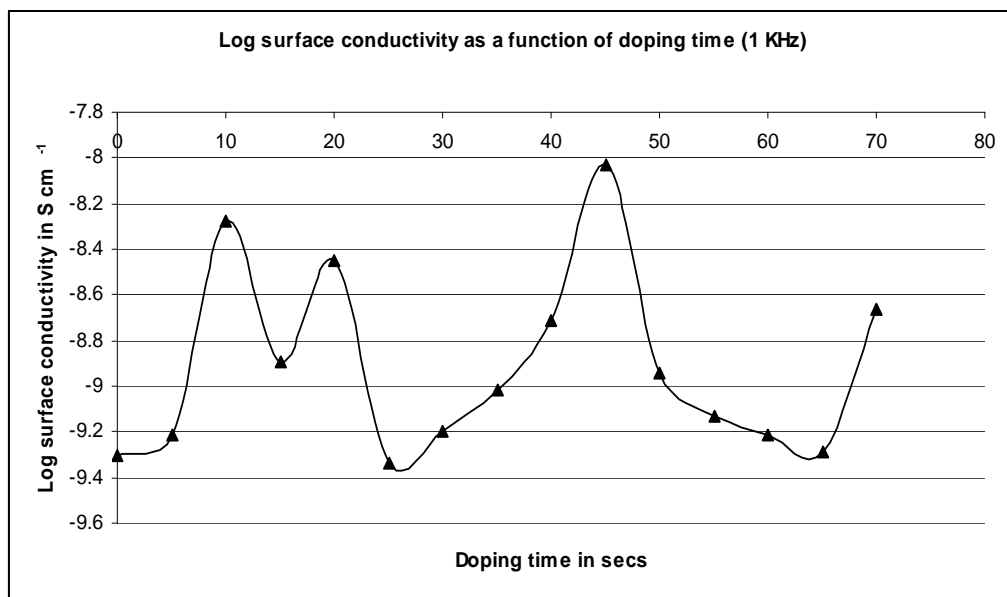


Figure 3.3.5(3) Surface conductivity measurements at different doping intervals
at 2 KHz

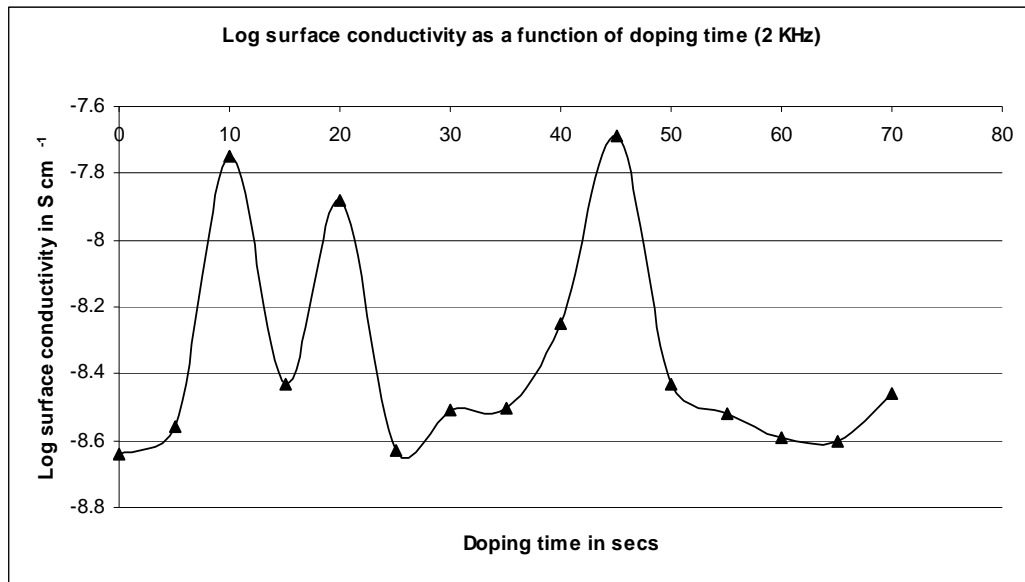


Figure 3.3.5(4) Surface conductivity measurements at different doping intervals
at 5 KHz

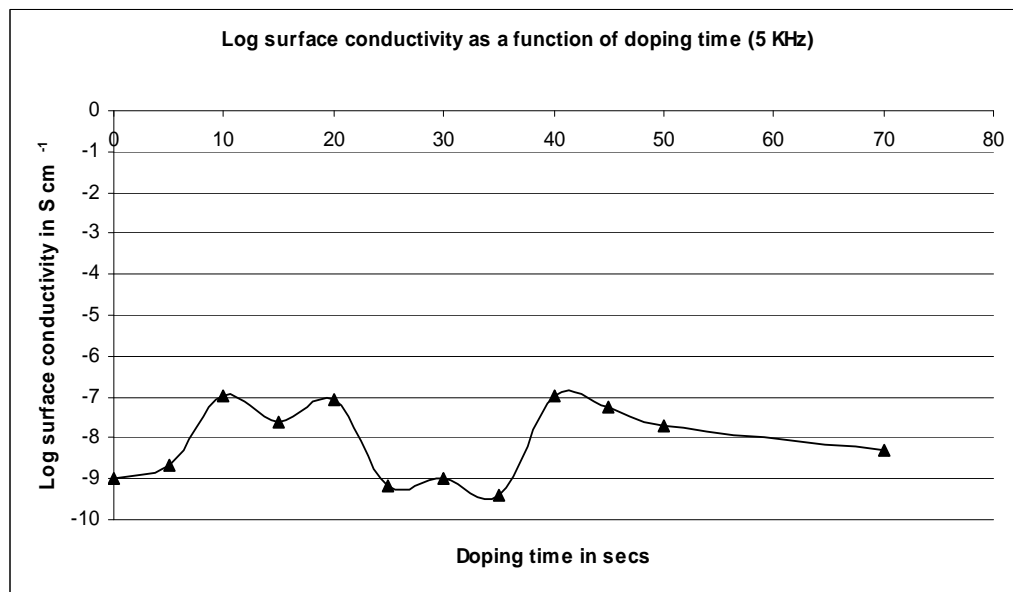


Figure 3.3.5(5) Surface conductivity measurements at different doping intervals
at 10 KHz

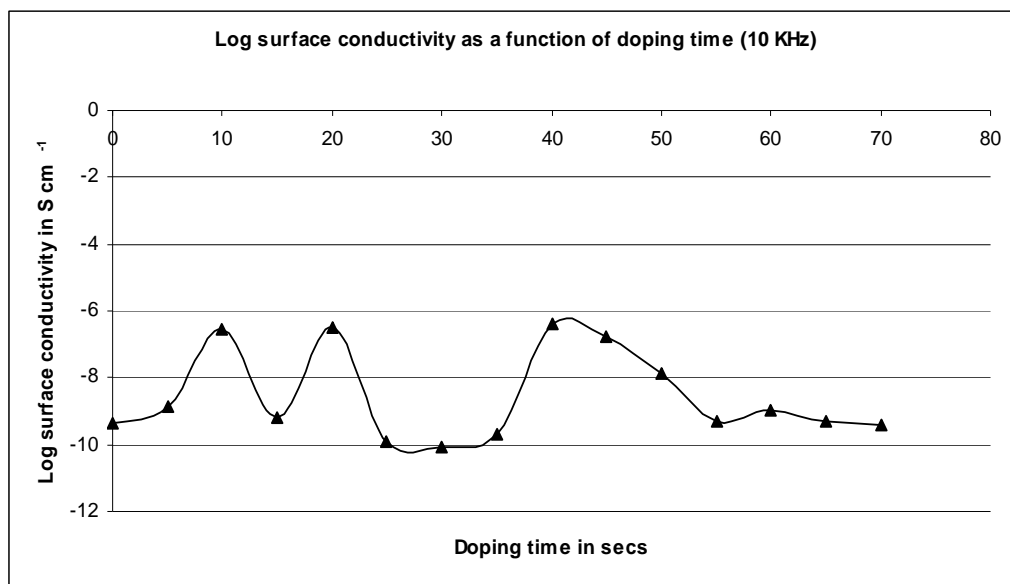


Table 3.3.5(6) Summary of surface conductivity values at different doping intervals observed at 1 KHz are given in Figure 3.3.5(2)

| Doping time in seconds | Log surface conductivity in S cm⁻¹ |
|-----------------------------------|--|
| Freshly prepared sample (undoped) | -9.30 |
| Exposing to iodine for 5 seconds | -9.21 |
| Exposing to iodine for 10 seconds | -8.28 |
| Exposing to iodine for 15 seconds | -8.89 |
| Exposing to iodine for 20 seconds | -8.45 |
| Exposing to iodine for 25 seconds | -9.34 |
| Exposing to iodine for 30 seconds | -9.20 |
| Exposing to iodine for 35 seconds | -9.02 |
| Exposing to iodine for 40 seconds | -8.71 |
| Exposing to iodine for 45 seconds | -8.03 |
| Exposing to iodine for 50 seconds | -8.94 |
| Exposing to iodine for 55 seconds | -9.13 |
| Exposing to iodine for 60 seconds | -9.21 |
| Exposing to iodine for 65 seconds | -9.29 |
| Exposing to iodine for 70 seconds | -8.66 |

The emphasis will be on the results obtained at 1 KHz applied frequency. The 2-nitro-1,4-phenylenediamine/titanocene polymer was initially exposed to iodine vapors for 5 seconds and a modest increase in the conductivity was observed as shown in Figure 3.3.5(2) and given in Table 3.3.5(6)

Further exposure of the pellet to iodine vapors for an additional 5 seconds (total exposure time of 10 seconds) resulted in larger increases in the conductivity of about 10 fold. The disk was allowed to reside in the open atmosphere for 24 hours. The conductivity decreased to the original value. The pellet was again exposed to iodine vapors for an additional 5 seconds for a total exposure time of 15 seconds. The conductivity increased slightly about $-\log 8.9$. The pellet was exposed further to iodine vapors for an additional 5 seconds giving a total exposure time of 20 seconds (total exposure time of 10 seconds for this exposure interval) with the conductivity increasing to about $-\log 8.5$. The pellet was allowed to reside in open atmosphere for a period of 48 hours. The conductivity again decreased to the original value. The pellet was again exposed to various increments of 5 seconds of iodine vapors finally giving a total exposure time of 45 seconds. At this point, the conductivity increased about 20 fold. The pellet was further allowed to reside in the open atmosphere for 17 days with the accompanying decrease in conductivity to about $-\log 9.3$. After exposing the pellet to additional iodine for a total exposure time of 70 seconds (total interval exposure time of 15 seconds), the conductivity again increased to $-\log 8.6$. Thus, the changes in the conductivity appear cyclic, increasing when the pellet was exposed to iodine vapors and decreasing when the pellet was allowed to reside in the open atmosphere. Further, for decent increases in the conductivity, an exposure time of ten seconds appears to be needed.

The behavior of conductivity decreasing on exposing to the atmosphere is consistent with the behavior of other doped polymers. [220, 221]. The rates of these decreases vary with the particular polymer. The decreases in the conductivity are easily

overcome by simply covering the material with a coating that prevents exposure of the doped surface to the air.

3.3.6 Bulk conductivity studies for the product of 2-nitro-1, 4-phenylenediamine and titanocene dichloride

The initial section dealt with the effects of surface doping on the conductivity. This section presents the results from studying the effect of addition of the doping agent, iodine, on the bulk conductivity along with the effect of varying heating times. Heating is employed to assist in the iodine being better distributed throughout the sample. Heating may also lead to the formation of the active compound that allows for better conductivity. Measurements were obtained as a function of applied frequency.

The same procedures were performed three times employing the same conditions to gauge reproducibility. The results are reported in section 3.4

3.4 Standard deviation plots (n=3) and comparison of conductivity of 2-nitro-1,4-phenylenediamine titanocene dichloride polymer in undoped and 10% iodine phase

3.4.1 Standard deviation plots (n=3) for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer containing 10% iodine concentration

To illustrate how data was obtained and treated, the raw data for one set of measurements is given for three data points. The initial set deals with the undoped sample. The raw data for the undoped sample for one set of measurements appears in Table 3.4.1(1)

Table 3.4.1(1) Electrical properties for the **undoped** product of 2-nitro-1,4,-phenylenediamine and titanocene dichloride sample as a function of applied frequency

| Frequency in KHz | C _s | C _p | Δ C | D _{sample} | D _s | K | Bulk conductivity in S cm ⁻¹ | Log bulk conductivity in S cm ⁻¹ |
|---------------------|----------------|----------------|------|---------------------|----------------|------|---|---|
| 0.4KHz | 1.41 | 0.77 | 0.64 | 0.34 | 0.39 | 1.46 | 1.11 x 10 ⁻¹⁰ | -9.95 |
| 1KHz | 1.31 | 0.49 | 0.82 | 1.01 | 0.83 | 1.87 | 1.05 x 10 ⁻⁹ | -8.98 |
| 2KHz | 1.04 | 0.34 | 0.70 | 1.77 | 1.40 | 1.59 | 3.14 x 10 ⁻⁹ | -8.50 |
| 5KHz | 0.46 | 0.24 | 0.22 | 1.57 | 1.10 | 0.51 | 2.19 x 10 ⁻⁹ | -8.66 |
| 10KHz | 0.38 | 0.20 | 0.18 | 0.79 | 0.60 | 0.41 | 1.81 x 10 ⁻⁹ | -8.74 |

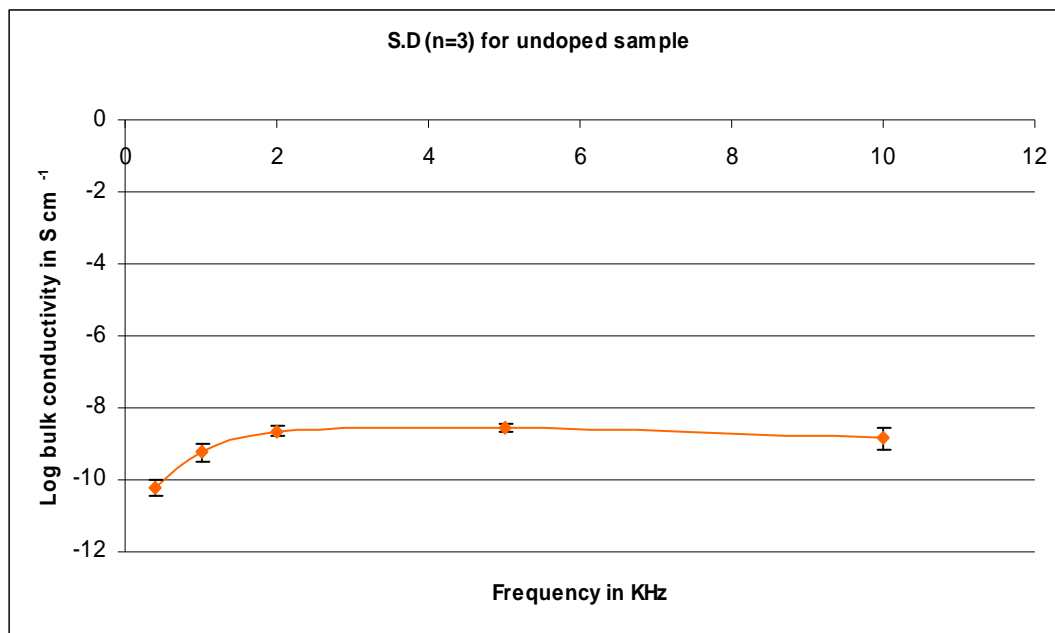
Table 3.4.1(2) contains the conductivity data derived from Table 3.4.1(1) plus two additional like measurements along with the standard deviation values.

Table 3.4.1(2) Log conductivity and standard deviation values for **undoped** sample as a function of applied frequency

| | Analysis | | | | |
|-----------------------------|-----------------|----------|----------|--------------------|-------------------------------|
| Frequency in KHz | 1 | 2 | 3 | Average Log | Standard Deviation |
| 0.400 | -9.95 | -10.28 | -10.40 | -10.21 | 0.23 |
| 1.00 | -8.98 | -9.24 | -9.50 | -9.24 | 0.26 |
| 2.00 | -8.50 | -8.60 | -8.82 | -8.64 | 0.16 |
| 5.00 | -8.66 | -8.52 | -8.49 | -8.56 | 0.09 |
| 10.00 | -8.74 | -8.63 | -9.17 | -8.85 | 0.29 |

Figure 3.4.1(3) contains the conductivity plot for the data given in Table 3.4.1(2).

Figure 3.4.1(3) Conductivity plot for **repeat** experiments (n=3) for the **undoped** sample as a function of applied frequency



The results are consistent with the measurements carried out with good reproducibility for the undoped samples.

The second set of measurements described in detail is for the doped sample but unheated. The raw data appears in Table 3.4.1(4). The conductivity data for three repetitions along with the standard deviations are given in Table 3.4.1(5). Figure 3.4.1(6) contains a plot based on the data given in Table 3.4.1(5).

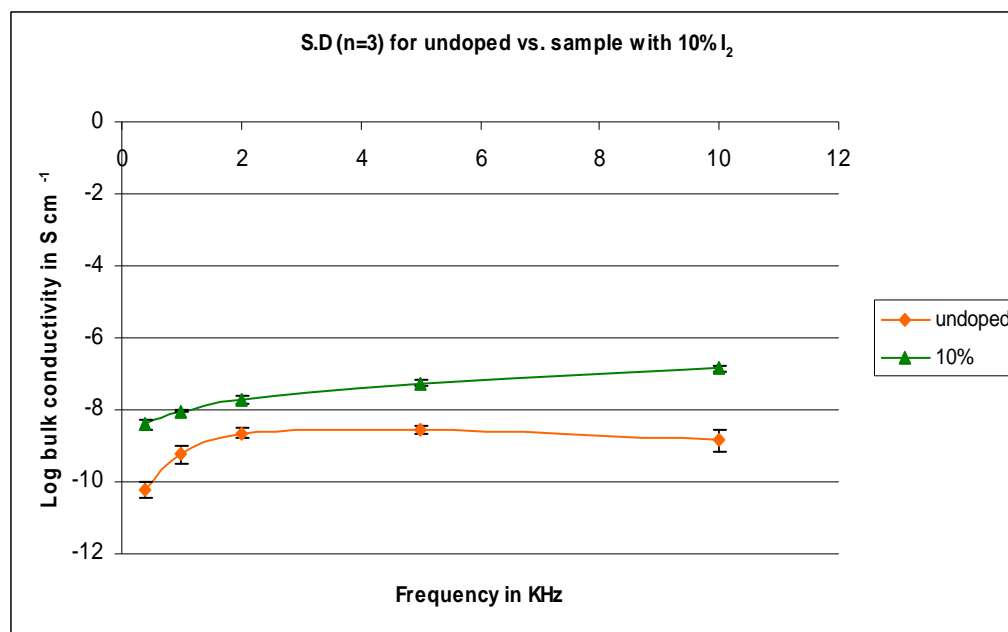
Table 3.4.1(4) Electrical properties for the product of 2-nitro-1,4,-phenylenediamine and titanocene dichloride sample containing **10% iodine** as a function of applied frequency without heating.

| Frequency in KHz | C _s | C _p | Δ C | D _{sample} | D _s | K | Bulk conductivity in S cm ⁻¹ | Log bulk conductivity in S cm ⁻¹ |
|---------------------|----------------|----------------|-------|---------------------|----------------|-------|---|---|
| 0.4KHz | 24.00 | 0.77 | 23.23 | 0.40 | 0.40 | 37.11 | 3.28 x 10 ⁻⁹ | -8.48 |
| 1KHz | 11.70 | 0.49 | 11.21 | 0.92 | 0.90 | 17.91 | 9.21 x 10 ⁻⁹ | -8.04 |
| 2KHz | 6.30 | 0.34 | 5.96 | 1.46 | 1.40 | 9.52 | 1.55 x 10 ⁻⁸ | -7.81 |
| 5KHz | 5.50 | 0.24 | 5.26 | 2.03 | 1.95 | 8.40 | 4.74 x 10 ⁻⁸ | -7.32 |
| 10KHz | 5.10 | 0.20 | 4.90 | 2.80 | 2.70 | 7.83 | 1.22 x 10 ⁻⁷ | -6.91 |

Table 3.4.1(5) Log conductivity and standard deviation values for samples containing **10% iodine** as a function of applied frequency

| | Analysis | | | | |
|---------------------|----------|-------|-------|-------------|-----------------------|
| Frequency in KHz | 1 | 2 | 3 | Average Log | Standard Deviation |
| 0.400 | -8.48 | -8.49 | -8.24 | -8.40 | 0.14 |
| 1.00 | -8.04 | -7.99 | -8.05 | -8.03 | 0.03 |
| 2.00 | -7.81 | -7.61 | -7.79 | -7.74 | 0.11 |
| 5.00 | -7.32 | -7.17 | -7.32 | -7.27 | 0.09 |
| 10.00 | -6.91 | -6.75 | -6.90 | -6.85 | 0.09 |

Figure 3.4.1(6) Conductivity plot for **repeat** experiments (n=3) for polymer containing **10% iodine** as a function of applied frequency



Bulk conductivity increased about 100 fold in comparison to the undoped sample with the standard deviation values indicating good reproducibility.

The third set of measurements described in detail is for the doped sample but heated for 10 seconds. The raw data appears in Table 3.4.1(7). The conductivity data for three repetitions along with the standard deviations are given in Table 3.4.1(8). Figure 3.4.1(9) contains a plot based on the data given in Table 3.4.1(8).

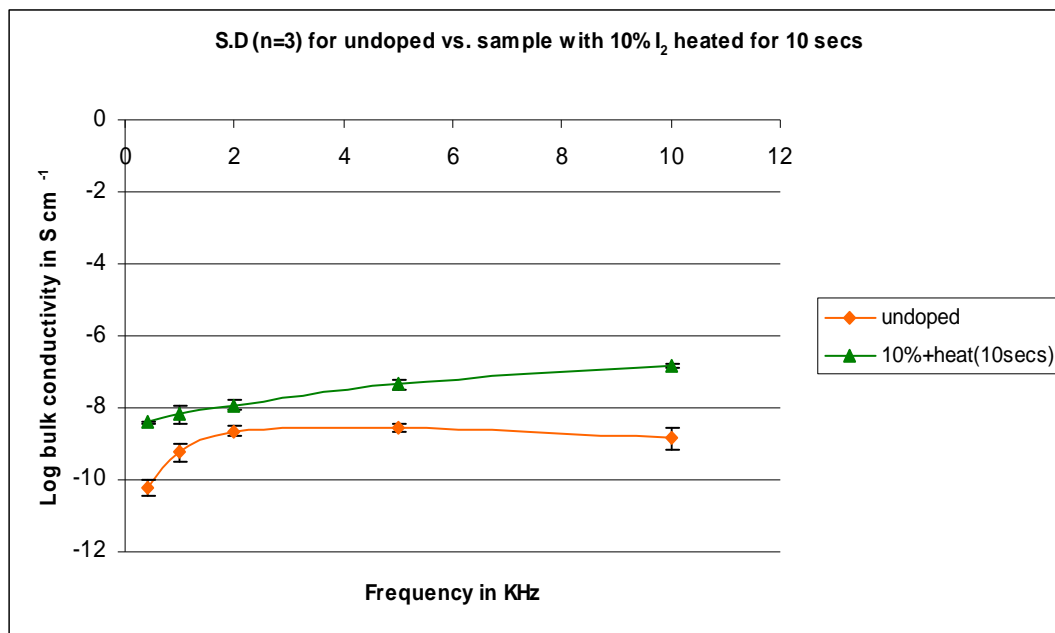
Table 3.4.1(7) Electrical properties for the product of 2-nitro-1,4,-phenylenediamine and titanocene dichloride containing **10% iodine** heated for **10 seconds** as a function of applied frequency

| Frequency in KHz | C _s | C _p | Δ C | D _{sample} | D _s | K | Bulk conductivity in S cm ⁻¹ | Log bulk conductivity in S cm ⁻¹ |
|---------------------|----------------|----------------|-------|---------------------|----------------|-------|---|---|
| 0.4KHz | 28.00 | 0.77 | 27.23 | 0.40 | 0.40 | 43.51 | 3.85 x 10 ⁻⁹ | -8.41 |
| 1KHz | 11.70 | 0.49 | 11.21 | 1.03 | 1.00 | 17.91 | 1.02 x 10 ⁻⁸ | -7.99 |
| 2KHz | 4.65 | 0.34 | 4.31 | 1.43 | 1.35 | 6.89 | 1.09 x 10 ⁻⁸ | -7.96 |
| 5KHz | 4.15 | 0.24 | 3.91 | 2.00 | 1.90 | 6.25 | 3.47 x 10 ⁻⁸ | -7.46 |
| 10KHz | 3.95 | 0.20 | 3.75 | 4.40 | 4.20 | 5.99 | 1.47 x 10 ⁻⁷ | -6.83 |

Table 3.4.1(8) Standard deviation results for the polymer containing **10% iodine** heated for **10 seconds** as a function of applied frequency

| | Analysis | | | | |
|---------------------|----------|-------|-------|-------------|-----------------------|
| Frequency in KHz | 1 | 2 | 3 | Average Log | Standard Deviation |
| 0.400 | -8.41 | -8.43 | -8.40 | -8.41 | 0.02 |
| 1.00 | -7.99 | -8.46 | -8.10 | -8.18 | 0.25 |
| 2.00 | -7.96 | -8.01 | -7.79 | -7.92 | 0.12 |
| 5.00 | -7.46 | -7.41 | -7.19 | -7.35 | 0.14 |
| 10.00 | -6.83 | -6.88 | -6.75 | -6.82 | 0.07 |

Figure 3.4.1(9) Conductivity values for **repeat** experiments (n=3) for samples containing **10% iodine** heated for **10 seconds** as a function of applied frequency



The conductivity increases vary from about 10 to 100 fold. Again, reproducibility is decent.

This procedure was carried out for the remainder of the data presented in this section.

3.5 Standard deviation plots (n=3) for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer with varying iodine concentrations

3.5.1 Comparison plots for 3%, 5%, 10% and 15% iodine concentrations for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer

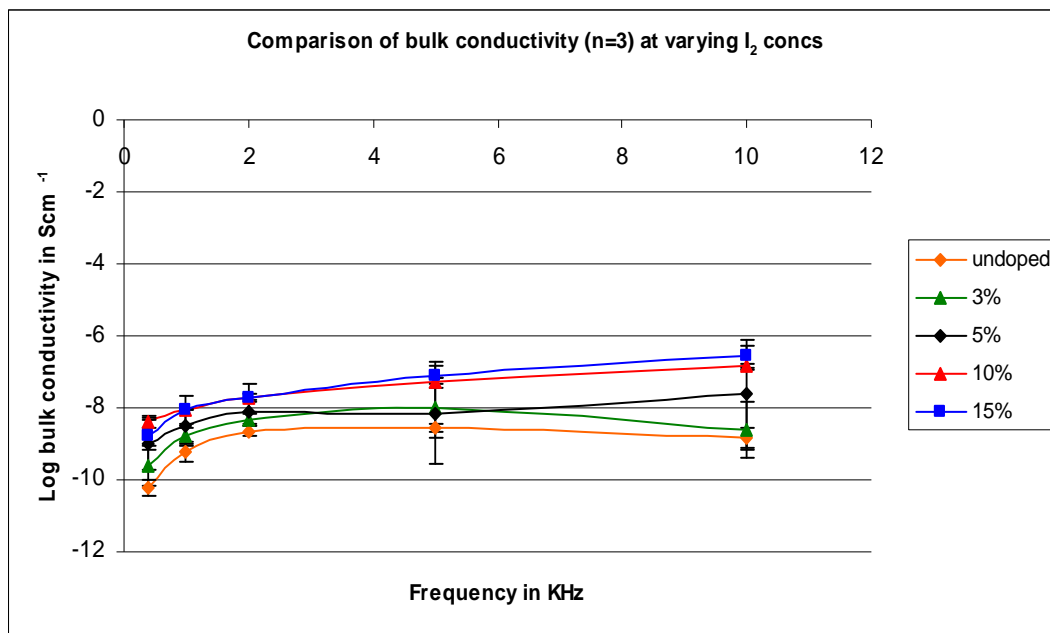
The electrical properties for 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer employing varying iodine concentrations were studied as a function of applied frequency and different heating times.

Here the effect on bulk conductivity by varying the amounts of iodine concentrations and varying the heating times are given. The standard deviation values are incorporated in the conductivity plots and tables given below. Results for unheated samples are given in Table 3.5.1(1) and Figure 3.5.1(2)

Table 3.5.1(1) Bulk conductivity results for **unheated** samples containing **varying** iodine concentrations as a function of applied frequency

| | Average log bulk conductivity in S cm⁻¹ | | | | |
|-----------------------------|---|------------------------------------|-------------------------------------|-------------------------------------|--|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration | |
| 0.400 | -9.62 | -8.98 | -8.40 | -8.77 | |
| 1.00 | -8.80 | -8.49 | -8.03 | -8.07 | |
| 2.00 | -8.35 | -8.12 | -7.74 | -7.72 | |
| 5.00 | -7.98 | -8.14 | -7.27 | -7.12 | |
| 10.00 | -8.61 | -7.63 | -6.85 | -6.58 | |

Figure 3.5.1(2) Conductivity for **repeat** experiments (n=3) for **unheated** samples mixed at **varying** iodine amounts as a function of applied frequency

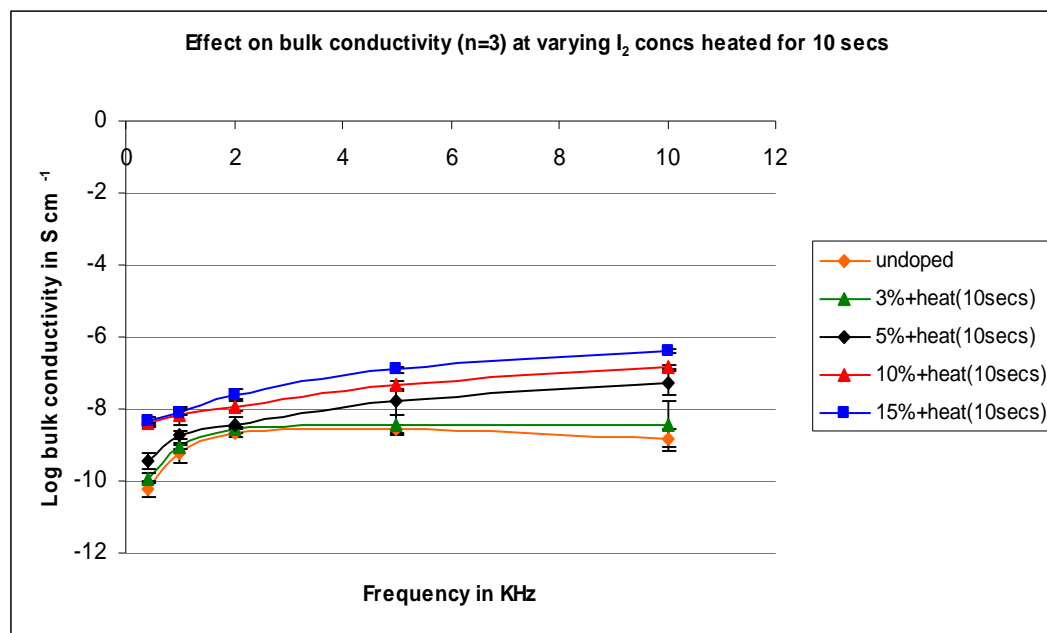


Bulk conductivity generally increases with increased amounts of iodine with the increases about the same for additions of 10% to 15% where conductivity increases are in the range of 10^2 to 10^3 fold are similar.

Table 3.5.1(3) Bulk conductivity results for samples containing **varying** iodine concentrations heated for **10 seconds** as a function of applied frequency

| | Average log bulk conductivity in S cm^{-1} | | | |
|---------------------|---|----------------------------|-----------------------------|-----------------------------|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration |
| 0.400 | -9.92 | -9.44 | -8.41 | -8.36 |
| 1.00 | -9.03 | -8.73 | -8.18 | -8.09 |
| 2.00 | -8.53 | -8.44 | -7.92 | -7.59 |
| 5.00 | -8.45 | -7.79 | -7.35 | -6.91 |
| 10.00 | -8.43 | -7.29 | -6.82 | -6.41 |

Figure 3.5.1(4) Conductivity for **repeat** experiments (n=3) for samples mixed at **varying** iodine amounts heated for **10 seconds** as a function of applied frequency



A similar pattern to that found for the unheated samples is found for the samples heated for 10 seconds as seen in Table 3.5.1(3) and Figure 3.5.1(4). Conductivity increases as the concentration of iodine is increased with the difference between the conductivity of the undoped and doped being in the range of 10^2 to 10^3 fold. The results are similar for the samples heated for 20 seconds as seen in Table 3.5.1(5) and Figure 3.5.1(6) and 30 seconds heating as seen in Table 3.5.1(7) and Figure 3.5.1(8).

Table 3.5.1(5) Bulk conductivity results for samples containing **varying** iodine concentrations heated for **20 seconds** as a function of applied frequency

| | Average log bulk conductivity in S cm^{-1} | | | |
|---------------------|---|----------------------------|-----------------------------|-----------------------------|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration |
| 0.400 | -10.07 | -9.49 | -8.85 | -9.20 |
| 1.00 | -9.03 | -8.72 | -8.36 | -8.51 |
| 2.00 | -8.45 | -8.46 | -8.02 | -8.07 |
| 5.00 | -8.63 | -7.82 | -7.57 | -7.39 |
| 10.00 | -8.90 | -7.30 | -7.46 | -6.83 |

Figure 3.5.1(6) Conductivity for **repeat** experiments (n=3) for samples mixed with **varying** iodine amounts heated for **20 seconds** as a function of applied frequency

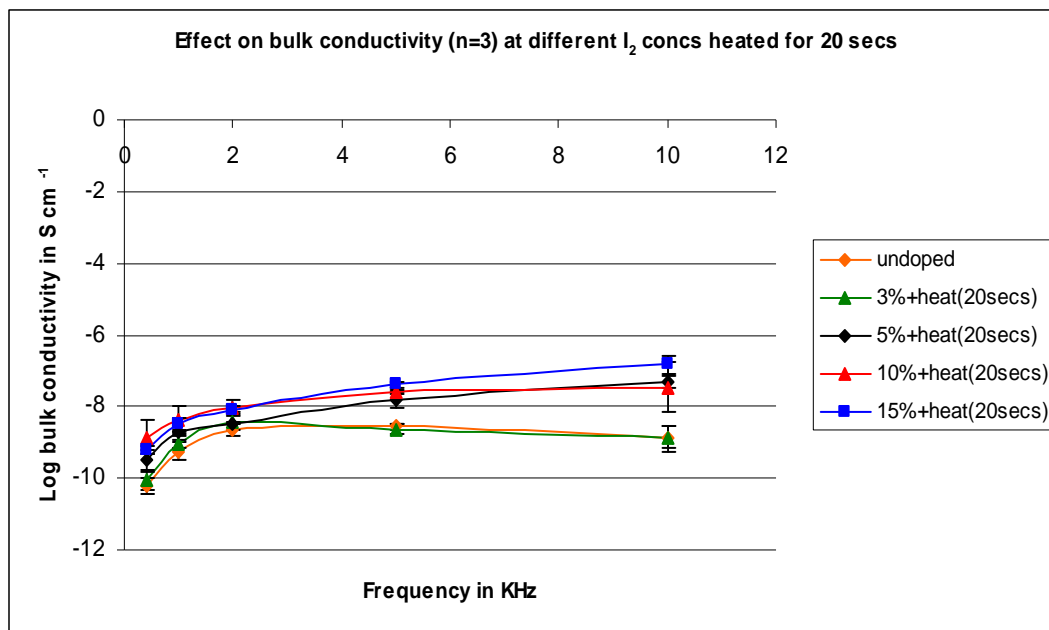
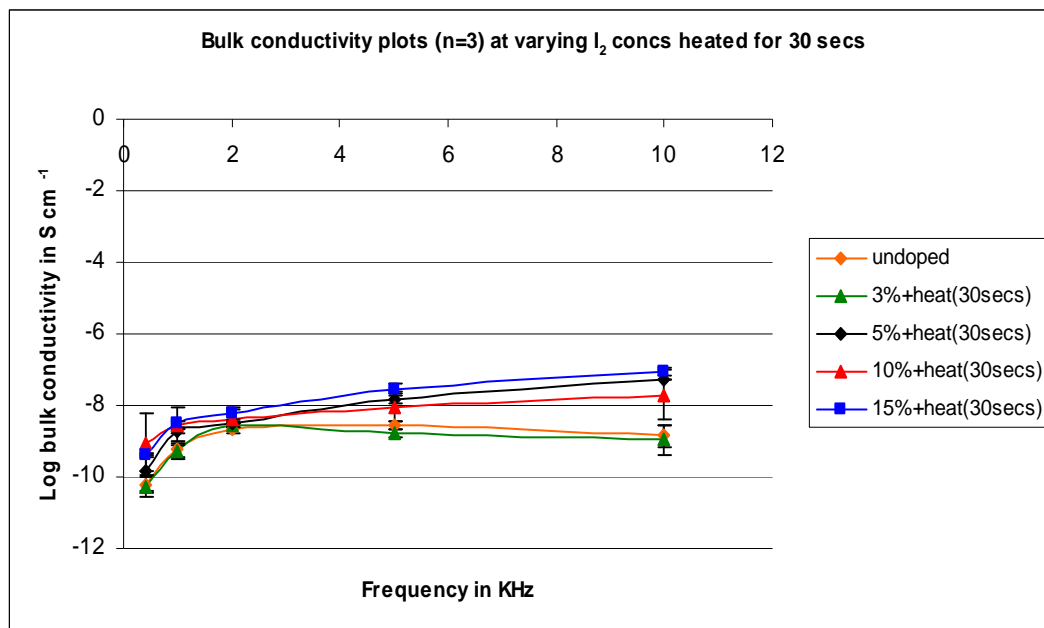


Table 3.5.1(7) Bulk conductivity results for samples containing **varying** iodine concentrations heated for **30 seconds** as a function of applied frequency

| | Average log bulk conductivity in S cm ⁻¹ | | | |
|---------------------|---|----------------------------|-----------------------------|-----------------------------|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration |
| 0.400 | -10.25 | -9.85 | -9.04 | -9.41 |
| 1.00 | -9.26 | -8.73 | -8.57 | -8.52 |
| 2.00 | -8.54 | -8.48 | -8.37 | -8.22 |
| 5.00 | -8.77 | -7.82 | -8.04 | -7.55 |
| 10.00 | -8.97 | -7.28 | -7.70 | -7.03 |

Figure 3.5.1(8) Conductivity for **repeat** experiments (n=3) for samples mixed with **varying** iodine amounts heated for **30 seconds** as a function of applied frequency

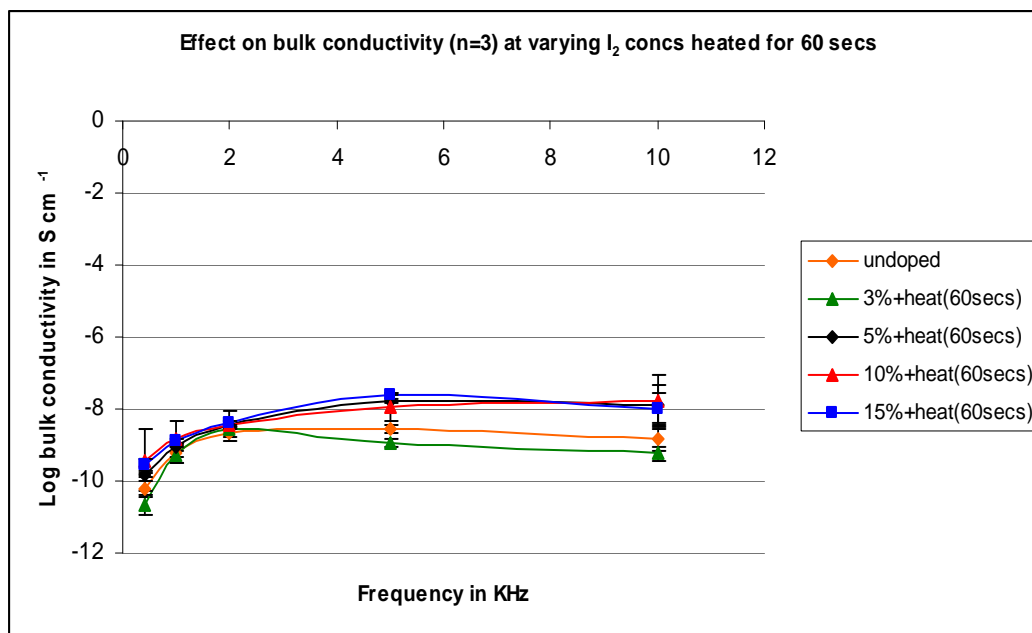


For heating time of 60 seconds as seen in Table 3.5.1(9) and Figure 3.5.1(10), the conductivity difference between the doped and undoped samples are less, with differences being several fold to 10 fold with the conductivity of the 3% doped sample approximating that of the undoped sample.

Table 3.5.1(9) Bulk conductivity results for samples containing **varying** iodine concentrations heated for **60 seconds** as a function of applied frequency

| | Average log bulk conductivity in S cm^{-1} | | | |
|---------------------|---|----------------------------|-----------------------------|-----------------------------|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration |
| 0.400 | -10.65 | -9.84 | -9.42 | -9.57 |
| 1.00 | -9.27 | -9.07 | -8.84 | -8.89 |
| 2.00 | -8.54 | -8.47 | -8.46 | -8.38 |
| 5.00 | -8.93 | -7.77 | -7.95 | -7.59 |
| 10.00 | -9.24 | -7.89 | -7.79 | -7.98 |

Figure 3.5.1(10) Conductivity for **repeat** experiments (n=3) for samples mixed with **varying** iodine amounts heated for **60 seconds** as a function of applied frequency

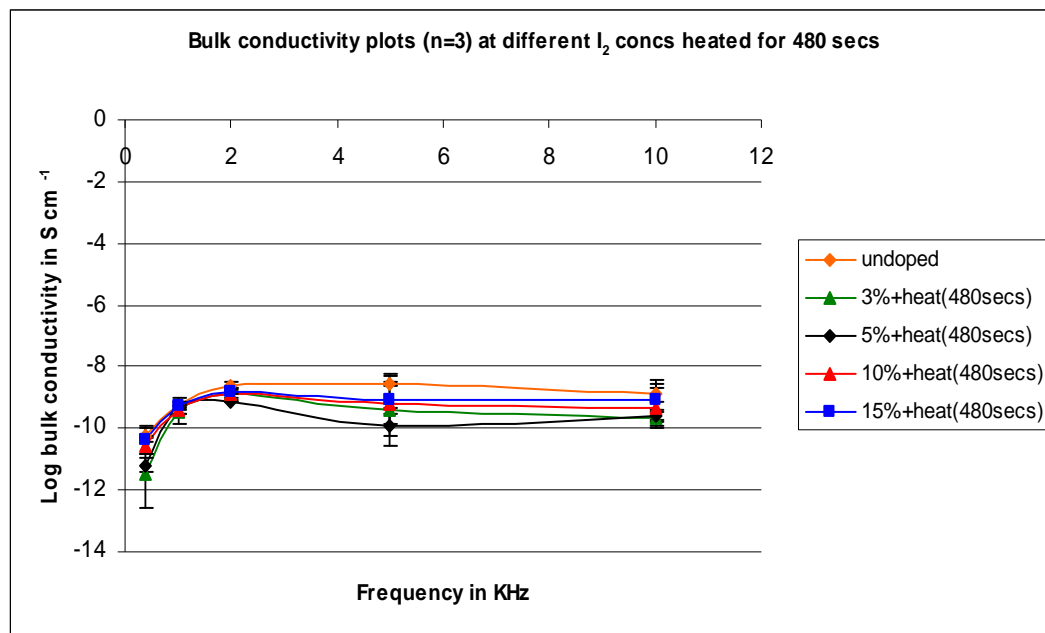


After heating for 480 seconds (Table 3.5.1(11) and Figure 3.5.1(12), all of the samples approximate the conductivity of the undoped sample.

Table 3.5.1(11) Bulk conductivity results for samples containing **varying** iodine concentrations heated for **480 seconds** as a function of applied frequency

| | Average log bulk conductivity in S cm⁻¹ | | | |
|-----------------------------|---|------------------------------------|-------------------------------------|-------------------------------------|
| Frequency in KHz | 3% iodine concentration | 5% iodine concentration | 10% iodine concentration | 15% iodine concentration |
| 0.400 | -11.44 | -11.19 | -10.56 | -10.38 |
| 1.00 | -9.49 | -9.30 | -9.37 | -9.29 |
| 2.00 | -8.86 | -9.12 | -8.90 | -8.79 |
| 5.00 | -9.43 | -9.89 | -9.22 | -9.07 |
| 10.00 | -9.68 | -9.59 | -9.32 | -9.06 |

Figure 3.5.1(12) Conductivity for **repeat** experiments (n=3) for samples mixed with **varying** iodine amounts heated for **480 seconds** as a function of applied frequency



The next series of figures (Figure 3.5.1(13) to Figure 3.5.1(15)) are for data presented for the same doping extent but for different heating times.

Figure 3.5.1(13) Conductivity for **repeat** experiments (n=3) for sample with **3% iodine** concentration heated at different intervals as a function of applied frequency

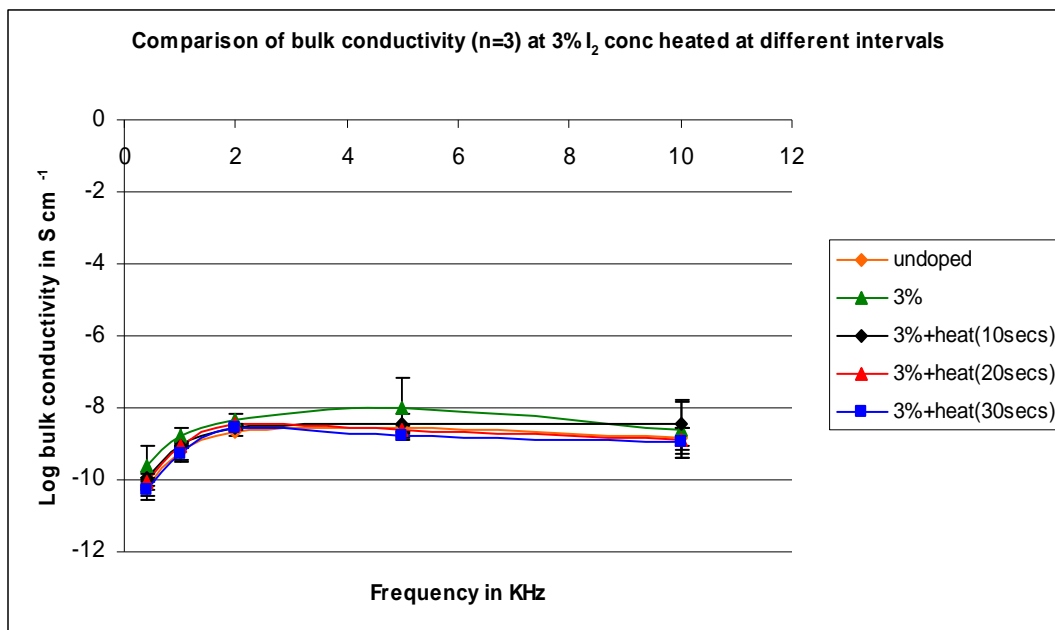


Figure 3.5.1(14) Conductivity plot for samples containing **10% iodine** heated at different intervals as a function of applied frequency

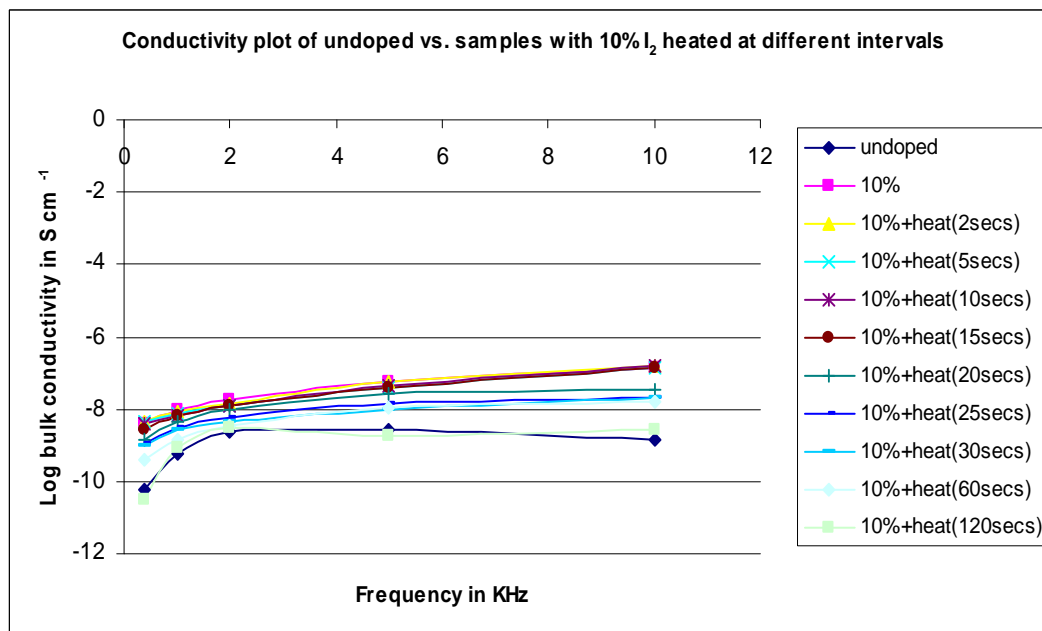
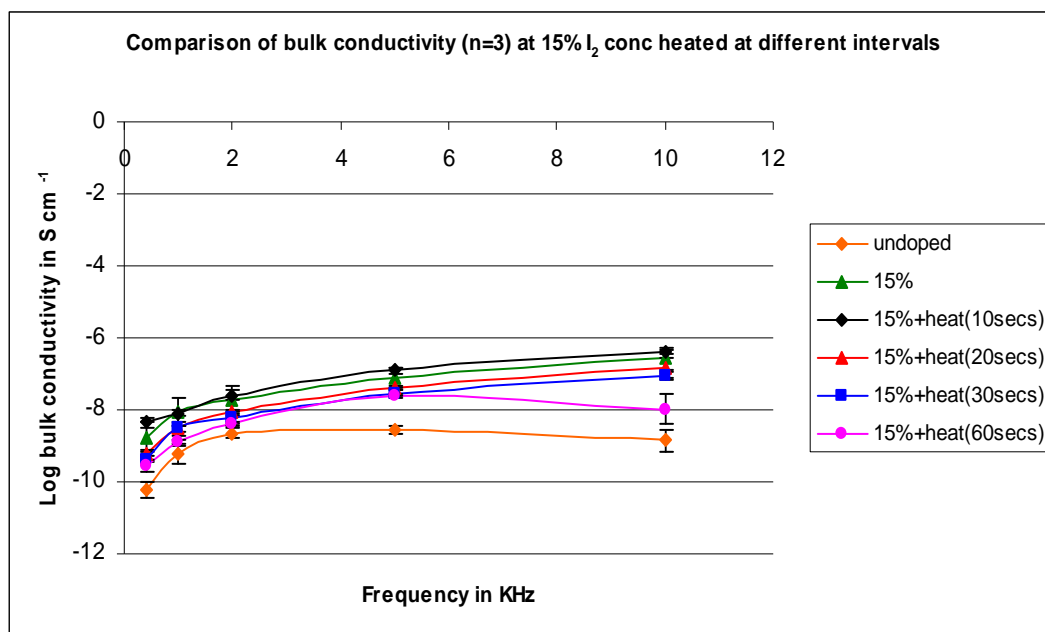


Figure 3.5.1(15) Conductivity for **repeat** experiments (n=3) for sample with **15% iodine** concentration heated at different intervals as a function of applied frequency



Again, the conductivity difference between the undoped and doped samples decreases as the heating time increases.

Several conclusions are evident from these studies. First, conductivity varies with the applied frequency. This is normal. As noted elsewhere, the precise causes for this variation are varied and the precise extent and identity of the factors are generally unknown. It is customary to simply report the results and note the tendency. Second, conductivity generally decreases with increased heating times. This is due to evaporation of iodine from the surface of the sample. For longer heating times, the conductivity approached that of the undoped sample. Third, the standard deviations generally increase with increases in the heating times. This is reasonable since each successive heating time contains the uncertainties from previous heating times. Even so, standard deviations were generally one log function and less for shorter heating times. Fourth, conductivity

generally increases with the amount of iodine added to the sample with 10% and 15% additions offering generally similar conductivities. Fifth, the increases in conductivity are similar to the same magnitude found for surface doping. Further, the variability of conductivity with respect to applied voltage is also similar to that found for the surface-doped samples. Since most electrical measurements on polymers involve only surface measurements, the relationship between surface and bulk conductivities is not established.

3.6 Study of variety of metal atoms (Sn, Zr and Hf) containing 10% iodine and their effect on electrical conductivity

The finding that doping with iodine increases the conductivity of the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride encourages further related structures to be synthesized and their electrical properties to be evaluated. The results of these studies are given in this section.

3.6.1 Effect of metal atom on the electrical conductivity

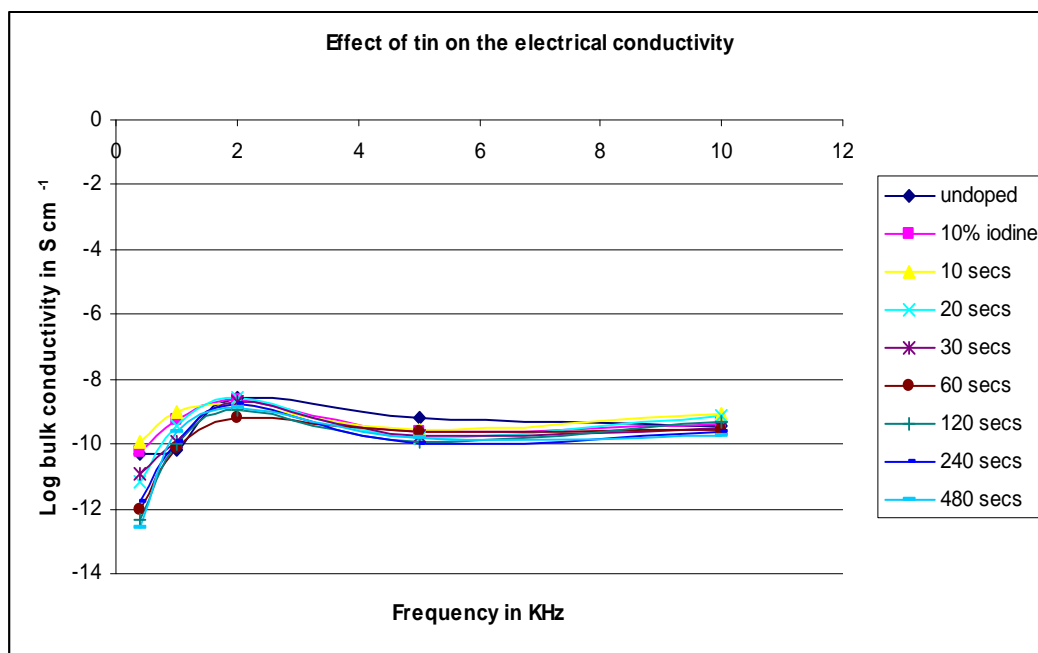
While there are many metals that can be incorporated, we chose to look at the analogous products from tin since we have lot of experience with organotin-containing materials and the corresponding metallocenes but derived from zirconocene dichloride and hafnocene dichloride since these metals are in the same family as titanium and should offer similar tendencies.

3.6.2 Effect of tin on conductivity of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride product

Electrical properties for 2-nitro-1,4-phenylenediamine/dibutyltin dichloride polymer were studied as a function of applied frequency with different heating intervals

for samples containing 10% by weight of iodine. Figure 3.6.2(1) shows the conductivity plot for the product of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride as a function of heating times. The results are consistent with there being little or no effect on the conductivity of the undoped and doped samples heated for different times.

Figure 3.6.2(1) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride containing 10% iodine heated at different time intervals.

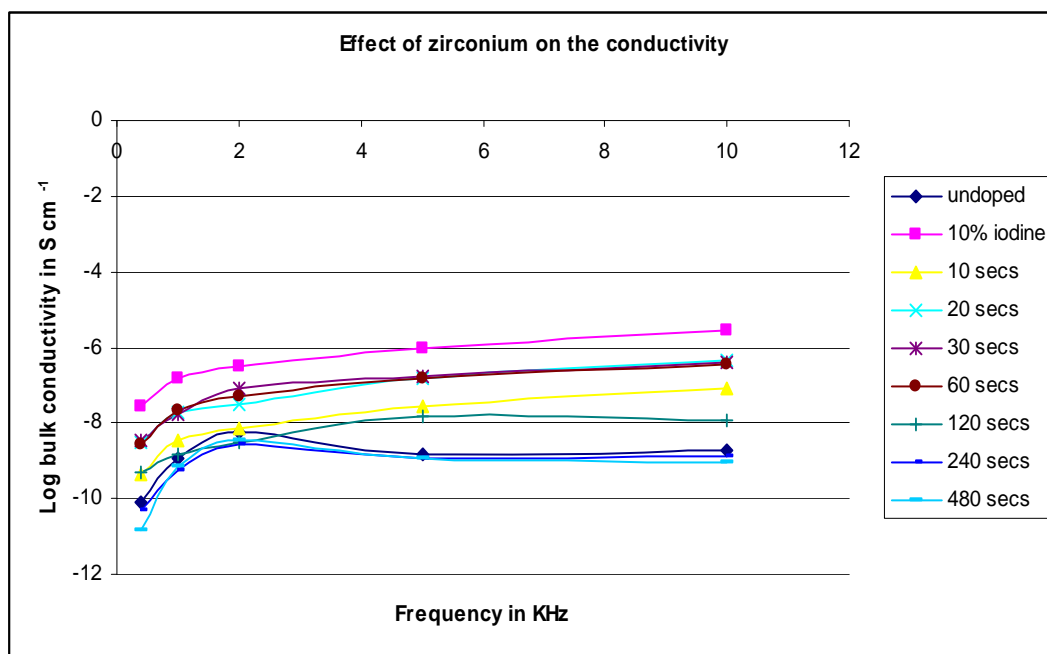


3.6.3 Effect on conductivity by changing the nature of the Group IVB metal

Electrical properties for materials formed from the reaction of 2-nitro-1,4-phenylenediamine with zirconocene dichloride and with hafnocene dichloride containing 10% by weight of iodine were studied as a function of applied frequency and different heating times. The results appear in Figure 3.6.3(1) and Figure 3.6.3(2) respectively. The initial plot is for a doped sample that is unheated. It shows the greatest increase in

conductivity on the order of 10^3 to 10^4 fold for both the zirconocene and hafnocene polymers. In general, the conductivity decreases with heating time possibly due to the vaporization of iodine from the surface of the pellet. Finally, after heating for 480 seconds for the zirconocene product and 60 seconds for the hafnocene product, the conductivity approaches the undoped sample value.

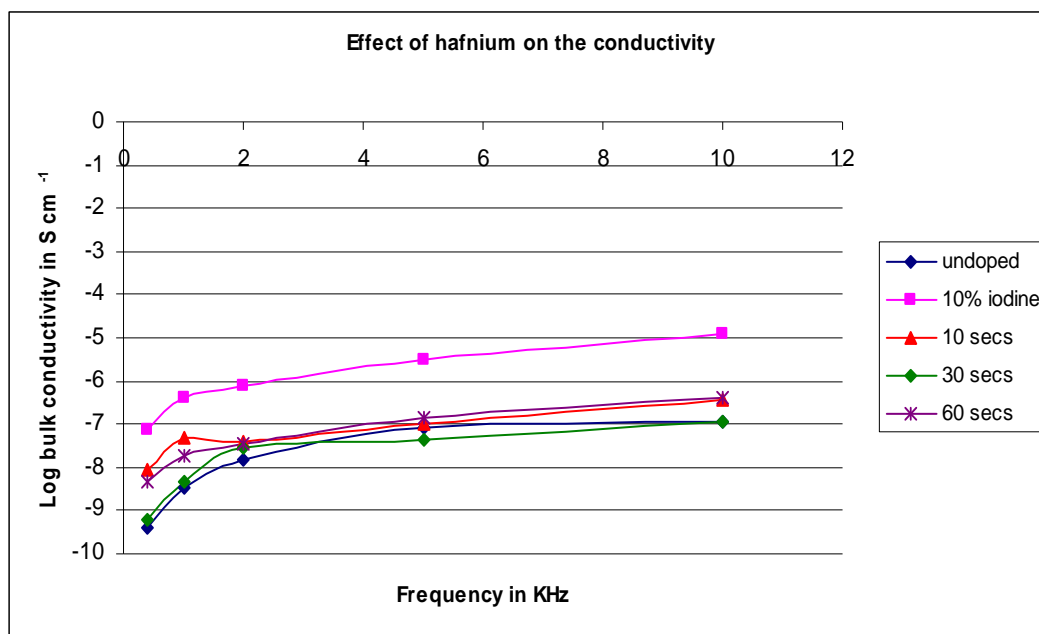
Figure 3.6.3(1) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and zirconocene dichloride containing 10% iodine heated at different times.



As in the case with the corresponding zirconocene dichloride product, there was a marked increase in conductivity for the doped unheated sample, on the order of 10^4 fold. Further, conductivity decreases with increases in heating times until at longer heating times, the conductivity approaches that of the undoped conductivity value. A similar situation also occurs with the hafnocene dichloride product. While there was no increase

in conductivity as the organotin product was doped, there was an increase in conductivity similar to that found for the hafnocene dichloride product. Thus, all of the Group IVB metallocene products showed similar behavior with increases in conductivity on the order of 10^3 to 10^4 fold.

Figure 3.6.3(2) Conductivity plot (single experiment) for the product of 2-nitro-1,4-phenylenediamine and hafnocene dichloride containing 10% iodine heated for different periods.



3.7 Electron donating and electron withdrawing substituents and their effect on electrical conductivity

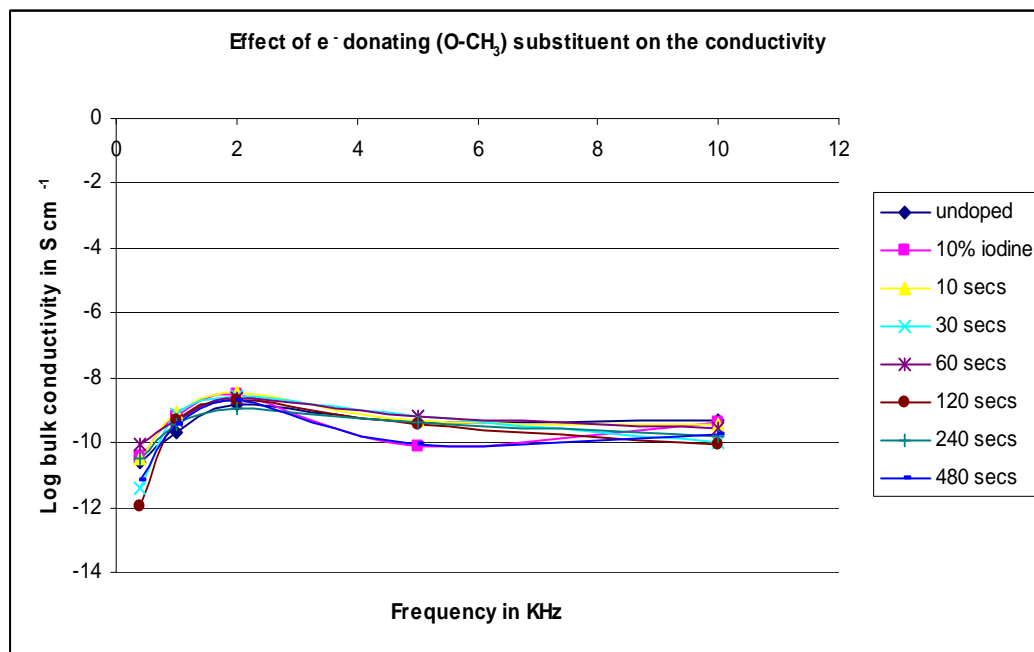
The second structural window involved investigating the varying nature of the substituents on the 1,4-phenylenediamines. These are commercially available a wide range of substituted 1,4-phenylenediamines. In the present study we looked at the effect of both electron donating and electron withdrawing substituents on the electrical

conductivity of the resulting titanocene polyamines. Following are the results for these studies.

3.7.1 Effect on conductivity for 2-methoxy-1,4-phenylenediamine and titanocene dichloride product

Electrical properties for 2-methoxy-1,4-phenylenediamine/titanocene dichloride polymer containing 10% by weight of iodine were studied as a function of applied frequency and different heating times. The heating times are cumulative. Thus, for a heating time of 10 seconds means the sample was heated for a total of 10 seconds. For a heating time of 30 seconds means the same sample that was heated for 10 seconds was heated for an additional time of 20 seconds. The results are given in Figure 3.7.1(1).

Figure 3.7.1(1) Conductivity plot (single experiment) for the product of 2-methoxy-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different periods.

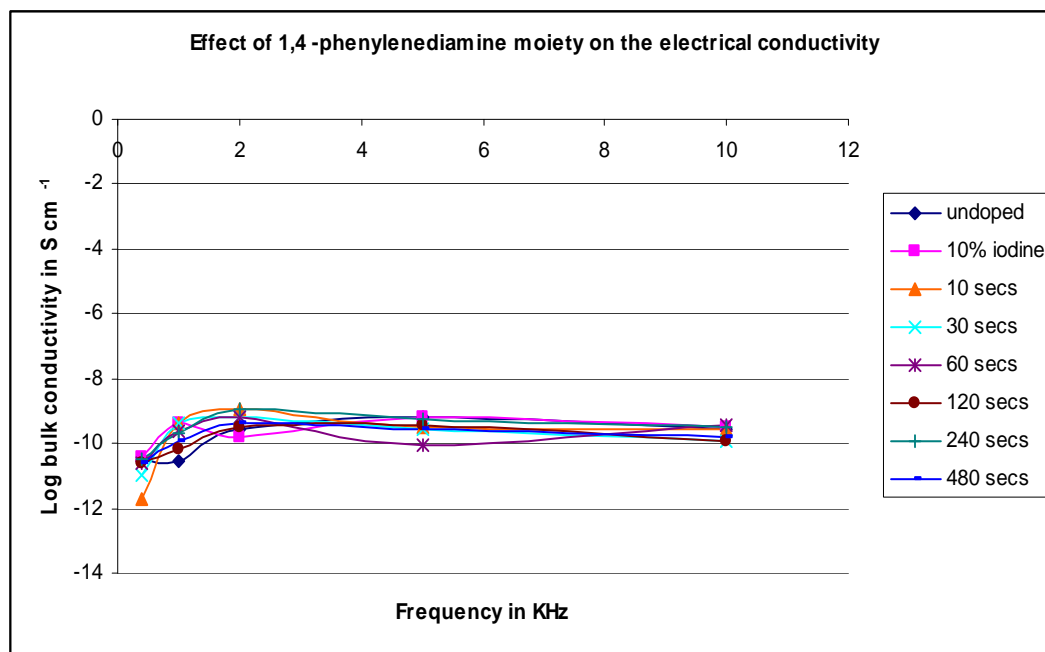


From the above plot, little or no change in the conductivity is observed for the product of 2-methoxy-1,4-phenylenediamine and titanocene dichloride between the undoped sample and the doped sample.

3.7.2 Effect on conductivity for 1,4-phenylenediamine and titanocene dichloride product

Electrical properties for 1,4-phenylenediamine and titanocene dichloride product containing 10% by weight of iodine were studied as a function of applied frequency and different heating intervals and are reported in Figure 3.7.2(1).

Figure 3.7.2(1) Conductivity plot (single experiment) for the product of 1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different intervals.

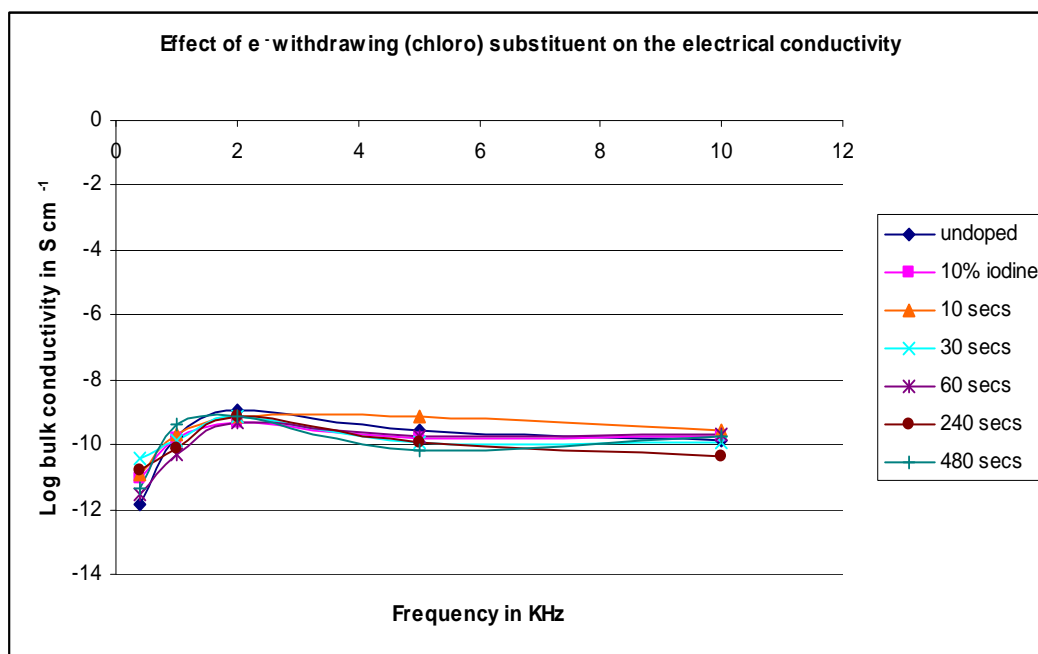


Again, there appears to be little or no change in the conductivity between the undoped and the doped samples.

3.7.3 Effect on conductivity for the product of 2,5-dichloro-1,4-phenylenediamine and titanocene dichloride

Electrical properties for 2,5-dichloro-1,4-phenylenediamine/titanocene dichloride polymer containing 10% by weight of iodine were studied as a function of applied frequency and different periods of heating. Results are reported in Figure 3.7.3(1)

Figure 3.7.3(1) Conductivity plot (single experiment) for the product of 2,5-dichloro-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different times.



Little or no change in the electrical conductivity was found between the undoped and doped product of 2,5-dichloro-1,4-phenylenediamine and titanocene dichloride.

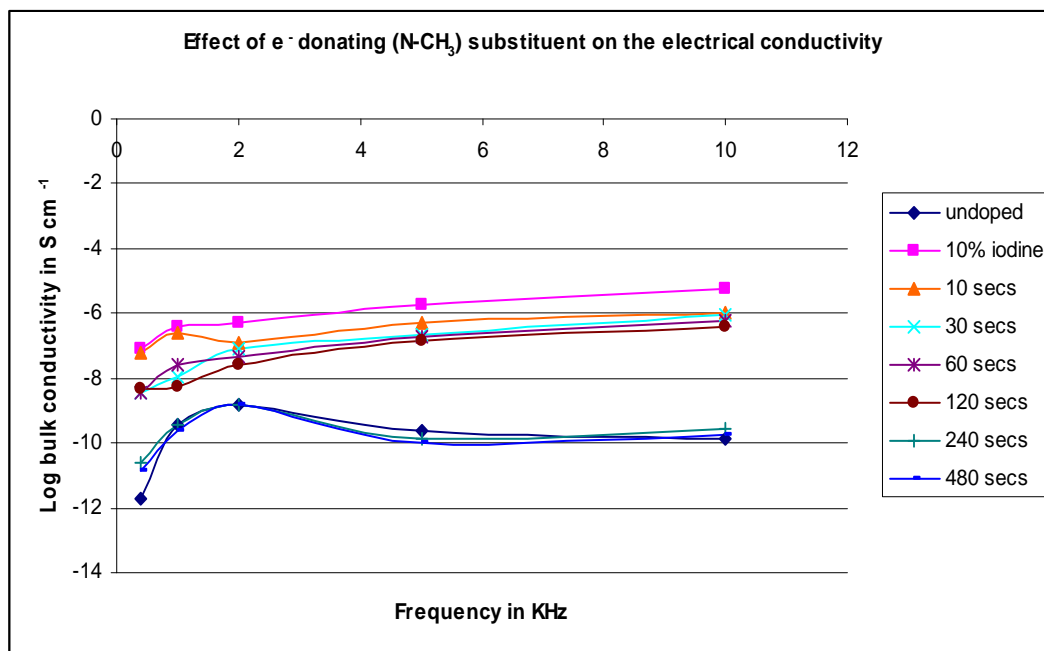
There was no change observed in the conductivity of the undoped and the doped samples whether the substituents are electron donating (2-methoxy-1,4-phenylenediamine) or electron withdrawing (2,5-dichloro-1,4-phenylenediamine). Thus,

there is something special about the nitro group and its ability to allow for an increased conductivity. Future studies might consider dinitrodiamine products.

3.7.4 Effect on conductivity for the product of N-methyl -1,4-phenylenediamine and titanocene dichloride

In another approach, products were synthesized from N-methyl-1,4-phenylenediamine and titanocene dichloride. The electrical properties for the N-methyl-1,4-phenylenediamine and titanocene dichloride product containing 10% iodine heated at different durations were studied as a function of applied frequency with results appearing in **Figure 3.7.4(1)**.

Figure 3.7.4(1) Conductivity plot (**single experiment**) for the product of N-methyl-1,4-phenylenediamine and titanocene dichloride containing 10% iodine heated at different time intervals.



The results are similar to those found for the 2-nitro-1,4-phenylenediamine products. As in the case with the nitrophenylenediamine products, the greatest increase is found for the unheated sample containing 10% iodine with 10^5 fold increases throughout the frequency range. The conductivity decreases to the value of undoped sample at longer heating times.

3.8 Determination of degradation rate for the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride containing 10% iodine

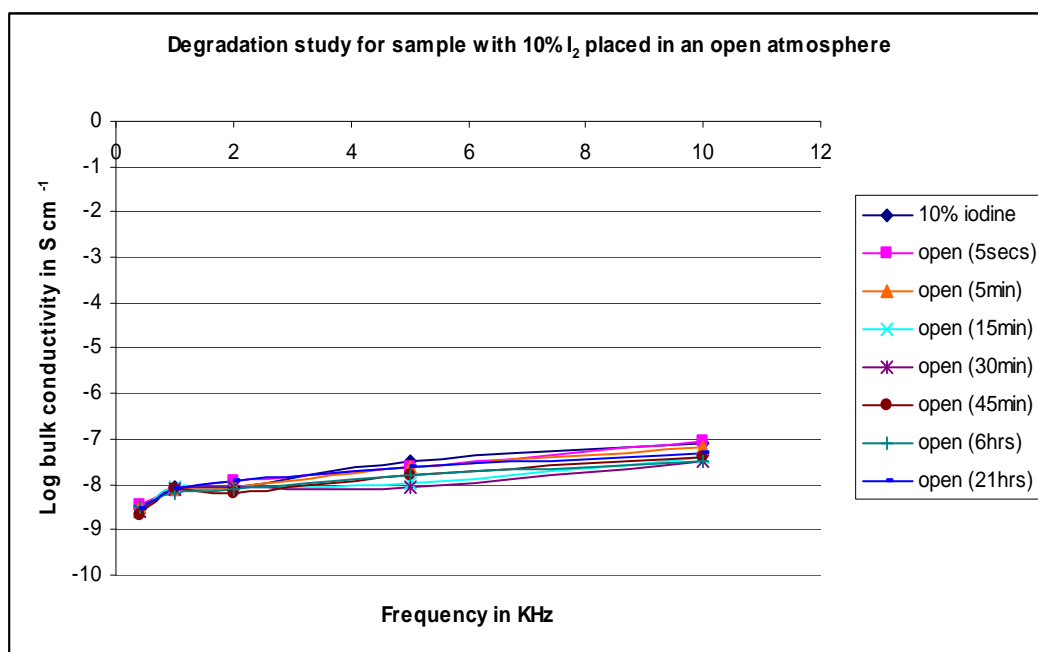
3.8.1 Degradation study for 2-nitro-1,4-phenylenediamine and titanocene dichloride product containing 10% iodine concentration

The stability of the samples in the atmosphere was studied by simply placing a freshly doped sample in the open (atmosphere) and determining its conductivity as a function of time. Results are given in Figure 3.8.1(1). The sample conductivity remained approximately constant even after exposure to the atmosphere for about a day. This may be in contrast with the results found for the surface doped samples where degradation in the conductivity occurred for samples exposed to the atmosphere for times of about one day. For other doped samples, such as doped organic polymers like polyacetylene, it is believed that this inability to retain enhanced conductivity when in the open is due to the ability of oxygen to react with free radicals thus reducing the ability of doped samples to have holes or excess electrons that are necessary for enhanced conductivity of electrical currents.

Tentatively, it appears that the bulk doped samples show superior ability to retain their enhanced conductivity. This may be due to the presence of protective layers of non-iodine product in the bulk-doped materials preventing ready deactivation by oxygen.

Before this observation is accepted with confidence, further studies should be carried out including one where the bulk samples are simply allowed to remain in the open atmosphere for longer periods of time.

Figure 3.8.1(1) Conductivity plot (**single experiment**) representing the degradation rate for the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride by placing in the open atmosphere for different time durations.



While there is a minimal or no change in the bulk conductivity values even after placing the sample in the open atmosphere for 21 hours, it is believed that it is best to carry out measurements on pellets the same day that they are prepared. This has been done in the studies reported here unless noted otherwise.

3.9 Structural Analysis

While the synthesis of Group IVB metallocene polyamines was reported over 30 years ago, [222-224] and recently reviewed [225, 226], it is important that the current

material employed in the electrical studies be structurally analyzed. Further, one of the aims of our research is to see if the nature of the doped structure can be determined. Towards this end, spectral analysis of doped and undoped materials were studied to see if differences were apparent and attempt to identify the reasons for these differences. Following are the spectral results that contribute to this aim as well as serving to identify the structural units present in the polymer.

3.9.1 Determination of functional groups for the 1,4-phenylenediamine-derived polymers employing IR spectroscopy

Infrared spectra were obtained for the monomers and doped and undoped polymers employing the KBr pellets. **Table 3.9.1(1)** contains assignments for important bands for titanocene dichloride itself [227]. **Table 3.9.1(2)** contains a summary table for important bands for 2-nitro-1,4-phenylenediamine monomer, undoped and doped products of 2-nitro-1,4-phenylenediamine and titanocene dichloride [228, 229]. **Figures 3.9.1(3) – 3.9.1(5)** contain IR spectra for the monomer derived from 2-nitro-1,4-phenylenediamine and undoped and doped products derived from 2-nitro-1,4-phenylenediamine and titanocene dichloride.

Table 3.9.1(1) IR assignments for titanocene dichloride (Cp_2TiCl_2)

| Assignments | Cp_2TiCl_2 |
|----------------------|----------------------------|
| CH stretch | 3103 |
| CH out of plane bend | 821 |
| Ring breathing | 1130 |
| CH in plane bend | 1271 |
| CH in plane bend | 1015 |
| CH out of plane bend | 871 |
| CC stretch | 1440 |
| CH out of plane bend | 1074 |
| CC stretch | 1364 |
| CC in plane bend | 927 |
| CC out of plane bend | 597 |

Table 3.9.1(2) IR assignments for 2-nitro-1,4-phenylenediamine monomer and undoped and doped products with titanocene dichloride

| | 2-nitro-1,4-phenylenediamine and Cp₂TiCl₂ | | | |
|-----------------------------|--|---------------------|-----------------------------|-------------------|
| Assignments | Monomer | Polymer | Polymer (iodine) | Literature |
| C-H st aromatic | 3017, 3121, 3168 | 3027, 3100, 3168 | 3030, 3064, 3168 | 3200-3000 |
| C=C stretch | 1420 | 1489 | 1470 | 1475 |
| C-H bend(para) | 854 | 850 | 850 | 850-800 |
| CH in plane bend, Cp | 1015 [*] | 1034 | 1030 | 1015 |
| CH out of plane bend, Cp | 1074 [*] , 871 [*] | 1078, 871 | 1080, 870 | 1074, 871 |
| Ring breathing, Cp | 1130 [*] | 1120 | 1119 | 1130 |
| C-N stretch (alkyl) | 1164 | 1160 | 1167 | 1200-1025 |
| N-H stretch | 3393 | 3378 | 3393 | 3500-3300 |
| N-H bend | 1577 | 1593 | 1602 | 1640-1500 |
| N-H bend (oop) | 802 | 815 | 814 | 800 |
| NO ₂ aromatic | 1473 | 1489 | 1470 | 1550-1400 |
| NO ₂ aromatic | 1366 | 1334 | 1330 | 1355-1315 |
| Ti-N stretch | - | 493 | 481 | 480 |
| C-I stretch | - | - | 664 | 700-485 |

Monomer = 2-nitro-1,4-phenylenediamine; * designates the titanocene dichloride monomer.

Polymer = 2-nitro-1,4-phenylenediamine and Cp_2TiCl_2 and

Polymer (iodine) = 2-nitro-1,4-phenylenediamine and Cp_2TiCl_2 doped with iodine

Figure 3.9.1(3) IR spectrum for 2-nitro-1, 4-phenylenediamine monomer

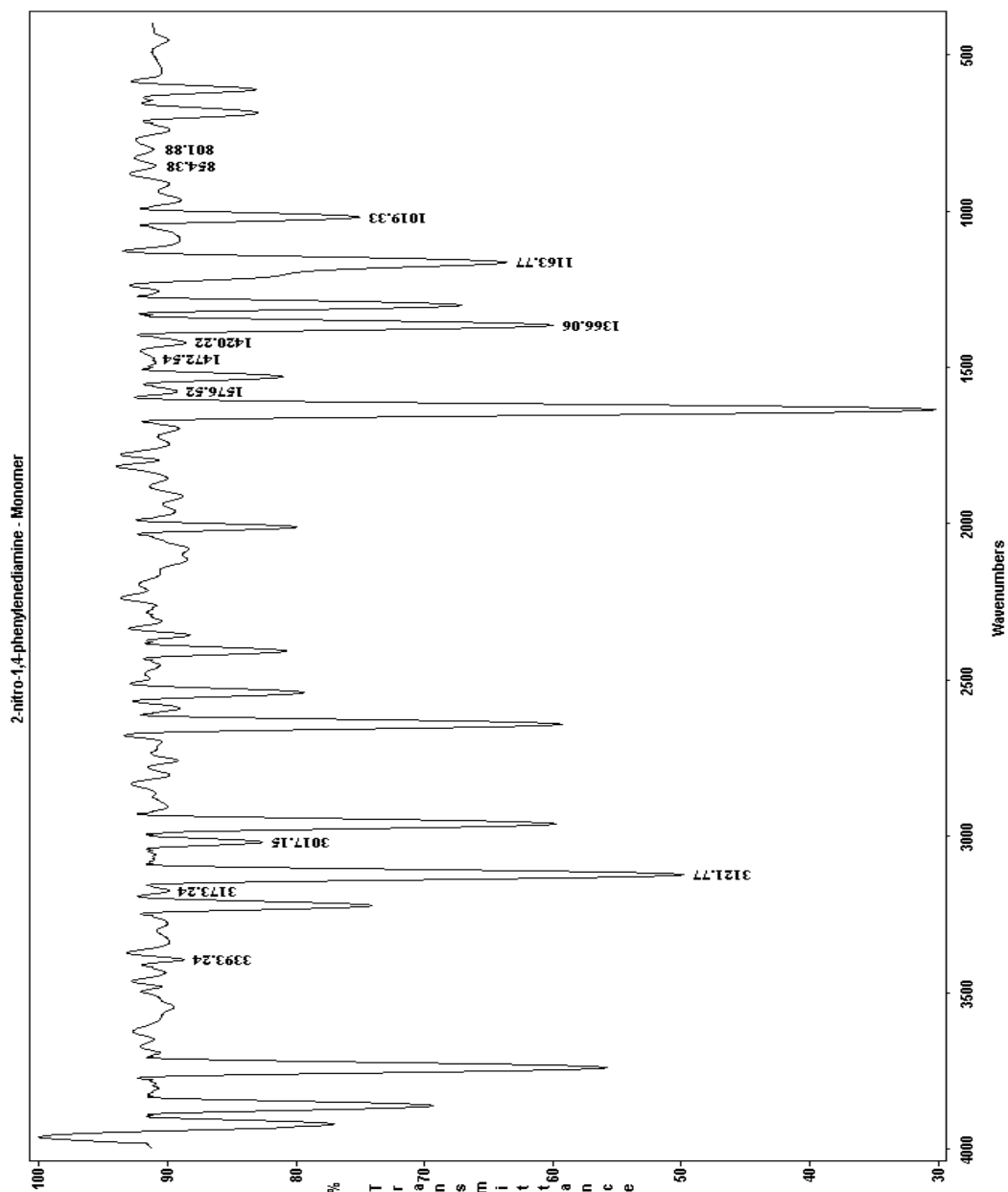


Figure 3.9.1(4) IR spectrum for the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride

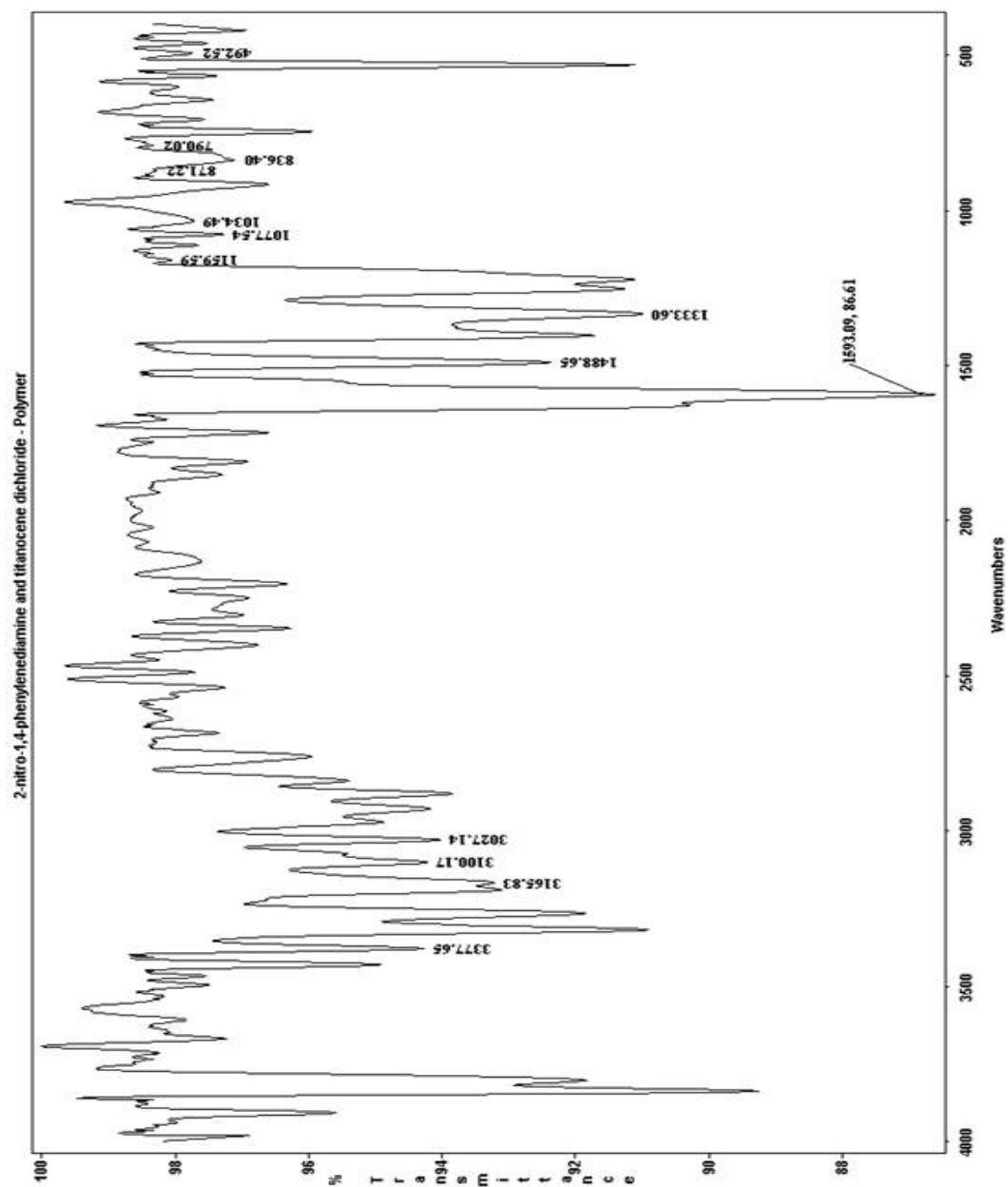
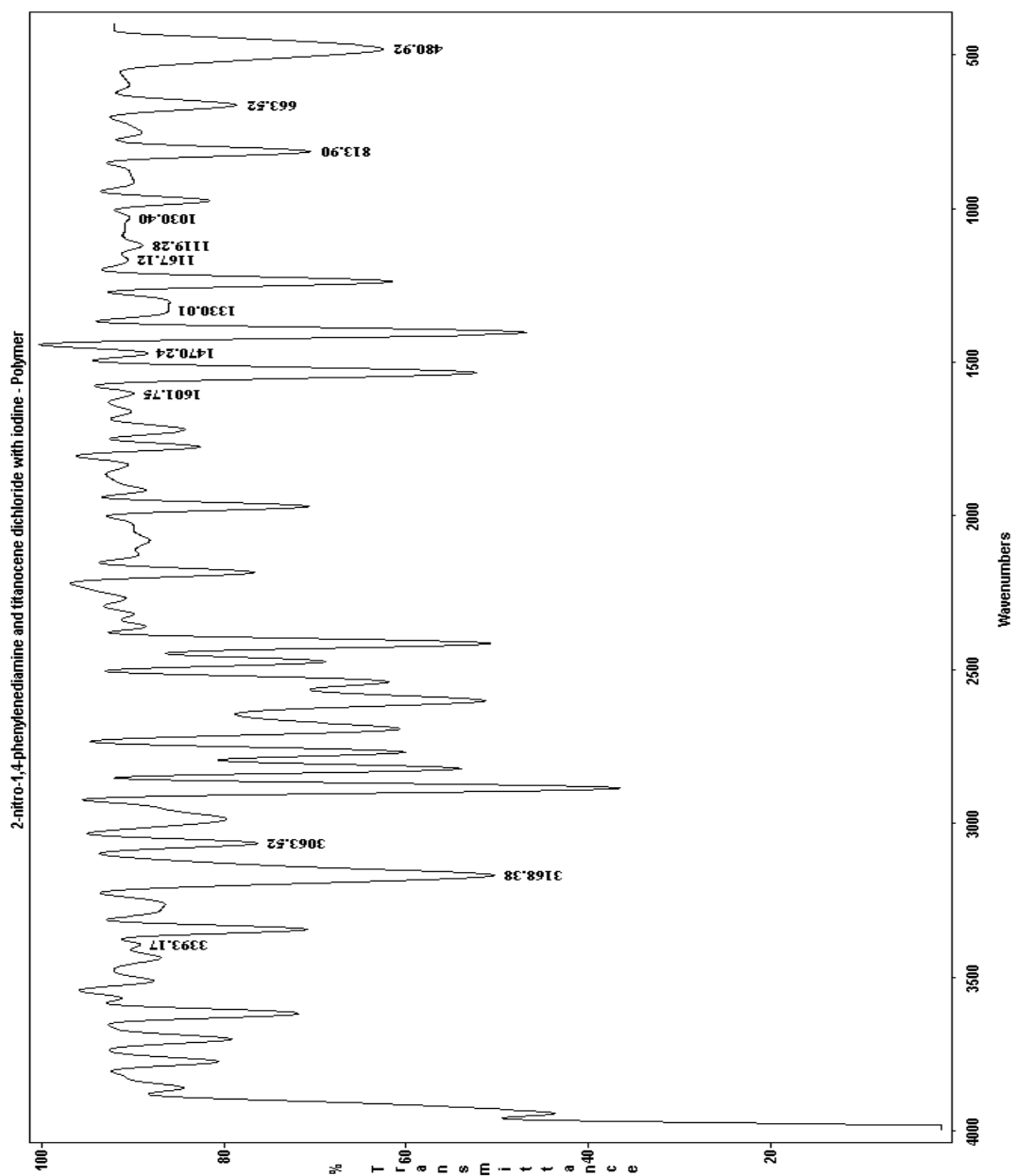


Figure 3.9.1(5) IR spectrum for the product of 2-nitro -1,4-phenylenediamine and titanocene dichloride doped with iodine



For the product of 2-nitro-1,4-phenylenediamine and titanocene dichloride polymer, the N-H stretches for monomer and polymer are in the range of 3546-3317 cm^{-1} (all values are given in cm^{-1}) which lies within the range of literature values 3500-3300.

The N-H group gives both an out of plane or antisymmetric stretch in the range of 3510 to 3390 (for aromatic amines) and in plane or symmetric stretch at about 3420 to 3330 (for aromatic amines). The monomer has N-H stretching bands at about 3545 and 3393 associated with the out-of-plane stretching. Secondary amines, here formed from the reaction of the titanocene dichloride with the primary amine, has only one band grouping about 3300. The polymer has a band at about 3317. The N-H bending is assigned to 1577 for the monomer and 1593 for the polymer. The NO₂ aromatic stretches appear in the general range of 1550 to 1400 for antisymmetric stretching and 1355 to 1315 for symmetric stretching. Both are strong bands. For the monomer these appear at 1473 and 1366. For the polymer they appear at about 1489 (part of a larger band) and 1334. The Ti-N is assigned to be in the general area of 480. A new band appears at about 490 is assigned to this moiety. The band assigned to C-I stretching is listed as a strong band. It is found in the range of about 700 to 485. A new band for the doped sample compared with the undoped sample appears at 664 which is tentatively identified as the C-I stretch consistent with the formation of this moiety for the doped sample.

Tables 3.9.1(6) – 3.9.1(8) contain the IR data for products derived from 2-nitro-1,4-phenylenediamine and zirconocene dichloride, 2-nitro-1,4-phenylenediamine and hafnocene dichloride and N-methyl-1,4-phenylenediamine and titanocene dichloride respectively.

Even for the product of N-methyl-1,4-phenylenediamine and titanocene dichloride polymer, similar bands were observed in the same region with slight difference in Ti-N stretch at 496 and 473 for polymer and polymer mixed with iodine.

The products of 2-nitro-1,4-phenylenediamine with hafnocene and zirconocene exhibit similar bands when compared with titanocene dichloride polymer except, Zr-N observed in the region of 480-410 and Hf-N stretch observed in the region of 480-420 respectively. The Zr-Cp and Hf-Cp asymmetric stretches are observed in the range of 421 and 418 respectively which correspond to the actual literature values. In addition to those bands, C-I band is seen in the region between 700-485.

Table 3.9.1(6) IR assignments for the undoped and doped products derived from 2-nitro-1,4-phenylenediamine and zirconocene dichloride [228, 230].

| | 2-nitro-1,4-phenylenediamine and Cp₂ZrCl₂ | | |
|-----------------------------|--|-----------------------------|-------------------|
| Assignments | Polymer | Polymer (iodine) | Literature |
| C-H st aromatic | 3024, 3070, 3134, 3178 | 3024, 3059, 3080, 3184 | 3200-3000 |
| C=C stretch | 1456 | 1448 | 1475 |
| C-H bend(para) | 856 | 860 | 850-800 |
| CH in plane bend, Cp | 940 | 938 | 927 |
| CH out of plane bend, Cp | 1071 | 1072 | 1074 |
| Ring breathing, Cp | 1119 | 1120 | 1130 |
| C-N stretch (alkyl) | 1180 | 1182 | 1200-1025 |

| | | | |
|--------------------------|------|------|-----------|
| N-H stretch | 3400 | 3403 | 3500-3300 |
| N-H bend | 1592 | 1595 | 1640-1500 |
| N-H bend (oop) | 810 | 813 | 800 |
| NO ₂ aromatic | 1450 | 1456 | 1550-1400 |
| NO ₂ aromatic | 1327 | 1327 | 1355-1315 |
| Zr-Cp asym. st. | 405 | 421 | 419 |
| Zr-N stretch | 474 | 468 | 480-410 |
| C-I stretch | - | 666 | 700-485 |

Table 3.9.1(7) IR assignments for the undoped and doped products derived from 2-nitro-1,4-phenylenediamine and hafnocene dichloride [228, 231].

| | 2-nitro-1,4-phenylenediamine and Cp₂HfCl₂ | | |
|-----------------------------|--|------------------------|-------------------|
| Assignments | Polymer | Polymer(iodine) | Literature |
| C-H st aromatic | 3010,3058, 3106 [*] , 3156 | 3059,3137 | 3200-3000 |
| C=C stretch | 1593 | 1577 | 1600 |
| C-H bend(para) | 848 | 846 | 850-800 |
| CH out of plane bend, Cp | 1071 | 1072 | 1074 |
| Ring breathing, Cp | 1125 | 1118 | 1130 |
| C-N stretch (alkyl) | 1160 | 1119 | 1200-1025 |
| N-H stretch | 3357 | 3382 | 3500-3300 |
| N-H bend | 1593 | 1577 | 1640-1500 |
| N-H bend (oop) | 776 | 781 | 800 |
| NO ₂ aromatic | 1523 | 1499 | 1550-1400 |
| NO ₂ aromatic | 1320 | 1320 | 1355-1315 |
| Hf-N stretch | 461 | 468 | 480-420 |
| Hf-Cp asym. st. | 419 | 418 | 419 |
| C-I stretch | - | 699 | 700-485 |

Table 3.9.1(8) IR assignments for N-methyl-1,4-phenylenediamine monomer and undoped and doped products with titanocene dichloride [228, 229].

| | N-methyl-1,4-phenylenediamine and Cp₂TiCl₂ | | | |
|-----------------------------|---|---------------------|-----------------------------|-------------------|
| Assignments | Monomer | Polymer | Polymer (iodine) | Literature |
| CH st. aromatic | 3006, 3061, 3151, 3188 | 3035, 3120, 3152 | 3035, 3157 | 3200-3000 |
| CH st. aliphatic | 2949, 2865 | 2991, 2838 | 2989, 2938, 2891, 2822 | 3000-2800 |
| C=C stretch | 1570 | 1557 | 1584 | 1600 |
| C-H bend(para) | 830 | 825 | 870 | 850-800 |
| CH in plane bend, Cp | 1005, -- | 1105 | 1005 | 1015 [*] |
| CH out of plane bend, Cp | -- | 1056 | 1054 | 1074 [*] |
| C-H st. Cp | 3103 | 3091 | 3107 | 3200-3000 |
| Ring breathing, Cp | - | 1126 | 1125 | 1130 [*] |
| C-N stretch (alkyl) | 1172 | 1169 | 1168 | 1200-1025 |

| | | | | |
|-----------------|------|------|------|-----------|
| N-H stretch | 3364 | 3344 | 3370 | 3500-3300 |
| N-H bend | 1504 | 1512 | 1509 | 1640-1500 |
| N-H bend (oop) | 791 | 779 | 780 | 800 |
| Ti-N stretch | - | 496 | 473 | 480 |
| Ti-Cp asym. st. | - | 434 | 431 | 419 |
| C-I stretch | - | - | 664 | 700-485 |

where,

Monomer = N-methyl-1, 4-phenylenediamine

Polymer = N-methyl-1, 4-phenylenediamine and Cp_2TiCl_2

Polymer (iodine) = N-methyl-1, 4-phenylenediamine and Cp_2TiCl_2 doped with iodine

For the product of N-methyl-1,4-phenylenediamine and titanocene dichloride, of interest is the presence of C-H aliphatic st. for the methyl group. The higher band(s), generally about 2960, are due to the antisymmetric stretch while the lower band(s), generally about 2870, are due to the symmetric stretch. These bands are present in the monomer and polymer consistent with their presence in the product.

Thus, IR results are consistent with the proposed structure with the appearance of new bands assigned to the formation of the M-N linkage, change in the amine bands consistent with formation of a secondary amine and presence of bands from both reactant moieties.

3.9.2 Determination of ion fragments for metal-containing polymers derived from various 1,4-phenylenediamines employing MALDI Mass Spectrometry

MALDI TOF MS was employed to assist in the structural characterization of the metal-containing polyamines derived from various 1,4-phenylenediamines. The mass spectra for the 2-nitro-1,4-phenylenediamine and titanocene dichloride polymer both in undoped and doped states are presented in **Figure 3.9.2(1)** and **Figure 3.9.2(2)** respectively.

Figure 3.9.2(1) MALDI MS for the polymer derived from 2-nitro-1,4-phenylenediamine and titanocene dichloride in the **undoped** state over the mass range of 100 to 500 Da

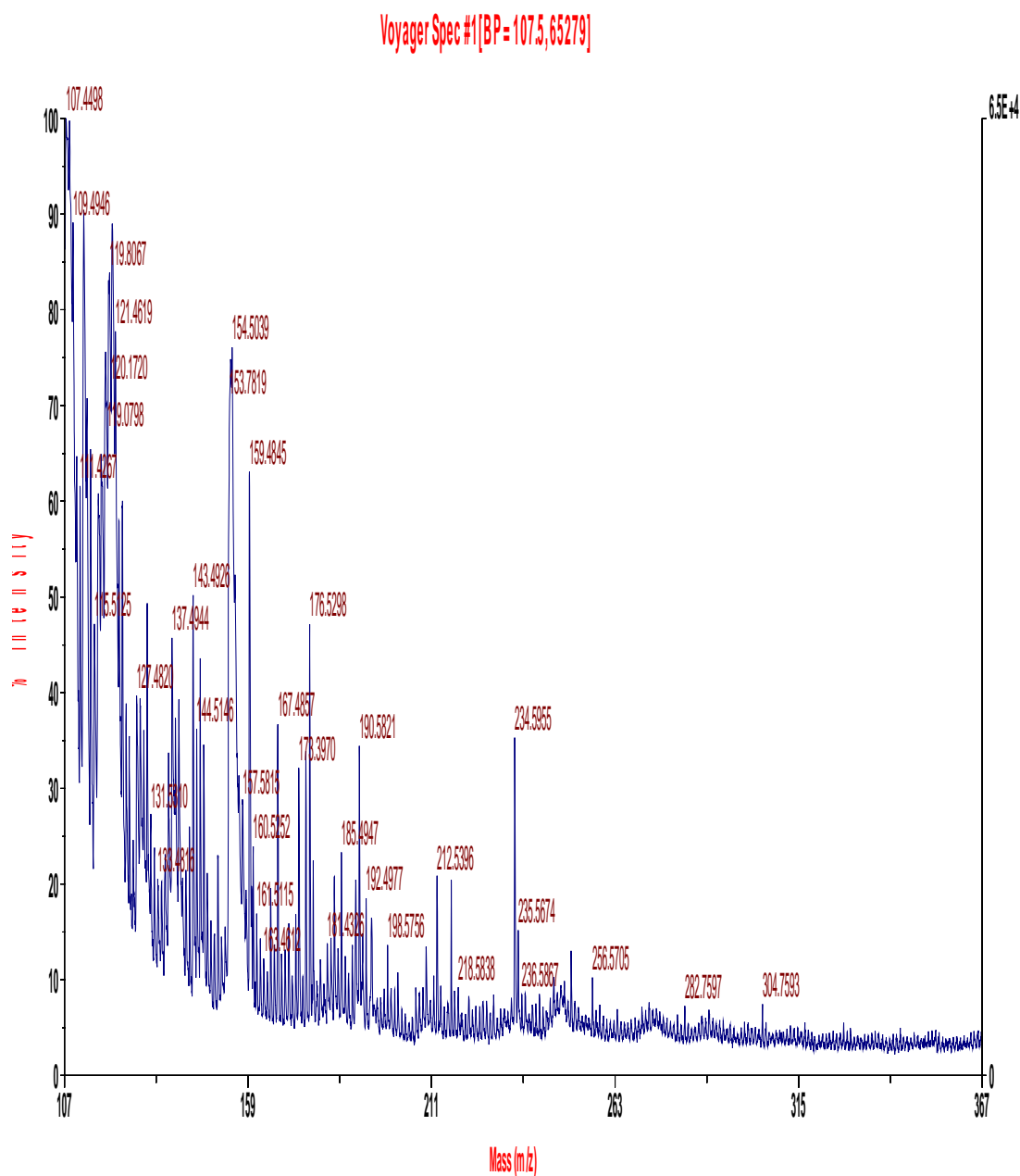
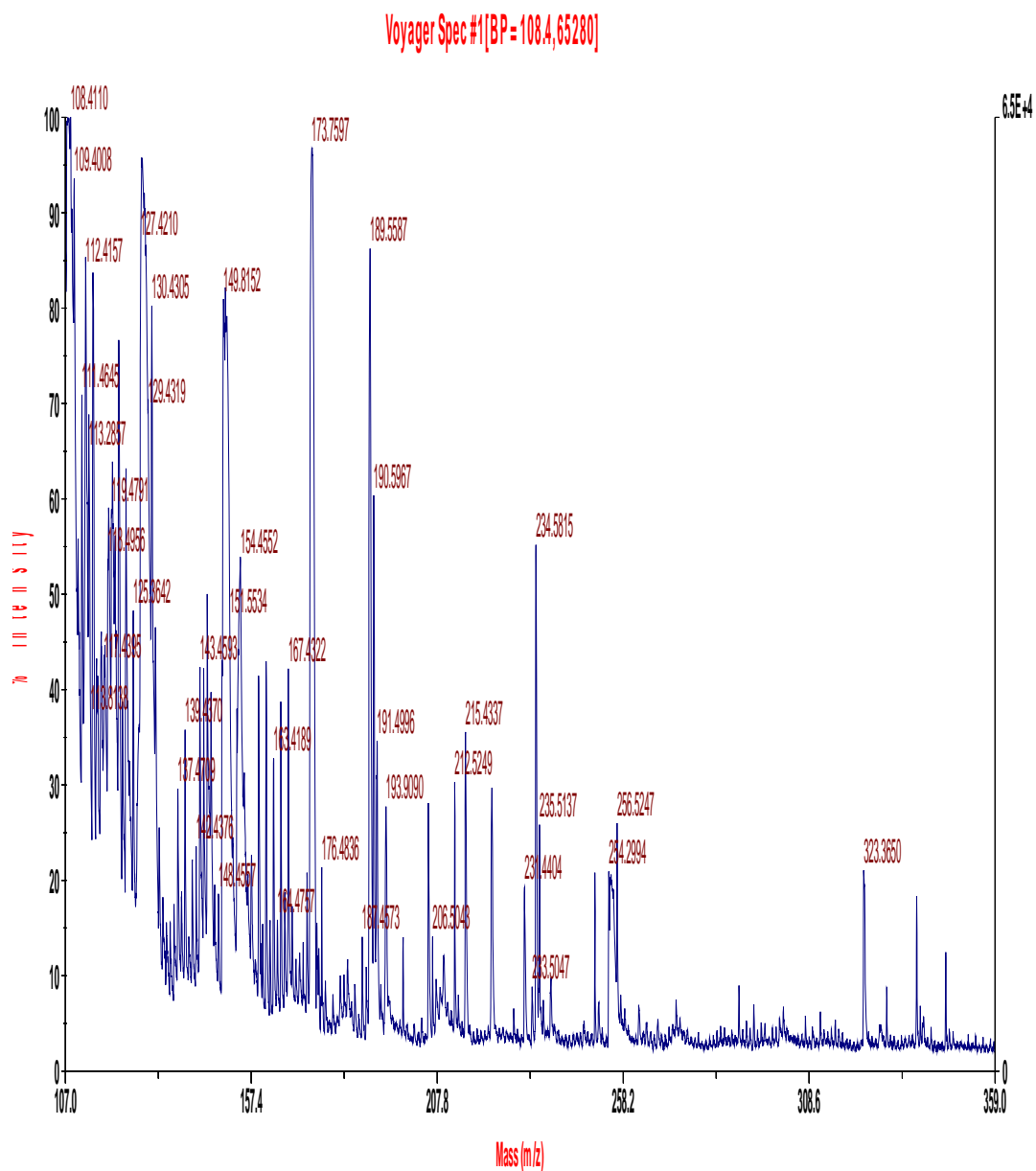


Figure 3.9.2(2) MALDI MS for the polymer derived from 2-nitro-1,4-phenylenediamine and titanocene dichloride in the **doped** state over the mass range of 100 to 500 Da.



The significant ion fragments for the undoped and doped products of 2-nitro-1,4-phenylenediamine and titanocene dichloride in the mass range of 100 to 500 Da are presented in **Table 3.9.2(3)**

Table 3.9.2(3) Significant ion fragments (greater than three times the background) in the mass range of 100 to 500 Da for the undoped and the doped product of 2-nitro-1,4-phenylenediamine and titanocene dichloride

| m/e (undoped) | m/e (doped) | Possible Tentative assignments |
|---------------|-------------|----------------------------------|
| 107 | 108 | HNPhNH (106) |
| 155 | 154 | TiNHPhNH (154) |
| 173 | 174 | HNPhNHNO ₂ , Na (174) |
| 193 | 194 | Cp ₂ Ti-NH (193) |
| - | 231 | HNPhNHI (232) |
| - | 254 | I ₂ |
| - | 323 | TiNHPhNO ₂ NHI (325) |

The MALDI MS contains ion fragments from both the reactants. Here the focus is on the appearance of different ion fragments between the undoped and the doped samples. As expected, ion fragments are present that show the presence of iodine (at 254 Da). There are additional ion fragments that contain iodine at 231 and 323 Da. consistent with the formation of iodine-containing products from the doping of the sample. The ion fragment at 231 Da is particularly informative in that it can be envisioned as being formed from the substitution of iodine to the phenylene ring.

Table 3.9.2(4) and Table 3.9.2(5) contain the assignments for ion fragments for the undoped and the doped products of 2-nitro-1,4-phenylenediamine and zirconocene dichloride and 2-nitro-1,4-phenylenediamine and hafnocene dichloride. As in the case of the analogous titanocene, there are ion fragments derived from both reactant moieties. For the doped samples there is an expected ion fragment at about 255 assigned to the presence of I₂ as well as ion fragments characteristic of the presence of iodine substituted into the phenylene ring at 216, 233 and 324 for the zirconocene product and 216, 231 and 301 for the hafnocene product. As in the case of the titanocene product the appearance of new ion fragments are consistent with the formation of an iodine-phenylene product resulting from the doping of the products.

Table 3.9.2(4) Significant ion fragments (greater than three times the background) in the mass range of 100 to 500 Da for the undoped and doped product of 2-nitro-1,4-phenylenediamine and zirconocene dichloride

| m/e (undoped) | m/e (doped) | Possible Tentative assignments |
|---------------|-------------|----------------------------------|
| 107 | 108 | HNPhNH (106) |
| 159 | 159 | PhNO ₂ NH, Na (160) |
| 173 | 174 | HNPhNHNO ₂ , Na (174) |
| - | 216 | HNPhI (217) |
| - | 233 | HNPhNHI (232) |
| - | 255 | I ₂ (254) |
| 274 | 274 | HNCp ₂ ZrNH, Na (274) |
| - | 324 | ZrNHPhNHI (323) |

Table 3.9.2(5) Significant ion fragments (greater than three times the background) in the mass range of 100 to 500 Da for the undoped and doped product of 2-nitro-1,4-phenylenediamine and hafnocene dichloride

| m/e (undoped) | m/e (doped) | Possible Tentative assignments |
|---------------|-------------|--|
| 107 | 107 | HNPhNH (106) |
| 151 | 151 | HNPhNHNO ₂ (151) |
| 173 | 175 | HNPhNHNO ₂ , Na (174) |
| - | 216 | HNPhI (217) |
| - | 231 | HNPhNHI (232) |
| - | 255 | I ₂ (254) |
| - | 301 | HNPhNO ₂ NHI, Na (300) |
| 364 | 364 | HNCp ₂ HfNH ₂ , Na (363) |

The mass spectra for N-methyl-1,4-phenylenediamine and titanocene dichloride polymer both in the undoped and the doped states are presented in **Figure 3.9.2(6)** and **Figure 3.9.2(7)** respectively.

Figure 3.9.2(6) MALDI MS for the polymer derived from N-methyl-1,4-phenylenediamine and titanocene dichloride in the **undoped** state over the mass range of 100 to 500 Da

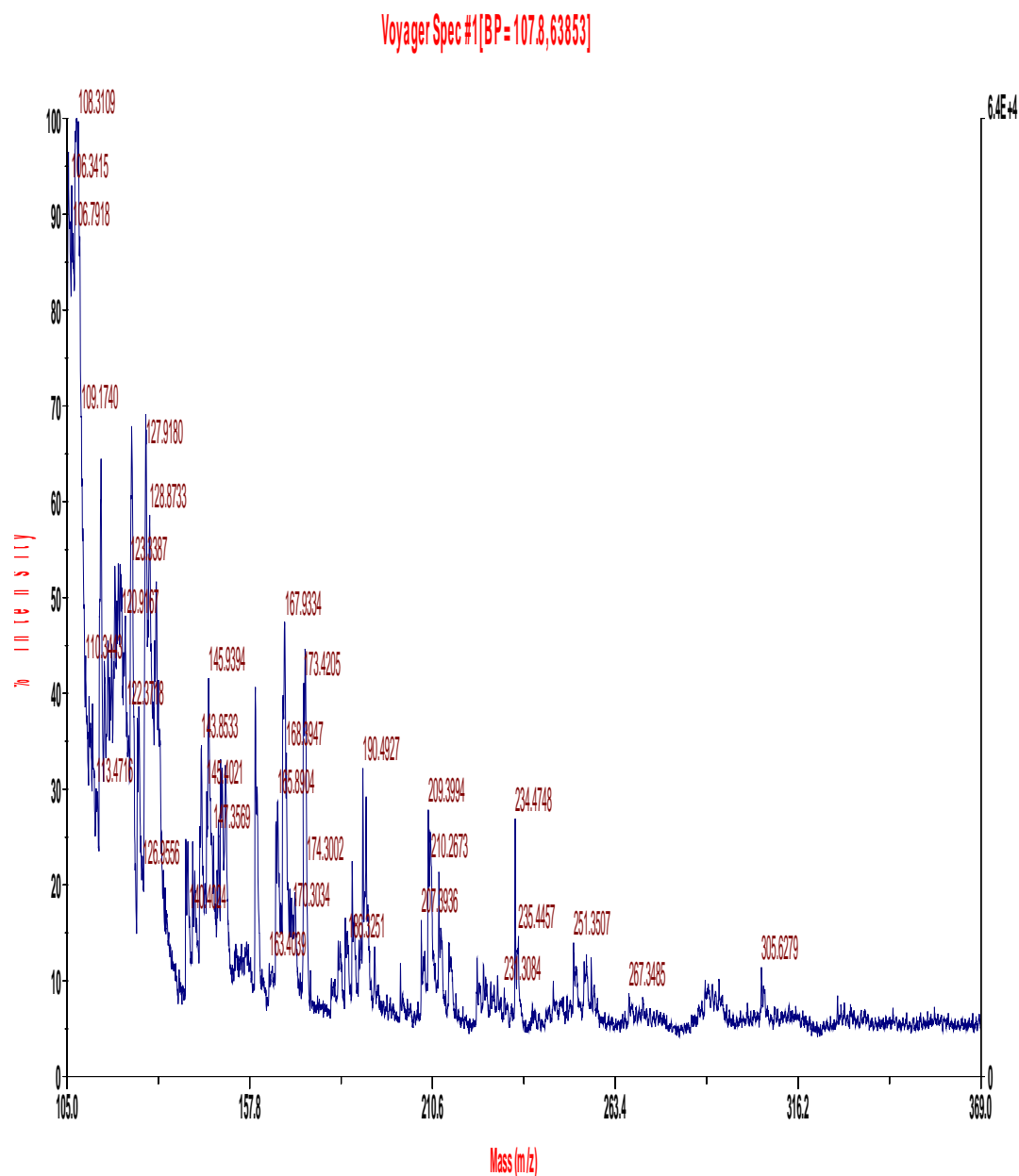


Figure 3.9.2(7) MALDI MS for the polymer derived from N-methyl-1,4-phenylenediamine and titanocene dichloride in the **doped** state over the mass range of 100 to 500 Da.

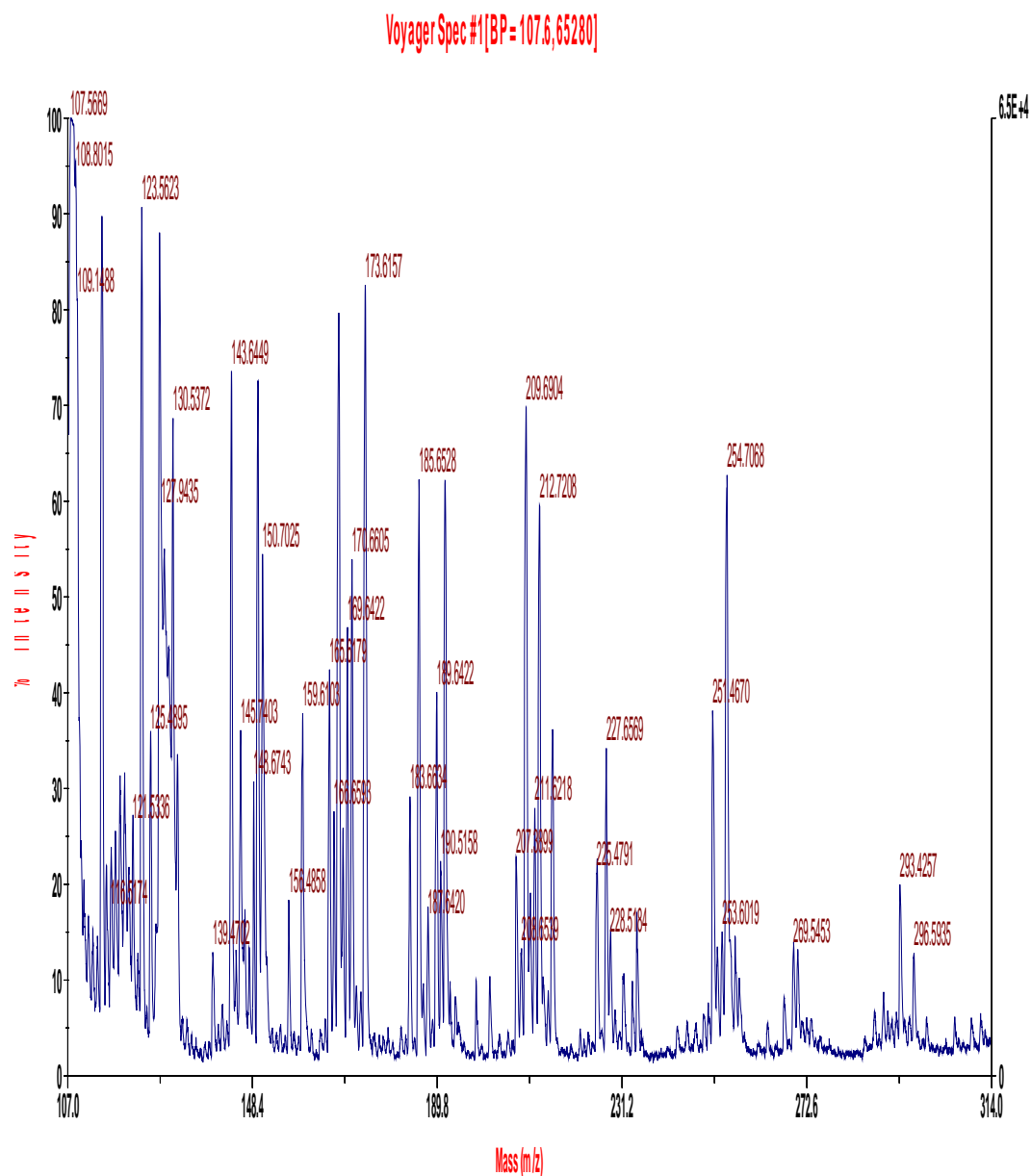


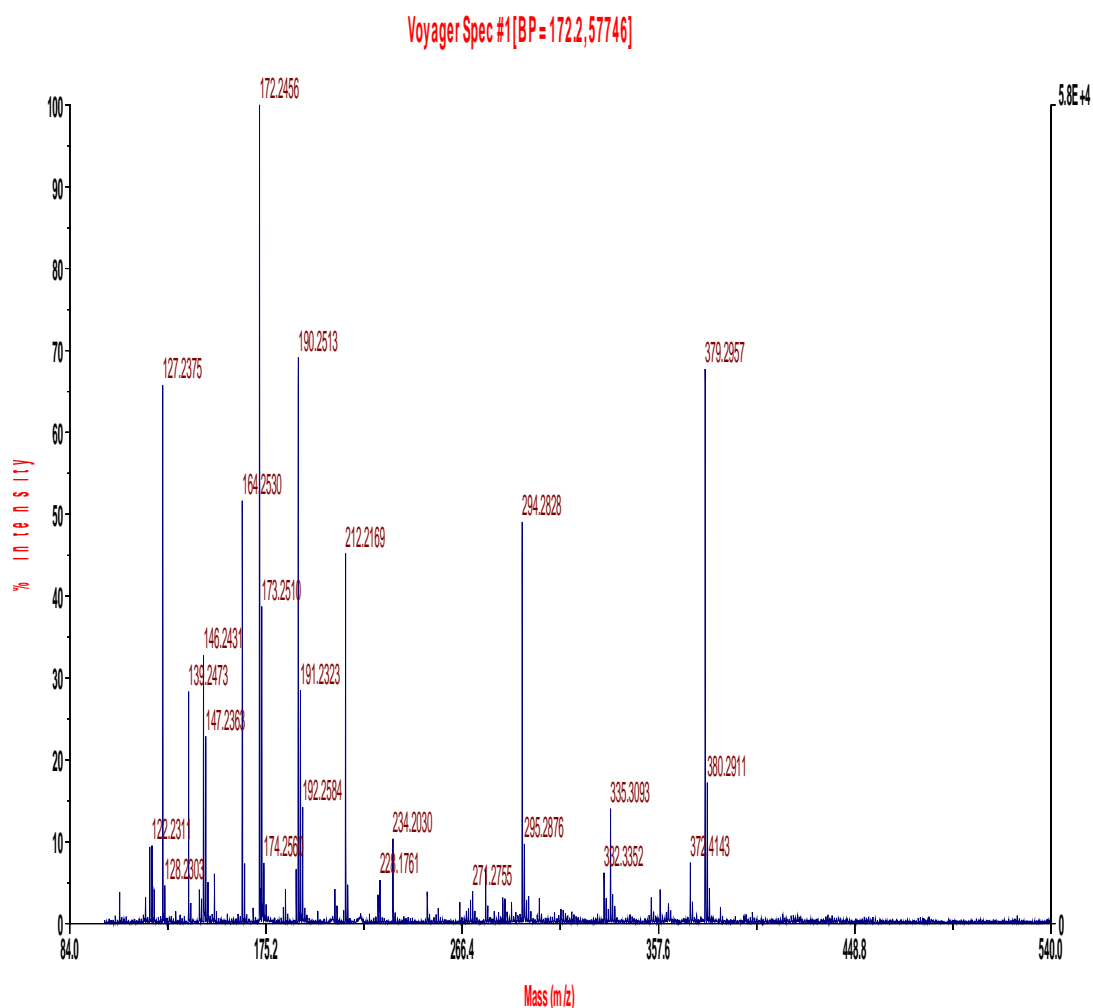
Table 3.9.2(8) contains ion fragments generated from the product of N-methyl-1,4-phenylenediamine and titanocene dichloride. As in the case with the nitrophenylene products, there are ion fragments that contain iodine at 255 and iodine-containing fragments at 151 and 227 respectively.

Table 3.9.2(8) Significant ion fragments (greater than three times the background) in the mass range of 100 to 500 Da for the undoped and the doped product of N-methyl-1,4-phenylenediamine and titanocene dichloride

| m/e (undoped) | m/e (doped) | Possible Tentative assignments |
|----------------------|--------------------|--|
| 108 | 108 | HNPhNH (106) |
| 144 | 144 | HNPhN-CH ₃ , Na (143) |
| - | 151 | NaI (150) |
| 168 | 168 | N-CH ₃ PhNHTi (168) |
| 209 | 210 | NHCp ₂ TiNH (208) |
| - | 227 | PhI, Na (227) |
| - | 255 | I ₂ (254) |
| 270 | 270 | Cp ₂ TiNHPh (269) |
| 297 | 297 | Cp ₂ TiNHPhN(CH ₃)(297) |

Figure 3.9.2(9) contains ion fragments derived from the matrix (CHCA) in the mass range of 100 to 500 Da. These have been omitted in interrupting with the MALDI MS for the various products since they are derived from the matrix and not the products.

Figure 3.9.2(9) Significant ion fragments derived from the matrix (α -cyano-hydroxy cinnamic acid) (CHCA)



Thus, MALDI MS results are consistent with the proposed repeat unit. Further, it is consistent with the formation of ion fragments containing iodine-phenylene moiety.

3.9.3 Molecular weight determination of 1,4-phenylenediamines by light scattering photometry

Light Scattering Photometer was employed for determining the molecular weights for series of 1,4-phenylenediamines. Most of the polymers were soluble in 1-methyl-2-pyrrolidinone solvent (MP) with the exception of 2-nitro-1,4-phenylenediamine and titanocene dichloride polymer which is soluble in dimethyl sulfoxide (DMSO) solvent. The molecular weights for this series were found in the range of 10^4 .

Table 3.9.3(1) Molecular weight and chain length for the metallocene polyamines

| 1,4-phenylenediamine/metallocene dichloride | Molecular weight (Mw) | DP |
|---|------------------------------|-----------|
| 2-nitro-1,4-phenylenediamine/titanocene dichloride polymer | 2.2×10^4 | 67 |
| 2-nitro-1,4-phenylenediamine/zirconocene dichloride polymer | 1.5×10^4 | 40 |
| 2-nitro-1,4-phenylenediamine/hafnocene dichloride polymer | 2.8×10^4 | 61 |
| N-methyl-1,4-phenylenediamine/titanocene dichloride polymer | 6.0×10^4 | 201 |

Molecular weight was studied as a function of time for one month and found to be unchanged. For instance, for the product of N-methyl-1,4-phenylenediamine and titanocene dichloride, the molecular weight was initially 6.0×10^4 Da. and after one month was 5.7×10^4 Da. For the product of 2-nitro-1,4-phenylenediamine and zirconocene dichloride the initial molecular weight was 1.5×10^4 Da. and after one month was 1.4×10^4 Da.

3.10 Physical characterization summary

Infrared spectroscopy shows bands derived from both the reactants. In addition, there is presence of a new band assigned to the formation of the M-N for the metallocene products. There is also an appropriate shift from bands assigned to primary to secondary amines as expected. Finally, there is formation of a new band assigned to the C-I stretching found for the doped samples.

MALDI MS shows ion fragment clusters consistent with the presence of structures derived from bond scission of the proposed polymer structure. New ion fragments are also found that contain the phenylene-iodine moiety for doped materials consistent with the formation of such moieties when doping is employed.

The polymeric nature is supported by the light scattering photometry.

Thus, physical characterization is consistent with the proposed structures for the metallocene polyamines.

CHAPTER 4. DISCUSSION & SUMMARY

The focus of this research is to learn about the electrical properties of a number of metal-containing condensation polymers. The particular electrical property focused on the conductivity because it is this property that determines if a material can be used as an insulator, semiconductor or a conductor. Towards this end two areas were emphasized. The initial area involved a general survey of a number of polymers while the second area focused on the ability to enhance conductivity through doping.

4.1. Hypothesis

The **hypothesis** of the current research is that metal-containing condensation polymers which allow delocalization of electrons are near semiconductors and can be successfully doped to increase their conductivity to within the near conductive region.

4.2 Specific aims

There are two specific aims of the current research:

- 1) Determine the electrical conductivity of a variety of metal-containing polymers that can exhibit whole chain electron delocalization.
- 2) Study the effects of doping selected metal-containing polymers with iodine to see if increases in the conductivity are obtained.

4.3 Discussion

Following are the conclusions reached from these research efforts. All of the surveyed samples were condensation polymers formed from reaction with various organometallic dihalides and various Lewis bases. All of the compounds fit our criteria where the repeat unit could show delocalization of electrons throughout the polymer backbone. About 50 samples were surveyed for several purposes. The first purpose was to determine if any of the materials were inherently conductors or near conductors. None of the samples were inherently conductors. The product from dimethyltin dichloride and Eosin Y was near the conductive region with log conductivities between -7 and -8 in the general range of near conductors. The other samples ranged from being semiconductors to near nonconductors as given in Table 4.3.1(1)

Table 4.3.1(1) General conductivity values for the polymer samples surveyed. (The conductivity values are minus log conductivity)

| Sample grouping | Frequency in KHz | | |
|-----------------------------------|------------------|-------|--------|
| | 0.4 KHz | 5 KHz | 10 KHz |
| Group IV B polyethers | 11 | 9-11 | 9-10 |
| Group IV B polyesters | 11-12 | 10-11 | 10 |
| Phenylsulfonphthalein polydyes | 11 | 10-11 | 10 |
| Flourescein polydyes | 11 | 8-10 | 7-10 |
| Cobalticene-containing polyesters | 9-11 | 9 | 9 |
| Organotin polyamines | 11 | 9-11 | 9-10 |

The second purpose was to see if there were structural relationships that contributed to the conductivity. Several series were tested to see if the electronic nature of the Lewis acid had a pronounced effect on the conductivity. Results were consistent with there being no pronounced electronic effect within a grouping of similar polymers varying the Lewis acid but holding the metal atom constant. While the general conductivities varied from about 7 to 12, there appeared to be no single metal that gave better conductivities. For instance, for the cobalticene polymers tested, there appeared to be little difference between whether the metal was tin, antimony or bismuth. For the polyesters derived from phenylsulfonphthalein dyes, there was little difference as to whether the metal was Group IVB or tin. It must be noted that the number of metals were

necessarily small focusing on Group VA, Group IVB and tin. In summary, while disappointing, no particular trend was established between the conductivity and the identity of the metal. Again, while a number of polymers were tested, more needs to be studied before this trend is firmly established.

Another aspect was to vary the nature of the Lewis base but holding the metal atom constant. Again, there appeared to be little or no variance as the nature of the Lewis base was varied. Thus, the titanocene polyethers derived from hydroquinone and various substituted hydroquinone derivatives show similar behavior in terms of electrical conductivity of the materials with log conductivities varying from about -10 to -12 which are within the semiconductor range. There appears to be no direct relationship between the conductivity and electronic nature of the phenylene ring. For instance, the behavior of the tetrachlorohydroquinone and dimethylhydroquinone derived polymers were essentially the same yet the tetrachlorohydroquinone features a phenylene ring that is electron poor while the dimethylhydroquinone polymer features a phenylene ring that is electron rich.

A similar situation exists for a series of polyamines derived from reaction of dibutyltin dichloride and 4,6-diaminopyrimidines. The series was sufficiently wide as to see if there was a relationship between the conductivity and the steric nature of the 4,6-diaminopyrimidine derivatives and no relationship was observed. Thus, the product from 4,6-diaminopyrimidine itself, which offers the least steric hindrance, has a conductivity about the same as that found for the most sterically cluttered diamine, 4,6-diamino-5-(p-chlorophenyl)-6-ethylpyrimidine. Further, conductivity appears to be independent of the chain length. Again, for the dibutyltin polyamines, the longest chain length product

derived from 4,6-diaminopyrimidine itself has essentially the same conductivity as the shortest chain length product derived from 4,6-diamino-5-(p-chlorophenyl)-6-ethylpyrimidine.

The lone exception for the insensitivity of conductivity to the electron density for the Lewis base is for the titanocene polyesters. While the magnitude and behavior is similar for the titanocene polyesters, a mild difference is found between those containing electron donating substituents with log bulk conductivity values clearly within the near semiconductor to non-conductor range while those containing electron withdrawing groups were a little higher, being within the semiconductor region. The difference is on the order of 10^2 to 10^3 fold, so may be significant.

Even so, in general, it appears that almost all of the materials are semiconductors to near nonconductors regardless to the nature of the metal or Lewis base.

Further results related to doping are discussed in this section. Iodine was used as the doping agent because of its widespread use and ease of application [37]. In the current research, doping with iodine was carried out employing both the iodine chamber method [38] for surface doping and the in situ method [40] for bulk doping. The product of 2-nitro-1,4-phenylenediamine and titanocene dichloride was found to be receptive to doping with increases in conductivity routinely on the order of 10^2 fold and greater. Initial studies involved surface doping through simple exposure of the product to the iodine vapors. Several sets of experiments were carried out that were consistent with doping being cyclic. Thus, a sample was exposed to iodine vapor and showed increased conductivity of about 10^2 fold. Iodine was removed either through exposure to the air for a day or more or through heating. Conductivity decreased to non-doped levels but

increased when the disk was again exposed to the iodine vapors. Conductivity was dependent on the time the sample disk was exposed to iodine such that at high exposure times the conductivity falls to the non-doped levels. The optimum doping time was ten seconds.

This system, while simple to operate, it is difficult to control the amount of iodine deposited on the sample disk. Thus, further studies were carried out using a bulk doping system where samples were prepared using known amounts of the iodine along with the test material. While this bulk doping technique is employed industrially to make silicon semiconductors, it is not typically used for organic polymers since the major use for the organic polymers is the formation of conductive “wires”.

Conductivity was measured as a function of applied frequency, heating times and amounts of added iodine. Several conclusions were drawn from these studies. First, as expected, conductivity varied as the frequency varied. Conductivity was the least for the lowest applied frequency of 0.4 KHz. This frequency is often employed to illustrate constant voltage. Second, conductivity decreased with increased heating times. There is a slight loss in weight as heating time increases but it does not approach the amount of iodine within the sample. It is believed that increased heating removes surface and near surface iodine resulting in a lack of continuous “activated” sites at the surface leading to a decrease in the conductivity. Third, conductivity increases as the amounts of iodine is increased with the highest amounts of 10% and 15% iodine respectively showing similar conductivities. Fourth, the magnitude of conductivity increases about 10^2 to 10^4 fold are similar for both the bulk and surface doped systems and the behavior as a function of applied frequency are also similar. The similarity in conductivity behavior between

surface and bulk doped systems is also found for polymeric vinyl systems. [232-234]. It appears that the limit of conductivity increases may be due to the intrinsic conductivity of the activated material. This is consistent with the observation that no significant change in the conductivity is found when the sample contains 3% iodine where the lack of change may be due to lack of sufficient iodine to effect the required structural changes to allow increased conductivity to occur. At 5% iodine, increased conductivity of 10^1 to 10^2 fold occurs.

Since the nitro group is an electron withdrawing substituent, it is suggested that the electron density on the phenylene ring might be a key to whether doping successfully allowed increased in the conductivity. A number of titanocene polyamines were synthesized from 1,4-phenylenediamine and its derivatives. No increases in the conductivity were observed when these compounds were doped. Thus, it appears that there is another structural key that is not yet discovered that dictates which compounds can be successfully doped.

Another polymer was synthesized employing N-methyl-1,4-phenylenediamine with titanocene dichloride and this polymer was found to exhibit about 10^3 to 10^5 fold magnitude increases in the conductivity when doped with iodine. It is currently not known why this particular product gave such increases in the conductivity but suggests another structural window to be investigated is the modification of the amine such as employing N, N'-dimethyl-1,4-phenylenediamine. From a brief search it was found that N,N'-bis(1-ethyl-3-methyl-pentyl)-1,4-phenylenediamine is commercially available and would be one of the initial diamines to try.

The nature of the metal was next tested. The analogous polyamine was made from the reaction of 2-nitro-1,4-phenylenediamine and dibutyltin dichloride and its electrical properties were studied. There was little or no change in the conductivity as the polymer was doped. Next, polymers from reaction of 2-nitro-1,4-phenylenediamine with the other two Group IVB metallocene dichlorides, namely zirconocene dichloride and hafnocene dichloride, were synthesized and their electrical properties were measured. They behaved similar to the titanocene product exhibiting increases in the conductivity of about 10^2 to 10^4 fold when doped with iodine. Thus, the identity of the metal atom is critical to the materials behavior to doping. Since all of the Group IVB materials exhibited increased conductivity when doped, further studies might include additional metallocenes such as vanadocene dichloride and niobocene dichloride in place of the Group IVB metallocene dichlorides as the metal-containing reactant.

In doping, while it is assumed that some chemical reaction involves activation of the increased conduction from doping, the nature of the reaction site is normally not given. To attempt to gain some knowledge concerning the identity of the activated site or species, infrared spectroscopy and MALDI MS spectroscopy were carried out on doped and undoped samples for products that responded with increased conductivity to doping. For doped samples, MALDI MS showed the formation of iodine containing species, namely iodine-containing phenylene and infrared spectroscopy showed the formation of a new C-I bond.

Figure 4.3.1(2) shows a possible mechanism for the formation of the iodine-containing phenylene ring. It is not known if this might be in fact the initial step that assists in the increase in the conductivity or if this is simply one of the steps involved in

the doping process resulting in the formation of an iodine-phenylene product. Here, addition of I^+ occurs. It might be considered that such step would be favored for electron rich sites and not electron poor sites as envisioned for the nitro-substituted phenylene moiety. Even so, this is a plausible sequence leading to the formation of the iodine-phenylene structure. While iodine is believed to act as an oxidizing agent for vinyl-derived polymers, studies with doping for condensation polymers have not been reported so it is possible that iodine acts as a reducing agent (adding I^- to create an excess electron site). This would account for the inability to enhance conductivity through doping for electron withdrawing substituted 1,4-phenylenediamines (not consistent with the ability to successfully dope 2-nitro-1,4-phenylenediamine) but it does not explain the failure of electron-donating substituents to exhibit enhanced conductivity when doped. An additional study might include use of dinitro compounds such as 2,5-dinitro-1,4-phenylenediamine. A caution should be taken on using dinitro and trinitro diamines and their stability should be checked before use because of the instability of trinitrotoluene, TNT.

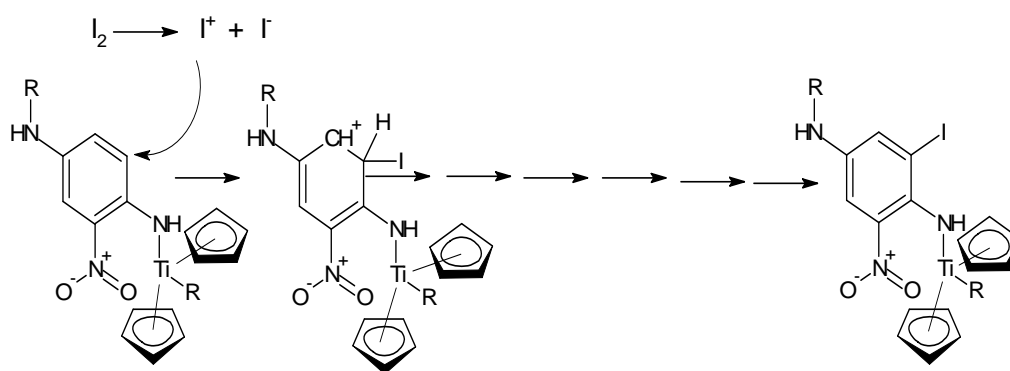


Figure 4.3.1(2) Possible mechanistic scheme for the substitution of iodine on the phenylene ring.

Often said about research is that good research raises many questions. This research raises a number of questions including the precise mechanism of activation and which structures will give materials that can be successfully doped.

The Group IVB metallocene polyamines derived from 2-nitro-1,4-phenylenediamines are somewhat ideal materials because they can be rapidly made within 15 seconds from commercially available materials utilizing the classical interfacial polycondensation system that is commercially employed for the synthesis of polycarbonates and aromatic nylons. This makes the scale up easier.

4.4. Critical Issues

Lack of appropriate solubility is one of the critical issues in the present research. As with other polymers that have been successfully doped to achieve conductive materials, solubility is a critical problem. This has been partially overcome through the use of “solubilizing arms” chemically attached to the conducting polymer backbone. One group of solubilizing arms that have been successfully employed is based on the poly(ethylene glycols). The use of poly(ethylene glycol) solubilizing arms has allowed water soluble polypyrrole to be produced. [235-239]. For the current polymers, obtaining a decent solubility for the conducting core polymer chain will allow the further determination of other important physical values. For instance, water solubility will allow a better characterization of the breadth of chain length through the use of various chromatographic techniques including size exclusion chromatography and MALDI MS. In turn, this will allow determination of the presence or absence of unwanted smaller chain segments. Solubility in a solvent such as DMSO would allow further comparative structural characterization between the undoped and successfully doped compounds

assisting the identification of the activating species by employing ^1H and ^{13}C NMR spectroscopy. The organotin polyamines were soluble in DMSO and ^1H and ^{13}C NMR spectroscopy was carried out on the products. The problem of solubility is further discussed in the following section.

Another critical issue is the alignment of polymer chains in the direction of magnetic field in order to enhance the conductivity of the test material. This is also discussed in the following section.

4.5 Future Directions

Several areas where additional work is needed have already been described in the discussion section. Here are some additional ones.

Conductivity is believed to occur from the transfer of charge along the polymer chains and also hopping from one chain to another. It is known for conductive polymers that conductivity varies dramatically for isotropic systems in comparison to directionally heterogeneous systems. Thus, for aligned polyacetylene chains conductivity is about 10^6 times greater in the direction of the alignment compared with that found at right angles to this alignment [240, 241]. For the present system, pressing of the polymer into pellets may cause alignment against the direction of applied pressure resulting in the chains being aligned along the face of the pellet and not at right angles to the face of the pellet. Since bulk conductivity is measured through the face of the pellet, any favorable enhancement due to the chain alignment is opposed. In the future, conductivity should be measured with electrodes connected to the sides of the pellets and not through the faces of the pellets. Application of a strong magnetic field to pre-pressed material may also

encourage preferential alignment. This process is called polling and is regularly employed to align materials.

Since it is believed that the formation of the iodo-substituted 2-nitro-1,4-phenylenediamine may be involved in the increased conductivity, the corresponding polymer that is iodo-2-nitro-1,4-phenylenediamine could be synthesized and its electrical properties can be measured. If it has a significantly larger conductivity than the corresponding non-iodo product then this would be tentative evidence that formation of this structure is important in increasing its conductivity. If there is no increase in the conductivity for this product then it is evident that activation is needed and may or may not involve the formation of this compound.

Further efforts are needed to have a better structural key for compounds that might be successfully doped. Some of these efforts have been already given such as the use of additional metal-containing units such as vanadocene dichloride. Non-metal compounds might also be tested. Thus, reaction with 2-nitro-1,4-phenylenediamine and terephthaloyl chloride will give a polyamide that should be tested. The polymer should offer electron chain delocalization. Figure 4.5.1(1) shows the formation of 2-nitro-1,4-phenylenediamine and terephthaloyl chloride polymer

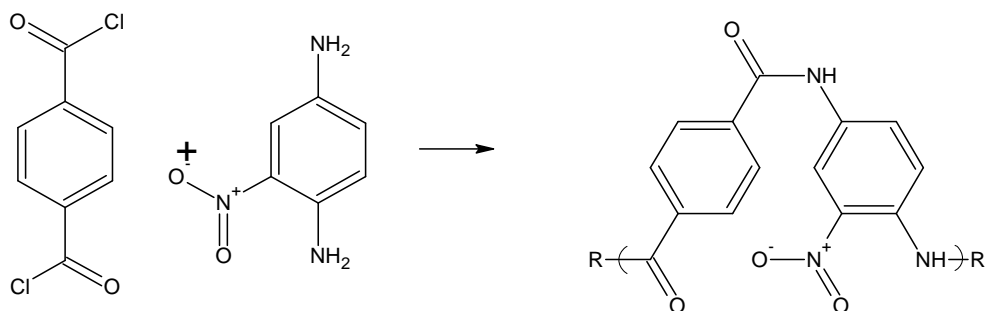
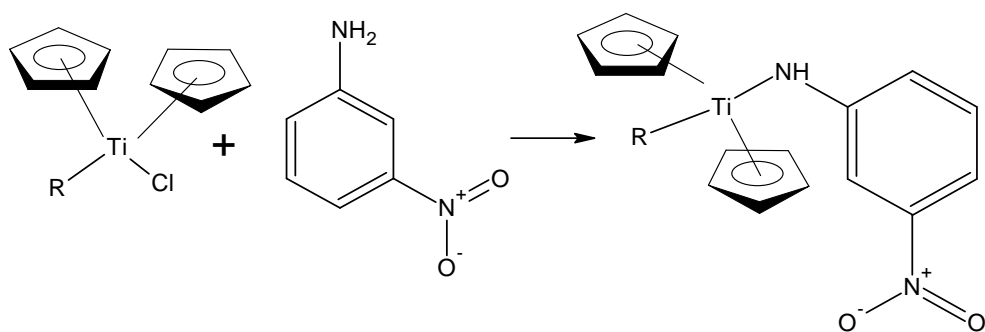


Figure 4.5.1(1) Reaction between 2-nitro-1,4-phenylenediamine and terephthaloyl chloride

Further characterization of the products needs to be undertaken. This includes looking at the effect of chain length and conductivity of the doped samples. Given the problem of solubility, determination of chain length distribution will be difficult. Even so, it should be possible to increase and decrease chain length and measure conductivity as a function of average chain length. Thus, chain length can be decreased through the addition of monofunctional reactants such as a variety of aromatic nitro-aminobenzenes. When one of these monofunctional molecules is added to the growing chain, further addition is not possible, stopping chain growth thus limiting the chain length of the polymer.



Growing chain Nitro-monophenyl amine Termination of chain growth

Figure 4.5.1(2) Illustration of chain growth termination through the use of monofunctional reactants.

Increase in chain length should be affected by the addition of a growing-chain solubilizing agent such as acetone to the system. Chain length is limited by the solubility of the growing chain. As long as the chain is able to grow, chain length increases but

when the polymer precipitates, it is no longer “fed” to the needed monomers to sustain continued chain growth, with precipitation effectively limiting chain extension. Acetone, while not a solvent for the polymer, is a better solvent than water or other generally employed organic solvents such as chloroform and heptane. Thus, its presence allows chain growth to continue in comparison to situations where acetone is not present. While increased chain length may increase conductivity, it decreases the solubility.

Most of the electrically conductive polymers are poorly soluble so that there has been a great effort to increase their solubility. It must be remembered that in order for the polymer to retain its conductivity, delocalization along its backbone must be retained so that efforts to increase solubility must retain the ability of the backbone to exhibit electron delocalization. These efforts fall into two general categories. The first effort involves disruption of the ordered backbone and consequently favoring amorphous structures. For the current research, addition of alkyl groups onto the 2-nitro-1,4-phenylenediamine moiety might be the easiest way to achieve this. The second approach is the addition of solubilizing units onto the polymer backbone. The most widely used solubilizing units are derived from mono-hydroxyl terminated poly(ethylene glycols). (Di-hydroxyl-terminated poly(ethylene glycols) will act to crosslink the polymer rendering it insoluble). It should be possible to react such poly(ethylene glycols) to the 2-nitro-1,4-phenylenediamine giving the product better solubility, hopefully water soluble. Water solubility would allow enhanced structural determination including chain length distribution through chromatography and solution NMR. It must be cautioned that before many of these time-consuming efforts are undertaken, a better understanding of the

structure-conductivity property relationship should be available so that the enhanced solubility efforts are carried out on the best of the products.

The products might be examined employing additional doping agents such as arsenic pentafluoride (oxidizing agent), bromine (oxidizing agent) and metallic sodium (reducing agent). None of these are easy to handle as iodine.

Depending on the perceived applications, additional measurements need to be carried out on the compounds for suitability. Thus, if the materials are considered for use in printing, then wettability, adhesion and printability needs to be tested.

4.6 Summary

The discovery of a condensation polymer that can be doped to improve its conductivity is potentially important. Such polymers may offer their own different and potentially valuable electrical profiles that can be employed in fashions different from the current vinyl-derived polymers. Combination of different polymers may be employed as a series of switches that allow more than the present off and on behavior. Further, the discovery of a condensation polymer that behaves in a manner similar to vinyl-derived polymers with respect to doping is significant and may open doors to a number of other condensation polymers that behave similarly including the non-metal containing condensation polymers.

REFERENCES

- 1) Roy, Kushal; Mishra, Ritesh K.; Sahana, Bikash Ch.; Karmakar, Krisnendu; **Application of conducting polymers in advanced electronic devices.** Acta Ciencia Indica; Phy; 32(4), 487-495, 2006.
- 2) Akhtar, Masud; Kleppinger, James; MacDiarmid, Alan G.; Milliken, JoAnn; Moran, Michael J.; Chiang, Chwan K.; Cohen, Marshall J.; Heeger, Alan J.; Peebles, Dale L.; J. A **'metallic' derivative of polymeric sulfur nitride: poly(thiazyl bromide), (SNBr_{0.4})_x.** Chem. Soc; Chem. Comm; (13), 473-4, 1977.
- 3) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, Alan G; **Conducting polymers: halogen-doped polyacetylene.** J. Chem. Phy; 69(11), 5098-5104, 1978.
- 4) Chiang, C. K.; Fincher, C. R., Jr.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, Alan G; **Electrical conductivity in doped polyacetylene** Phy. Rev. Letters; 39(17), 1098-101, 1977.
- 5) Shirakawa, Hideki; MacDiarmid, Alan; Heeger, Alan; Focus **article: twenty-five years of conducting polymers.** Chem. Comm; (1), 1-4, 2003.
- 6) Liu, Keke; Hu, Zhenglong; Xue, Rong; Zhang, Jianrong; Zhu, Junjie; **Electropolymerization of high stable poly(3,4-ethylenedioxythiophene) in ionic liquids and its potential applications in electrochemical capacitor.** J. Power Sources; 179(2), 858-862, 2008.

- 7) Kalendova, Andrea; Vesely, David; Stejskal, Jaroslav; **Organic coatings containing polyaniline and inorganic pigments as corrosion inhibitors.** Progress in Org. Coatings; 62(1), 105-116, 2008.
- 8) Schutze, Oliver; Jourdan, Laetitia; Legrand, Thomas; Talbi, El-Ghazali; Wojkiewicz, Jean-Luc; **New analysis of the optimization of electromagnetic shielding properties using conducting polymers and a multi-objective approach.** Polym. Adv. Tech.; 19(7), 762-769, 2008.
- 9) Niu, Yuhua; **Electromagnetic interference shielding with polyaniline nanofibers composite coatings.** Poly. Engg and Sci; 48(2), 355-359, 2008.
- 10) Otero, Toribio F; **Soft, wet, and reactive polymers. Sensing artificial muscles and conformational energy.** J. Mater. Chem.; 19(6), 681-689, 2009.
- 11) Street, R. A; **Bias-induced change in effective mobility observed in polymer transistors.** Phy. Rev. B: Condensed Matter and Mater. Phy.; 77(16), 2008.
- 12) Briseno, Alejandro L.; Mannsfeld, Stefan C. B.; Jenekhe, Samson A.; Bao, Zhenan; Xia, Younan; **Introducing organic nanowire transistors.** Materials Today; 11(4), 38-47, 2008.
- 13) Zou, Yingping; Zhou, Yi; Wu, Guanglong; Li, Yongfang; Pan, Chunyue; **Electroluminescent fluorene-based alternating polymers bearing triarylamine or carbazole moieties in the main chain: synthesis and properties.** J. App. Polym.Sci.; 111(2), 978-987, 2009.
- 14) de Boer, Bert; Facchetti, Antonio; **Semiconducting Polymeric Materials.** Polym. Rev.; 48(3), 423-431, 2008.

- 15) **"Synthetic metals ": A novel role for organic polymers (Nobel lecture);**
MacDiarmid, Alan G; 65(2), 8-17, 2001.
- 16) Peng, Hui; Zhang, Lijuan; Soeller, Christian; Travas-Sejdic, Jadranka; **Conducting polymers for electrochemical DNA sensing.** Biomater.; 30(11), 2132-2148, 2009.
- 17) Rajesh; Ahuja, Tarushee; Kumar, Devendra; **Recent progress in the development of nano-structured conducting polymers/nanocomposites for sensor applications.** Sensors and Actuators, B: Chem; B136 (1), 275-286, 2009.
- 18) Al-Saleh, Mohammed H.; Sundararaj, Uttandaraman; **A review of vapor grown carbon nanofiber/polymer conductive composites.** Carbon; 47(1), 2-22, 2009.
- 19) Spinks, Geoffrey M.; Whitten, Philip G.; Wallace, Gordon G.; Truong, Van-Tan; **An introduction to conducting polymer actuators.** Optical Science and Engineering; 133(Introduction to Organic Electronic and Optoelectronic Mater. and Devices), 733-763, 2008.
- 20) Joo, Jinsoo; Kim, Bo Hyun; Park, Dong Hyuk; Sung, Jun Hee; Choi, Hyoung Jin; **Conducting polymer nanotubes, nanowires, and nanocomposites: synthesis, characteristics, and applications.** Handbook of Organic Electronics and Photonics; 1, 51-83, 2008.
- 21) Fang, Fei Fei; Choi, Hyoung Jin; Joo, Jinsoo; **Conducting polymer/clay nanocomposites and their applications.** J. Nanoscience and Nanotechnology; 8(4), 1559-1581, 2008.
- 22) Gonzalez-Tejera, M. J.; de la Blanca, E. Sanchez; Carrillo, I; **Polyfuran conducting polymers: Synthesis, properties, and applications.** Synth. Metals; 158(5), 165-189, 2008.

- 23) Lange, Ulrich; Roznyatovskaya, Nataliya V.; Mirsky, Vladimir M; **Conducting polymers in chemical sensors and arrays**. *Analytica Chim. Acta*; 614(1), 1-26, 2008.
- 24) Hatchett, David W.; Josowicz, Mira; **Composites of intrinsically conducting polymers as sensing nanomaterials**. *Chem. Rev.*; 108(2), 746-769, 2008.
- 25) Thompson, Barry C.; Frechet, Jean M. J; **Polymer-fullerene composite solar cells**. *Angew. Chem., Int. Edition*; 47(1), 58-77, 2008.
- 26) C. Carraher, **Introduction to Polymer Chemistry**, Taylor & Francis, NY, USA, 2007.
- 27) Facchetti, Antonio; Marks, Tobin J.; Katz, Howard E.; Veinot, Jonathan; **Organic semiconductor materials**. *Printed Organic and Molecular Electronics*; 83-159, 2004.
- 28) Kittel, Ch. **Introduction to Solid State Physics**. John Wiley and Sons; NY, USA, 2004.
- 29) Neamen, Donald A; **Semiconductor Physics and Devices: Basic Principles (3rd ed.)**. McGraw-Hill Higher Education, NY, USA, 2003.
- 30) Facchetti, Antonio; Marks, Tobin J.; Katz, Howard E.; Veinot, Jonathan. Northwestern University, Evanston, IL, USA; **Organic semiconductor materials**. *Printed Organic and Molecular Electronics* 83-159, 2004.
- 31) Zhou, Qin; Swager, Timothy M; **Design and synthesis of conducting polymers with localized charge carriers: how important is delocalization?** *Polym. Preprints*; 35(1), 277-8, 1994.
- 32) Park, Y. W.; Yoon, C. O.; Na, B. C.; Shirakawa, H.; Akagi, K; **Metallic properties of transition metal halides doped polyacetylene: the solution liquid state**. *Synth. Metals*, 41(1-2), 27-32, 1991.

- 33) Das, G. P.; Yeates, A. T.; Dudis, D. S; OH, USA **Charge transport mechanism in trans-polyacetylene.** Proceedings of SPIE-The International Society for Optical Engineering; 3145(Optical Probes of Conjugated Polymers), 526-532, 1997.
- 34) Cho, Kwanghee; Cho, Sang Wan; Jeon, Pyung Eun; Lee, Hyunbok; Whang, Chung-Nam; Jeong, Kwangho; Kang, Seong Jun; Yi, Yeonjin; GyeongGi-Do; **Electronic structures of 8-hydroquinolatolithium on Au substrate: The organic electron injection layer having semiconducting properties.** Synth. Metals; 158(21-24), 984-987, 2008.
- 35) Koshino, Mikito; **Electron delocalization in bilayer graphene induced by an electric field.** Phy. Rev. B: Condensed Matter and Mater. Phy; 78(15), 155411/1-155411/5, 2008.
- 36) Jaiswal, Manu; Menon, Reghu; **Polymer electronic materials: a review of charge transport.** Polym. Int.; 55(12), 1371-1384, 2006.
- 37) K. Napo, G. Safoula, J. Bernede, K. Almeida, S. Tourihi, K. Alimi, A. Barreau, **Influence of the iodine doping process on the properties of organic and inorganic polymer thin films.** Poly. Degrad. Stability, 66, 257, 1999.
- 38) J. Mathai, S. Saravanan, M. Anantharaman, S. Venkitachalam, S. Jayalekshmi, **Effect of iodine doping on the bandgap of plasma polymerized aniline thin films.** J. Phy., D. Appl. Phy, 35(17), 2206-2210, 2002.
- 39) M. Cazayous; Sacuto, G. Horowitz; Ph. Lang, A; Zimmers and R. P. S. M. Lobo; **Iodine insertion in pentacene thin films investigated by infrared and Raman spectroscopy.** Phy.Rev. B: 70(8), 081309(R), 2004.

- 40) C.K. Chiang; **The bromine doping of polyacetylene.** Physica A; 321, 139 – 151, 2003.
- 41) H. Shirakawa; A. MacDiarmid; A. Heeger; **Focus article: twenty-five years of conducting polymers.** Chem. Comm., 1, 1, 2003.
- 42) A. Pron, A. MacDiarmid, A. Heeger; **Arsenic pentafluoride-doped polyacetylene: chemical composition of the dopant species.** Synth. Metals, 9, 115, 1984.
- 43) C. Fincher; D. Moses; A. Heeger; A. MacDiarmid; **Structure, morphology and electronic properties of trans-(CH)_x.** Synth. Metals, 6, 243, 1983.
- 44) C. Chiang; Y. Park; A. Heeger; H. Shirakawa; E. Louis; A. MacDiarmid; **Conducting polymers: halogen-doped polyacetylene.** J. Chem. Phys., 69, 5098, 1978.
- 45) C. M. Mikulski, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger; **Stability of polymeric sulfur nitride, (SN)_x, to air, oxygen, and water vapor.** Inorg. Chem; 15 (11), 2943-2945, 1976.
- 46) K.Ziegler and G. Natta, **Nobel Prize in Chemistry**, 1966.
- 47) H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger; **Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)_x.** J. Chem Soc; Chem Comm; 16, 578, 1977.
- 48) H. Shirakawa, E.J. Louis; A.G. MacDiarmid; C.K. Chiang and A.J. Heeger; **Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)_x.** J. Chem Soc; Chem Comm.; 579, 1977.
- 49) C.K. Chiang, C.R. Fischer, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau and A.G.MacDiarmid , **Electrical conductivity in doped polyacetylene.** Phys. Rev. Letters; 39, 1098-1101, 1977.

- 50) C.K. Chiang, M.A. Drury, S.C. Gau, A.J. Heeger, E.J. Louis, A.G. MacDiarmid*, Y.W. Park and H. Shirakawa; **Synthesis of highly conducting films of derivatives of polyacetylene, (CH)_x**. J. Am. Chem. Soc; 100 (3), 1013-1015, 1978.
- 51) Wang, C.; Wang, R; **Theoretical studies on anisotropic electrical conductivity of trans-polyacetylene doped with n-type dopants**. Solid State Communications; 117(2), 109-112, 2000.
- 52) Bischoff, Gerlinde; Schmidt, Werner F; **Electrical conductivity changes of polymers with conjugated double bonds induced by exposure to vapors and gases**. Angew. Makromolekulare Chem., 208, 151-65, 1993.
- 53) Plocharski, Janusz; Pukacki, Wojciech; Roth, Siegmur; **Electrical conductivity of iodine doped oriented polyacetylene**. Synth. Metals, 41(1-2), 133-6, 1991.
- 54) Sakamaki, K.; Akagi, K.; Shirakawa, H.; Kyotani, H; **Relationship between crystallinity and electrical conductivity of highly conducting polyacetylene film**. Synth. Metals; 84(1-3), 365-366, 1997.
- 55) MacDiarmid, Alan G; **Synthetic metals: a novel role for organic polymers**. Synth. Metals; 125(1), 11-22, 2001.
- 56) MacDiarmid, Alan G; **"Synthetic metals": A novel role for organic polymers (Nobel Lecture)**. Angew. Chem; 40(14), 2581-2590, 2001.
- 57) Shirakawa, Hideki; Zhang, Yu-Xi; Okuda, Tetsuo; Sakamaki, Kouichi; Akagi, Kazuo; **Various factors affecting the synthesis of highly conducting polyacetylene**. Synth. Metals; 65(2-3), 93-101, 1994.

- 58) Akagi, Kazuo; Shirakawa, Hideki; **Dependence of electrical conductivity on film thickness in polyacetylene - effects of mechanically forced parallel and in-plane alignments of fibrils.** Synth. Metals; 60(2), 85-92, 1993.
- 59) Hansen, George; **What we dreamt as children-how conductive polymers are bringing our dreams to reality.** J. Adv. Mater; 38(3), 68-74, 2006.
- 60) James Margolis, **Conductive Polymers and Plastics**, Chapman and Hall; P. 121, NY, USA, 1989.
- 61) James Margolis, **Conductive Polymers and Plastics**, Chapman and Hall; P. 120, NY, USA, 1989.
- 62) Lin, Y. C.; Zhong, Jue; **A review of the influencing factors on anisotropic conductive adhesives joining technology in electrical applications.** J. Mater. Sci; 43(9), 3072-3093, 2008.
- 63) Yim, Myung Jin; Li, Yi; Moon, Kyoung-sik; Paik, Kyung Wook; Wong, C. P; **Review of recent advances in electrically conductive adhesive materials and technologies in electronic packaging.** J. Adhesion Sci and Tech; 22(14), 1593-1630, 2008.
- 64) Lewis, H. J.; Coughlan, F. M; **An overview of the use of electrically conductive adhesives (ECAs) as a solder replacement.** J. Adhesion Sci and Tech; 22(8-9), 801-813, 2008.
- 65) Andrew Barlow, **Entone-OMI representative**, 1997.
- 66) Choudhary, R. B; **Lithographical utility of conducting polymers for information processing in molecular and micro-electronics industries.** Popular Plastics & Packaging; 53(10), 29-34, 36, 2008.

- 67) W. R. Salaneck D. T. Clark E. J. Samuelsen, **Science and Application of Conducting Polymers**, IOP Publishing Ltd; p135, Bristol, UK, 1991.
- 68) Luis Alcacer, **Conducting Polymers Special Applications**, D. Reidel Publishing Company; p192; Dordrecht, Holland/ Boston, USA, 1987.
- 69) James Margolis, **Conductive Polymers and Plastics**, Chapman and Hall; P. 33; NY, USA, 1989.
- 70) Huang, Yun-Hui; Goodenough, John B; **High-Rate LiFePO₄ Lithium Rechargeable Battery Promoted by Electrochemically Active Polymers**. Chem. of Mater.; 20(23), 7237-7241, 2008.
- 71) Zainudeen, U. L.; Careem, M. A.; Skaarup, S; **PEDOT and PPy conducting polymer bilayer and trilayer actuators**. Sensors and Actuators, B: Chem; B134 (2), 467-470, 2008.
- 72) W. R. Salaneck D. T. Clark E. J. Samuelsen, **Science and Application of Conducting Polymers**, IOP Publishing; p52, Bristol, UK, 1991.
- 73) M.G. Kanatzidis; **Conductive polymers**. Chem. Eng. News; 68, 36, 1990.
- 74) Roth, S.”**One-Dimensional Metals**” Weinheim VCH, 1995.
- 75) Nobel Symposium in Chemistry: **Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure**, W. R. Salaneck; I. Lundström and B. Rånby, Ed’s (Oxford Sci., Oxford, UK, 1993.
- 76) J.H. Burroughes; D.D.C. Bradley; A.R. Brown; R.N. Marks; K. Mackay; R.H. Friend; P.L. Burns and A.B. Holmes; **Light-emitting diodes based on conjugated polymers**. Nature; 347, 539, 1990.

- 77) R.H. Friend, R.W. Gymer, A. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Bredas, M. Lögdlund and W.R. Salaneck **Electroluminescence in conjugated polymers**. *Nature*; 397, 121, 1999.
- 78) Niu, Yuhua; **Electromagnetic interference shielding with polyaniline nanofibers composite coatings**. *Polym. Engg and Sci*, 48(2), 355-359, 2008.
- 79) Jing, Xinli; Wang, Yangyong; Zhang, Baiyu; **Electrical conductivity and electromagnetic interference shielding of polyaniline/polyacrylate composite coatings**. *J. App. Polym. Sci*; 98(5), 2149-2156, 2005.
- 80) Yoshioka, Yuka; Jabbour, Ghassan E; **Handbook of Conducting Polymers** (3rd Edition), 2 3/1-3/21, Taylor and Francis, NY, USA, 2007.
- 81) Nikolou, Maria; Malliaras, George G; **Applications of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) transistors in chemical and biological sensors**. *Chemical Record*; 8(1), 13-22, 2008.
- 82) Hoshino, Satoshi; Yoshida, Manabu; Uemura, Sei; Kodzasa, Takehito; Takada, Noriyuki; Kamata, Toshihide; Yase, Kiyoshi; **Influence of moisture on device characteristics of polythiophene-based field-effect transistors**. *J. App. Phy*, 95(9), 5088-5093, 2004.
- 83) Brady, S.; Lau, K. T.; Megill, W.; Wallace, G. G.; Diamond, D; **The Development and Characterisation of Conducting Polymeric-based Sensing Devices**. *Synth. Metals*; 154(1-3), 25-28, 2005.
- 84) Geetha, S.; Rao, Chepuri R. K.; Vijayan, M.; Trivedi, D. C; **Biosensing and drug delivery by polypyrrole**. *Analytica Chimica Acta*; 568(1-2), 119-125, 2006.

- 85) F. S. Kipping; J. Chem. Soc; **Organic derivatives of silicon. XXXII. The carbon-silicon binding.** 130, 104, 1927.
- 86) J. Montermoso, T. Andrews, L. Marinelli, **Polymers of tributyltin acrylate esters.** J. Polym. Sci., 32, 523, 1958.
- 87) D. Kochkin, V. Kotrelev, M. Shostakovskii, S. Kalinina, G. Kuenetsova, V. Borisenko, **Organotin polymers.** Vysokomolekul. Soeden; 1, 482, 1959.
- 88) C. Carraher, R. Damier, **Production of organometallic polymers by the interfacial technique. XII. Importance of hydrolysis in the interfacial synthesis of poly(tin esters).** J. Polym. Sci., A-1, 8, 3367, 1970.
- 89) T. Kealy and P. Pauson; **A new type of organo-iron compound.** Nature. 168, 1039, 1951.
- 90) F. A. Cotton and G. Wilkinson, **Advanced Inorganic Chemistry: A Comprehensive Text, Pt. 2. 4th Ed;** Wiley, NY, USA, 1988.
- 91) E. Neuse and H. Rosenberg, **Metallocene Polymers,** Dekker, NY, USA, 1979.
- 92) P. Wailes, R. Coutts, and H. Weigold, **Organometallic Chemistry of Titanium, Zirconium and Hafnium** Academic Press, NY, USA, 1974.
- 93) G. Wilkinson, F. Stone, and E. Abel, **Comprehensive Organometallic Chem.** Pergamon, Oxford, UK, 1982.
- 94) E. W. Neuse “**Metallocene Polymers**” in **Encyclopedia of Polym.Sci and Tech.,** Wiley-Interscience, NY, USA, Vol. 8; 1968.
- 95) A. Alaa Abd-El-Aziz, C. Carraher, C. Pittman, J. Sheats, and M. Zeldin, **Macromolecules Containing Metal and Metal-Like Elements, Vol. 2 Organoiron Polymers,** Wiley, Hoboken, NJ, USA, 2004.

- 96) F. S. Arimoto, A. Haven, **Derivatives of dicyclopentadienyliron**. J. Am. Chem. Soc; 77, 6295, 1955.
- 97) M. George, G. Hayes, **J. Polym. Sci. Chem. Ed**; 13, 1049, 1955.
- 98) C. U. Pittman, P. Grube, **Organometallic polymers. XIV. Copolymerization of vinylcyclopentadienyl manganese tricarbonyl and vinylferrocene with N-vinyl-2-pyrrolidone**. J. Polym. Sci; A1, 9, 3175, 1971.
- 99) P. Wailes, R. Coutts, and H. Weigold, **Organometallic Chem. Titanium, Zirconium, and Hafnium** Academic Press, NY, USA, 1974.
- 100) G. Wilkinson, F. Stone, and E. Abel, **Comprehensive Organometallic Chem.** Pergamon, Oxford, UK, 1982.
- 101) E. W. Neuse “**Metallocene Polymers**”, in **Encyclopedia of Polym. Sci and Tech**, Wiley-Interscience, NY, USA, Vol. 8, 1968.
- 102) A. Alaa Abd-El-Aziz, C. Carraher, C. Pittman, J. Sheats, and M. Zeldin, **Macromolecules Containing Metal and Metal-Like Elements, Vol. 2 Organoiron Polym.** Wiley, Hoboken, NJ, USA, 2004.
- 103) F. A. Cotton and G. Wilkinson, **Adv. Inorg. Chem**; Wiley, NY, USA, 1988.
- 104) C. Carraher, **Polym. Chem., 7th ed.** (Taylor and Francis, NY, 2008.
- 105) C. Carraher, **Synthesis of titanium polyesters**. J. Polym. Sci; A1, 9, 3661, 1971.
- 106) C. Carraher, **Production of organometallic polymers by the interfacial technique. XVI Importance of hydrolysis in the synthesis of poly[oxyadipoyloxy(diphenylsilylene)]**. Macromolecules, 4, 263, 1971.

- 107) C. Carraher, **Production of organometallic polymers by the interfacial technique. X. Influence of the nature of base employed on the synthesis of polysilylalkylene (arylene) diamines.** J. Polym. Sci; A1, 8, 3051, 1970.
- 108) C. Carraher, **Condensation metallocene polymers.** J. Inorg. Organ. Poly. Mater; 15, 121, 2005.
- 109) Carraher, Charles E., Jr.; Schroeder, Jack A.; Venable, Walter; McNeely, Christy; **Preliminary electrical measurements of selected organometallic polymers.** Organic Coatings and Plastics Chemistry; 38, 544-9, 1978.
- 110) Abd-El-Aziz, Alaa S.; Shipman, Patrick O, **Recent developments in organometallic polymers.** Frontiers in Transition Metal-Containing Polymers, 45-133, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2007.
- 111) Bekkali, Abd-El-Hakim; Thurzo, Ilja; Kampen, Thorsten U.; Zahn, Dietrich R. T. **Impedance spectroscopy study of metal-organic-metal structures.** App. Surf. Sci, 234(1-4), 149-154, 2004.
- 112) Cameron, Colin G.; Pittman, Timothy J.; Pickup, Peter G; **Electron Transport in Ru and Os Polybenzimidazole-Based Metallopolymers.** J. Phy. Chem. B; 105(37), 8838-8844, 2001.
- 113) de Souza, Solange; **Smart coating based on polyaniline acrylic blend for corrosion protection of different metals.** Surface and Coatings Tech; 201(16-17), 7574-7581, 2007.
- 114) Mu, Dan; Huang, Xu-Ri; Sun, Chia-Chung; **The adsorption of poly(vinyl alcohol) on the hydroxylated α -cristobalite.** Mol. Simulation, 34(6), 611-618, 2008.

- 115) Negri, R. Martin; Bernik, Delia L; **Critical revision of apparent dielectric constants calculations in lipid-water interfaces.** J. Colloid. and Interface Sci; 226(2), 364-366, 2000.
- 116) Kumazawa, H.; Kagimoto, T.; Kawabata, A; **Preparation of barium titanate ultrafine particles from amorphous titania by a hydrothermal method and specific dielectric constants of sintered disks of the prepared particles.** J. Mater. Sci; 31(10), 2599-2602, 1996.
- 117) Carraher, C; Linville, R; Manek, T; Blaxall, H; Taylor, R; Torre, L; **Cond. Polym;** R. Seymour, Ed., Plenum, NY, 1984.
- 118) Carraher, C; Nwufoh, V; Taylor, J. R; **Electrical properties of palladium polyamines with respect to the theory of whole chain resonance.** Polym. Mater. Sci. Eng; 60, 685, 1989.
- 119) M. V. N. V. D. Sharma; A. V. Sarma; R. Balaji Rao; **Electrical characterization and relaxation behavior of lithium-indium-phosphate glasses via impedance spectroscopy.** Turk J Phys; 33, 87 – 100, 2009.
- 120) A. K. Arof; S. R. Majid; **Electrical studies on chitosan based proton conductors and application in capacitors.** Mol. Cryst. Liq. Cryst., Vol. 484, pp. 107/[473]–116/[482], 2008.
- 121) L.C. Costa; C.P.L. Rubinger; C.R. Martins; **Dielectric and morphological properties of PANi-DBSA blended with polystyrene sulfonic acid.** Synth. Metals; 157, 945–950, 2007.

- 122) M. Marzantowicz; J.R. Dygas; F. Krok; Z. Florjan'czyk; E. Zygadło-Monikowska; **Conductivity and dielectric properties of polymer electrolytes PEO:LiN(CF₃SO₂)₂ near glass transition.** J. Non-Crystalline Solids; 353, 4467–4473, 2007.
- 123) Yinghong Xiao; Chang Ming Li; Shucong Yu; Qin Zhoua; Vee. S. Lee; Shabbir. M. Moochhala; **Synthesis and characterization of p-toluenesulfonate incorporated poly(3,4-ethylenedioxythiophene).** Talanta; 72, 532–538, 2007.
- 124) B. Normanda; H. Takenouti; M. Keddama; H. Liao; G. Monteil; C. Coddet; **Electrochemical impedance spectroscopy and dielectric properties of polymer: application to PEEK thermally sprayed coating.** Electrochim. Acta; 49, 2981–2986, 2004.
- 125) Runqing Ou; Rosario A. Gerhardt; Robert J. Samuels; **Structure and electrical properties of undoped oriented poly(phenylene vinylene) films.** J. Polym. Sci: Part B: Polym. Phys., Vol. 42, 98–116, 2004.
- 126) L.Valentinia; I. Armentanoa; J. Biagiottia; E. Frulloni; J. M. Kenny; S. Santucci; **Frequency dependent electrical transport between conjugated polymer and single-walled carbon nanotubes.** Diamond and Related Mater; 12, 1601–1609, 2003.
- 127) Christoph Jonda; Andrea B. R. Mayer; **Investigation of the Electronic Properties of Organic Light-Emitting Devices by Impedance Spectroscopy.** Chem. Mater; 11, 2429-2435, 1999.
- 128) R. Schrebler; H. Gómez; R. Córdova; L.M. Gassa b; J.R. Vilche; **Study of the aniline oxidation process and characterization of Pani films by electrochemical impedance spectroscopy.** Synth. Metals, 93,187-192, 1998.

- 129) A. Srivastava, A. Garg, F. D. Morrison; **Impedance spectroscopy studies on polycrystalline BiFeO₃ thin films on Pt/Si substrates.** J. Appl. Phys. 105, 054103, 2009.
- 130) Barford, W: **Electronic and Optical Properties of Conjugated Polym.**, Oxford University, Ithaca, NY, 2009.
- 131) Inzelt, G: **Conducting Polymers**, Springer, NY, 2008.
- 132) Rockett, A : **The Mater. Sci. of Semicond.**, Springer, NY, 2008.
- 133) Barford, W: **Electronic Properties of Conjugated Polymers**, Oxford University Press, Oxford, UK, 2005.
- 134) Blythe, T., Bloor, D: **Electrical Prop. of Polym.**, Cambridge University Press, Cambridge, UK, 2005.
- 135) Hadziioannou, G., Malliaras, G. G: **Semicond. Polym.: Chem, Phy and Engg**, Wiley, Hoboken, 2007.
- 136) T. Kealy and P. Pauson; **A new type of organo-iron compound.** Nature; 168, 1039, 1951.
- 137) S. A. Miller; J. Tebboth and J. Tremaine; **Dicyclopentadienyliron.** J. Chem. Soc; 632, 1952.
- 138) F. A. Cotton and G. Wilkinson; **Adv. Inorg. Chem**; Wiley, NY, 1988.
- 139) E. Neuse and H. Rosenberg; **Metallocene Polym.**; Dekker, NY, 1979.
- 140) P. Wailes; R. Coutts and H. Weigold; **Organometallic Chem. of Titanium, Zirconium and Hafnium** Academic Press; NY, 1974.
- 141) G. Wilkinson; F. Stone and E. Abel; **Comprehensive Organometallic Chem**; Pergamon, Oxford, 1982.

- 142) E. W. Neuse **“Metallocene Polymers”** in **Encyclopedia of Polym Sci and Tech**; Wiley-Interscience, Vol. 8, NY, 1968.
- 143) A. Alaa Abd-El-Aziz; C. Carraher; C. Pittman; J. Sheats and M. Zeldin; **Macromolecules Containing Metal and Metal-Like Elements; Vol. 2; Organoiron Polym**; Wiley, Hoboken, 2004.
- 144) F. A. Cotton and G. Wilkinson; **Adv. Inorg. Chem**; Wiley, NY, 1988.
- 145) P. W. Morgan; **Condensation Polymers by Interfacial and Solution Methods**; Interscience, NY, 1965.
- 146) C. Carraher and S. Bajah; **Effects of base nature, base concentration and method of synthesis on titanium polyethers**. Br. Polym; J. 7, 155, 1975.
- 147) C. Carraher and S. Bajah; **Synthesis of titanium polyethers by the interfacial and aqueous solution techniques**. Polymer (Br.); 14, 42, 1973.
- 148) C. Carraher and S. Bajah; **Tentative identification of reactive species in the interfacial and aqueous solution synthesis of titanium polymers**. Polymer (Br.); 15, 9, 1974.
- 149) Carraher, Charles E., Jr.; Peterson, George F.; Sheats, John E. **Synthesis of tin poly(cobalticinium esters)**. Org. Coat. and Plast. Chem; 33(2), 427-32, 1973.
- 150) C. Carraher and L. Reckleben; Polym. Modification; **Synthesis and structural characterization of titanocene-containing polyethers based on reaction with ethylene oxide-containing diols, including poly(ethylene glycol)**. Plenum, NY, p. 171, 1997.
- 151) C. Carraher and L. Reckleben; **Synthesis of metal-containing polymers utilizing hydroxyl-capped poly(ethylene oxides)**. Polym. Mater. Sci. Eng; 75, 184, 1996.

- 152) C. Carraher and L. Reckleben; **Synthesis and structural characterization of titanocene-containing polyethers based on hydroxyl-capped poly(ethylene oxides).** Polym. Mater. Sci. Eng; 69, 314, 1993.
- 153) C. Carraher and G. Burrish; **Synthesis and initial thermal characterization of titanium polyferrocene ethers.** J. Macromol. Sci.-Chem; A10 (8), 1451, 1976.
- 154) M. Williams; C. Carraher; F. Medina and M. Aloï; **Comparative Raman and infrared vibrational study of the polymer derived from titanocene dichloride and squaric acid.** Structure-Property Relations in Polymers; M. Urban and C. Craver; eds. Am. Chem. Soc; Washington, DC, p.769, 1993.
- 155) M. Williams and C. Carraher; **Inorg. and Metal-Containing Polym. Mater;** J. Sheats; C. Carraher; C. Pittman; M. Zeldin and B. Cutrell; eds, Plenum, NY, p.295, 1995.
- 156) M. Williams; C. Carraher; F. Medina and M. Aloï; **Synthesis and structural characterization of the condensation product of squaric acid and bis(cyclopentadienyl)titanium dichloride.** Polym. Mater. Sci. Eng; 61, 227, 1989.
- 157) M. Williams; C. Carraher; F. Medina and M. Aloï; **Raman and infrared spectroscopy of the polymer from squaric acid and titanocene dichloride.** Polym. Mater. Sci. Eng; 64, 6, 1991.
- 158) C. Carraher and L. Jambaya; Leonard M; **Reaction species in the aqueous solution and interfacial synthesis of zirconium polyethers.** J. Macromol. Sci.-Chem; A8 (7), 1249, 1974.
- 159) C. Carraher and L. Jambaya; Leonard M; **Initial synthesis and reactive species in low temperature condensations of dicyclopentadienylzirconium dichloride with diols.** Org. Coat. Plast. Chem; 34(2), 484, 1974.

- 160) C. Carraher and L. Jambaya; Leonard M; **Synthesis of zirconium polyethers.** Angew. Makromolekulare Chem; 39, 69, 1974.
- 161) C. Carraher and L. Jambaya; Leonard M; **Initial synthesis and thermal characterization of hafnium polyethers.** Angew. Makromolekular Chem; 52, 111, 1976.
- 162) C. Carraher; S. Bajah and L. Jambaya; **Crown Ethers and Phase Transfer Catalysis in Polymer Science;** L. Mathias; C. Carraher; eds, Plenum, NY, Chapt. 6, 1984.
- 163) Liu, Baijun; Hu, Wei; Chen, Chunhai; Wang, Guibin; Jiang, Zhenhua; Zhang, Wanjin; Wu, Zhongwen; **Novel fluorinated poly(aryl ether)s with low dielectric constants.** Polym. Preprints; 43(1), 448-449, 2002.
- 164) Chou, Shen; Lee, Ker-Sen; **A study of polyamide-imide resin/copper foil composite materials.** Polym. & Polym. Comp; 11(1), 57-67, 2003.
- 165) Carraher, Charles E., Jr; **Synthesis of titanium polyesters.** J. Polym. Sci, Part A-1: Polym. Chem; 9(12), 3661-70, 1971.
- 166) C. Carraher and J. Lee, **Tentative identification of reactive species in the synthesis of titanium polyesters.** Coat. Plastics; 34(2), 478, 1974.
- 167) C. Carraher and J. Sheats; **Synthesis, solution properties, and thermal characterization of titanium poly(cobalticinium esters).** Org. Coat. Plast. Chem; 33(1), 634, 1973.
- 168) C. Carraher and J. Lee, **Tentative identification of the reactive species in the reaction of dichlorobis(cyclopentadienyl)titanium with salts of diacids.** J. Macromol. Sci.-Chem; A9, 191, 1975.

- 169) C. Carraher; J. Sheats; **Synthesis of organometallic polymers by the interfacial technique. XXVI. Synthesis of poly[bis(oxycarbonylcyclopentadienyl)cobalt(III) (dicyclopentadienyltitanium(IV)) hexafluorophosphate].** Makromol. Chemie; 166, 23, 1973.
- 170) C. Carraher; **Synthesis of zirconium polyesters.** Europ. Polym. J. 8, 215, 1972.
- 171) C. Carraher; **Synthesis and thermal analysis of hafnium polyesters.** Angew. Makromolekular Chem; 28, 145, 1973.
- 172) Carraher, Charles E., Jr.. **Fiber forming and thermal properties of polyesters of group IV metals.** Chemical Technology; 2(12), 741-4, 1972.
- 173) Carraher, Charles E.; Reese, Charlene Deremo. **Solution synthesis and thermal characterization of lead(IV) polyesters.** Angew. Makromol. Chemie; 65, 95-102, 1977.
- 174) C. Carraher and J. Reimer; **Production of organometallic polymers by the interfacial technique. XXVII. Reaction variables in the synthesis of poly[oxy(dicyclopentadienylzirconium)oxycarbonylferrocenylcarbonyl].** J. Polym. Sci; Polym. Chem; Ed.10, 3367, 1972.
- 175) C. Carraher and J. Reimer; **Production of organometallic polymers by the interfacial technique. 24. Kinetics of polycondensation and thermal properties of poly[oxy(dicyclopentadienylzirconium)oxycarbonylferrocenylcarbonyl].** Polymer (Br.); 13, 153, 1972.
- 176) J. Sheats; C. Carraher; D. Bruyer and M. Cole; **Synthesis properties and thermal characterization of zirconocene poly(cobalticinium dicarboxylate).** Coat. Plast. Chem; 34(2), 474, 1974.

- 177) R. Benkeser; D. Goggin and G. Schroll; **A route to monosubstituted ferrocene compounds.** J. Amer. Chem. Soc; 76, 4025, 1954.
- 178) C. Carraher and R. Nordin; **Reaction variables in the aqueous solution synthesis of titanium poly(thio ethers).** Makromol. Chem; 164, 87, 1973.
- 179) C. Carraher and R. Nordin; **Synthesis of titanium polythioethers.** J. Polym. Sci; A-1. 10, 521, 1972.
- 180) C. Carraher and R. Nordin; **Synthesis of oligomeric zirconium polythioethers.** J. Appl. Polym. Sci; 18, 53, 1974.
- 181) C. Carraher; Polymer; **Synthesis and thermal characterization of hafnium polythioethers.** 17, 231, 1976.
- 182) C. Carraher; **Comparative synthesis and thermal stability of titanium, zirconium, and hafnium polythioethers.** Org. Coat. Plast. Chem; 33(1), 629, 1973.
- 183) C. Carraher and R. Nordin; **Comparative thermal stability and synthesis of Group IVB polythioethers.** J. Macromol. Sci.-Chem; A15 (1), 143, 1981.
- 184) Su, Yi-Che; Chen, Wan-Chun; Ou, Kai-Lin; Chang, Feng-Chih; **Study of the morphologies and dielectric constants of nanoporous materials derived from benzoxazine-terminated poly(ϵ -caprolactone)/polybenzoxazine co-polymers.** Polymer., 46(11), 3758-3766, 2005.
- 185) Blizzard, K. G.; Haghighat, R. R; **Processing and properties of polyimide melt blends containing a thermotropic liquid-crystalline polymer.** Polym. Engg and Sci, 33(13), 799-807, 1993.

- 186) C. Carraher; V. Foster; R. Linville; D. Stevison and R. Venkatachalam in **Adhesives, Sealants and Coatings for Space and Harsh Environments**, L.-H. Lee, eds, Plenum, NY, 1988.
- 187) C. Carraher; R. Schwarz; M. Schwarz and J. Schroeder, **Titanium polydyes derived from phenylsulfophthalein dyes, and Nigrosine, Eriochrome Black T and Indigo Carmine**. Org.Coat. Plast. Chem; 42, 23, 1980.
- 188) Carraher, Charles E., Jr.; Schwarz, Richard A.; Schroeder, Jack A.; Schwarz, Macy; Molloy, H. Michael. **Synthesis of titanium-xanthene polydyes as coatings and plastics additives**. Org. Coat. Plast. Chem; 43, 798-803, 1980.
- 189) C. Carraher and J. Kloss; **Synthesis of polydyes based on monoazo dyes and titanocene dichloride**. Polym. Mater. Sci. Eng; 64, 229, 1991.
- 190) C. Carraher; R. Schwarz; J. Schroeder and M. Schwarz; **Organotitanium polydyes derived from phenylsulfonphthalein dyes, and Congo Red, Eriochrome Black T, Nigrosine and Indigo Carmine-synthesis and doping characteristics**. J. Macromol. Sci. – Chem; A15 (5), 773; 1981.
- 191) C. Carraher; R. Schwarz; J. Schroeder and M. Schwarz; **Interfacial Synthesis; Vol. III, Recent Advances**; C. Carraher and J. Preston; eds, Dekker, NY, 1982.
- 192) C. Carraher; V. Foster; R. Linville and D. Stevison; **Characterization of metal-containing polydyes for severe environments**. Polym.Mater. Sci. Engg; 56, 401, 1987.
- 193) C. Carraher; A. Li; J. Kloss and A. Lombardo; **Structural characterization of monoazo-containing polydyes derived from titanocene dichloride using FT-NMR**. Polym.Mater. Sci. Engg; 70, 38, 1993.

- 194) C. Carraher; J. Kloss; F. Medina and A. Taylor; **Stability of films impregnated with Group IVB metallocene polydyes based on monoazo dyes to high-energy radiation.** Polym.Mater. Sci. Engg; 68, 253, 1993.
- 195) P. W. Morgan; **Condensation Polymers by Interfacial and Solution Methods;** Wiley, NY, Chapt. 3, 1965.
- 196) Carraher, Charles E., Jr.; Peterson, George F.; Sheats, John E. **Synthesis of tin poly(cobalticinium esters).** Org. Coat. Plast. Chem; 33(2), 427-32, 1973.
- 197) Carraher, C; **Organoantimony - containing polymers;** J. Polym. Mater; 24, 35, 2007.
- 198) C. Carraher, D. Winter, **Synthesis of organometallic polymers by the interfacial technique. XXVIII. Synthesis of oligomeric tin polyamines and polyhydrazides.** J. Macromol. Sci.-Chem., 7, 1349, 1973.
- 199) C. Carraher, D. Winter, **Production of organometallic polymers by the interfacial technique. XXI. Associated reaction variables in the synthesis of poly[imino-1,4-phenyleneimino(dibutylstannylene)].** Makromol. Chemie, 152, 55, 1972.
- 200) C. Carraher, D. Winter, D., **Production of organometallic polymers by the interfacial technique. XIX. Effect of leaving group in the synthesis of poly(stannylalkylenediamines).** Makromol. Chemie, 141, 259 and **Production of organometallic polymers by the interfacial technique. XIV. Synthesis of poly[stannylalkylene(arylene)diamines] and partial mechanistic study of their production.** 141, 237, 1971.
- 201) D. Mayo, F. Miller, R. Hannah, **Course Notes on the Interpretation of Infrared and Raman Spectra,** Wiley, Hoboken, NJ, 2004.

- 202) C. N. Rao, **Chemical Applications of Infrared Spectroscopy**, Academic Press, NY, 1963.
- 203) M. Tobin, **Rotational isomerism and the vibrational spectra of dibutyltin dichloride**. J. Molecular Spect., 5, 65, 1960.
- 204) T. Tanaka, **Vibrational spectra of organotin and organolead compounds**. Organomet. Chem. Revs., 5, 1, 1970.
- 205) L. Ronconi, C. Marzano, U. Russo, S. Sitran, R. Garziani, D. Fregona, **Organotin(IV) complexes of ethylsarcosine hydrochloride: synthesis, characterization and in vitro cytotoxic activity**. Appl. Organomet. Chem., 17, 9, 2003.
- 206) K. Nakanishi, P. Solomon, **Infrared Absorption Spectroscopy**, Holden-Day, NY, 1977.
- 207) G. Socrates, **Infrared Characteristic Group Frequencies**, Wiley, NY, 1980.
- 208) N. H. Ayachit; K. S. Rao; M. A. Shashidhar; **Infrared absorption spectra of some substituted pyrimidines**. Indian J. Pure Appl. Phy., 23, 225, 1985.
- 209) N. H. Ayachit; K. S. Rao; M. A. Shashidhar; **Infrared absorption spectra of some substituted pyrimidines**. Indian J. Pure Appl. Physics, 23, 225, 1985.
- 210) Matt Monroe; jjor.chem.unc.edu.
- 211) G. Barot; M. Roner; Y. Naoshima; K. Nagao; K. Shahi; C. Carraher; **Synthesis, Structural Characterization, and Preliminary Biological Characterization of Organotin Polyethers Derived from Hydroquinone and Substituted Hydroquinones**. J.Inorg.Org.Polym.Mater; 19, 12, 2009.

- 212) G. Barot; K. Shahi; M. Roner; C. Carraher; **Synthesis, anomalous fiber formation, and preliminary anticancer study of the organotin polyether derived from 2-butyne-1,4-diol.** J. Polym. Mater; 23, 423, 2006.
- 213) I. Omae, Organotin Chemistry, **J. Org. Chem. Library 21**, Elsevier, NY, 1989.
- 214) C. Carraher, M. Roner, K. Shahi, Y. Ashida, G. Barot, **Synthesis and Initial Cell Line Results of Organotin Polyethers Containing Diethylstilbestrol.** J. Inorg. Org. Polym. Mater., 18, 180, 2008.
- 215) C. Carraher, K. Morie, **Organotin Polyesters from 1,1'-Ferrocenedicarboxylic Acid.** J. Inorg. Org. Polym. Mater, 17, 127, 2007.
- 216) Chu, Hui-Juan; Zhu, Bao-Ku; Xu, You-Yi; **Polyimide foams with ultralow dielectric constants.** J.App. Polym. Sci; 102(2), 1734-1740, 2006.
- 217) Lin, Ching Hsuan; Chiang, Jung Chung; Wang, Chun Shan; **Low dielectric thermoset. I. Synthesis and properties of novel 2,6-dimethyl phenol-dicyclopentadiene epoxy.** J.App. Polym. Sci; 88(11), 2607-2613, 2003.
- 218) Lauchlan, L.; Woerner, T.; MacDiarmid, A. G.; Adar, Fran. **Raman microprobe analysis of pristine and iodine-doped polyacetylene films.** Microbeam Analysis, San Francisco, 17, 311-14, 1982.
- 219) Pron, A.; Bernier, P.; Rolland, M.; Lefrant, S.; Aldissi, M.; Rachdi, F.; Macdiarmid, A. G. **Thermal stability of highly conducting iodine derivatives of polyacetylene, (CH)_x.** Mater. Sci, 7(2-3), 305-12, 1981.
- 220) Bidez Paul R 3rd; Li Shuxi; Macdiarmid Alan G; Venancio Everaldo C; Wei Yen; Lelkes Peter I; **Polyaniline, an electroactive polymer, supports adhesion and proliferation of cardiac myoblasts.** J. Biomater. Sci; 17(1-2), 199-212, 2006.

- 221) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, Alan G; **Conducting polymers: halogen-doped polyacetylene.** J. Chem. Phys., 69(11), 5098-104, 1978.
- 222) Carraher, C.Jr.; Winter, Duane O; **Synthesis of organometallic polymers by the interfacial technique. XXVIII. Synthesis of oligomeric tin polyamines and polyhydrazides.** J. Macromol. Sci, Chem; 7(6), 1349-57, 1973.
- 223) Carraher, C. Jr.; Winter, Duane O. **Production of organometallic polymers by the interfacial technique. XIV. Synthesis of poly[stannylalkylene(arylene)diamines] and partial mechanistic study of their production.** Makromol. Chem; 141, 237-44, 1971.
- 224) Carraher, C. Jr; **Production of organometallic polymers by the interfacial technique. X. Influence of the nature of base employed on the synthesis of polysilylalkylene (arylene) diamines.** J. Polym. Sci, Part A-1: Polym. Chem; 8(11), 3051-9, 1970.
- 225) Zhou, Wei-Min; Tomita, Ikuyoshi; **Synthesis and Properties of Stannole-Containing Polymers by Reaction of Bis(cyclopentadienyl)titanacyclopentadiene-Containing Polymers and Tin(IV) Chloride.** J. Inorg. Org. Polym.Mater; 19(1), 113-117, 2009.
- 226) C. Carraher, **Condensation metallocene polymers.** J. Inorg. Org. Polym.Mater; 15, 121, 2005.

- 227) C. Carraher; D. Chamely; S. Carraher; G. Barot; H. Stewart; W. Learned; **Synthesis of group IVB metallocene polymers containing the plant growth hormone kinetin and their influence of on the seed germination of old and damaged food crop seed.** J. Polym. Mater; 24(2), 149-162, 2007.
- 228) M. Williams; C. Carraher; F. Medina; M. Aloï; **Comparative infrared and Raman spectroscopy of the condensation product of squaric acid and bis(cyclopentadienyl)titanium dichloride.** Inorg. and Metal-containing Poly.Mater; J. Sheats; Plenum Press; NY, 295-318, 1990.
- 229) L.I. Wei; Chen Jun-Fang, **Growth of TiN films at low temperature.** Appl. Surf. Sci; 253, 7019-7023, 2007.
- 230) S. Sinha; A.K. Srivastava; C. Tripathi, O.P. Pandey; S. K. Sengupta; **Synthesis, spectroscopic, and antimicrobial studies of binuclear metallocene (M = Ti, Zr, or Hf) derivatives of bis(mercaptoazoles).** Bioinorg. Chem. and Applications; Hindawi Publishing Corp, 2007.
- 231) S. Sinha; A.K. Srivastava; S. K. Sengupta, O.P. Pandey; **Microwave assisted synthesis, spectroscopic and antibacterial studies of bis(cyclopentadienyl) hafnium(IV) derivatives with benzil bis(aryl hydrazones).** Trans. Met. Chem.; 33, 563-567, 2008.
- 232) P. Carrasco; M. Cortazar; E. Ochoteco; E. Calahorra; J. Pomposo; **Comparison of surface and bulk doping levels in chemical polypyrroles of low, medium and high conductivity.** Surf. Interfac. Anal; 39, 26, 2007.

- 233) J. Lei; Z. Cai; C. R. Martin; **Effect of reagent concentrations used to synthesize polypyrrole on the chemical characteristics and optical and electronic properties of the resulting polymer.** Synth. Met., 46, 53, 1992.
- 234) K. G. Neoh; E. T. Kang; K. L. Tan; **Limitations of the X-ray photoelectron spectroscopy technique in the study of electroactive polymers.** J. Phys. Chem.; B, 101, 726, 1997.
- 235) C. Carraher; Reckleben, Lisa; **Synthesis of metal-containing polymers utilizing hydroxyl-capped poly(ethylene oxides.** Polym. Mater. Sci and Engg; 75, 184-185, 1996.
- 236) Carsten Spanka; Paul Wentworth Jr.; Kim D. Janda; **Developing soluble polymers for high-throughput synthetic chemistry.** Combinatorial Chem. & High Throughput Screening, 5, 233-240, 2002.
- 237) Cuihua Xue; Singaravelu Velayudham; Steve Johnson; Ratul Saha; Adrian Smith; Wilbel Brewer; Pushpalatha Murthy; Susan T. Bagley; Haiying Liu; **Highly water-soluble, fluorescent, conjugated fluorene-based glycopolymers with poly(ethylene glycol)-tethered spacers for sensitive detection of Escherichia coli.** Chem. Eur. J; 15, 2289 – 2295, 2009.
- 238) Haiqiao Wang; Huanfang Wang; Aiqing Zhang; Fangdai Wen; Na Song; Xiaoyu Li; **Structure-phase morphology - Property relationship of a series of light-emitting alternating copolymers with distyrylbenzenes segments and oligo(ethylene oxide) spacers.** Acta Materialia; 56, 3327–3337, 2008.

- 239) Gregg Caldwell; Eberhard W. Neuse; Axel G. Perlwitz; **Water-soluble monoamineplatinum(II) complexes bound to polyaspartamide carriers by a poly(ethylene oxide) spacer.** J. Inorg. and Org. Polym., Vol. 7(2), 111-119, 1997.
- 240) Goto, Hiromasa; Akagi, Kazuo; Itoh, Kikuo; **Side-chain liquid crystalline polyacetylene derivative - synthesis, chemical doping, and magnetically forced alignment.** Transactions of the Materials Research Society of Japan; 24(3), 473-476, 1999.
- 241) Lee, Kang I.; Jopson, Harriet; **Electrically conductive ethylene-propylene-diene terpolymer/polyacetylene blends.** Makromol. Chem., Rapid Comm., 4(6), 375-8, 1983.
- 242) S. A. Miller, J. Tebboth and J. Tremaine, **Dicyclopentadienyliron.** J. Chem. Soc. 632, 1952.