RECHARGEABLE BATTERIES BASED ON SPECIFIC NONCONJUGATED CONDUCTIVE POLYMERS; ELECTRICAL, OPTICAL AND STRUCTURAL STUDIES

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RECHARGEABLE BATTERIES BASED ON SPECIFIC NONCONJUGATED CONDUCTIVE POLYMERS; ELECTRICAL, OPTICAL AND STRUCTURAL STUDIES

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THESIS ABSTRACT

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Rechargeable batteries based on specific nonconjugated conductive polymers have been studied and developed. Quadratic electro-optic effect and electron paramagnetic resonance characterization of a specific polymer was investigated. These studies provide further insight regarding the structure of nonconjugated conductive polymers leading to technological applications.

The nonconjugated conducing polymers like *cis*-1, 4 polyisoprene and poly(β-pinene) have applications as energy storage device such as rechargeable batteries. The capacity measurements and its recharge cycle were made to study the battery life and performance. Emphasis was placed on the performance of the battery and finding optimal combinations of electrodes and electrolytes.

The electron paramagnetic resonance measurements show generation of radicals (spin- ½) species upon doping of poly(β-pinene). The number of radicals formed increased linearly with dopant concentration.

The electrical conductivity and nonlinear optical properties of a novel nonconjugated polymer, poly(β-pinene) was studied at low temperature. The quadratic electro-optic measurement of poly(β-pinene) at a wavelength of 633nm was found to be more prominent and the modulation depth was found to increase when measured at low temperature. The low temperature also helped to preserve the sample for a longer time.

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CHAPTER 1

INTRODUCTION

Photonics technology involves photons and electrons to carryout various operations in data acquisition, signal processing and communication industries. Photonics provide greater flexibility and advantages over its counterpart electronics in the filed of communication. They provide larger bandwidth, faster response time and less noise from extraneous electromagnetic fields. Nonlinear-optics plays a vital role in today's world of optical communication and in general the whole of photonics industry. The fact that fiber optics plays an important role in today's communication and transmission systems speaks volumes about the potential of optics. Nonlinear optical polymeric materials and organic crystals have been recognized as the important components of the promising data processing and communication technologies in today's world. Materials with excellent nonlinear optical properties are significant to the growth of photonic and electro-optical devices, such as those used in networking, communications, and storage equipment.

Novel polymers are not just restricted for use in photonics systems but they also extend their use in optical sensors, supercapacitors, rechargeable batteries and many other applications. For many years it was understood that polymers need to have a conjugate backbone to be conductive. Later it was proved by *Thakur* in 1988 that it is not necessary to have a conjugate structure and showed that polymers with nonconjugated structure also becomes conductive when doped with iodine at room temperature [1, 2].

In Chapter 2, a host of conjugated and nonconjugated system of polymers that were tested for their conductive nature and their usefulness in the field of rechargeable batteries and electro-optics are described. An introduction and basic information on rechargeable batteries is provided which forms the basis for the development of rechargeable batteries with these nonconjugated systems of polymers. A review of nonlinear optical phenomena is studied and emphasis is made on Maxwell's equation which governs the field of optics and propagation of optical waves. The origin and effects of second and third order susceptibility in relation with the field of electro-optics is discussed. Various nonlinear optical materials, their properties and their contribution to electro-optics are also explained.

In Chapter 3 the objectives of the research and specific goals to be achieved are stated.

In Chapter 4, the *cis* 1, 4 polyisoprene based rechargeable battery is discussed. Emphasis is given on the improvement of its performance, method of sealing and finding the right combination of electrodes and electrolyte. In this chapter a comparison of the battery performance in three different types of electrolytes tested.

In Chapter 5, the origin and development of a new conjugated polymer poly(β-pinene) as a rechargeable battery is explained. Battery composition and the types of electrode and electrolytes used will be explained. A study on the battery characteristics and capacity rating is presented.

In Chapter 6, the origin of rechargeable batteries and their development is discussed. The emergence of polymer based rechargeable batteries and their comparison with the polymer batteries that have been tested here which have a nonconjugated backbone are explained.

In Chapter 7, the basis and the results of electron paramagnetic resonance (EPR) measurements of poly(β-pinene) for different doping levels is explained.

In Chapter 8, the temperature dependence on the quadratic electro-optics effect is explained. The variation in modulation depth with respect to temperature change is discussed.

Finally, in Chapter 9, a summary of the work done is given. To sum up in this research two nonconjugated conductive polymers have been tested for their capacity in rechargeable batteries. The polymer poly(β-pinene) has been used to perform EPR measurements to prove the presence of radical cation upon doping. And finally temperature dependence on the quadratic electro-optic effect is explained.

CHAPTER 2

BACKGROUND

Conductive polymers, known as organic semiconductors are a special class of materials which play an important role in modern day electronics and devices like energy storage equipment. These polymers also found to possess good optical property which was utilized in the study of nonlinear optics. Nonlinear optics is a field of study that explains the interactions between a material system and light, wherein the material system is a nonlinear medium, that is, certain properties defining the material system are not proportional to the properties defining the light radiation. These nonlinear effects are produced using the high intensities of lasers of wavelength extending from far-infrared to the ultraviolet. This chapter explains the electrical properties of the novel nonconjugated conductive polymers which make them suitable to be used as storage device such as rechargeable batteries and a host of optical phenomena given by nonlinear optics using organic crystal and novel nonconjugated conductive polymers.

2.1 CONDUCTIVE POLYMERS

Conductive polymers are polymers with special molecular structures that become electrically conductive upon doping with specific electron acceptors or donors. The conductivity increases by more than eight orders of magnitude upon doping. A charge transfer between the polymer and the dopant occur and holes or electrons are created depending on acceptor or donor doping. These holes or electrons lead to the enhancement of conductivity. The charge transfer possibility of the polymer leads to various optical, nonlinear optical photovoltaic and light emission characteristics.

2.2 CONJUGATED SYSTEM

A polymer molecule in which the adjacent carbon atoms are joined together by alternating single and double bond is called a conjugated polymer. These conjugated polymers are found to consist of σ-sigma and π-bonds. The single bonds are called the σ-sigma bonds and the double bonds contain σ-sigma and π-bonds. These π-bonds are found to be delocalized throughout the molecule and are weaker than the σ-sigma bonds.

The chemical properties and its behavior can be changed by doping. Polymers like polypyrrole are partially oxidized to p-doped material which could be used in energy storage device, electrochromic devices etc. The π-bonds are responsible for their conductivity nature since the π-bonds are delocalized over the entire molecule and the p_z orbital produces a π bonding orbital and π* antibonding orbital[3, 4]. The two orbitals of different energy level produce the valance and conduction band and the difference in the energy level between the two bands give rise to band gaps of 1.5-3 eV. Conjugated polymers like PPV, Poly (p-phenylenevinylene) have been reported for electrical and optical characteristics especially its third order optical nonlinearity [5, 6]**.** These conjugated systems of polymers were found to show fast response time and large optical nonlinearities which can be used in optical switching and optical signal processing. The polymers like polyacetylene and polydiacetylene show large third order nonlinear susceptibility χ^3 [7, 8].

2.3 NONCONJUGATED SYSTEM

Till 1988 it was believed that a polymer needs a conjugated structure to electrically conduct. It was then proved by Thakur in 1988 that, a nonconjugated polymer becomes conductive when doped with proper dopants [1, 2]. The conductive nature of these polymers is due to the intersite hoping of the charges when doped. The conductivity studies of such nonconjugated polymers were based on 1, 4- *cis polyisoprene* as a prototype. This nonconjugated polymer was subjected to various conductivity studies and spectroscopic studies such as optical absorption, FTIR, Raman and EPR (electron paramagnetic resonance). The doped structure and mechanism of conductivity was established and a wide range of application is expected based on nonconjugated conductive polymer. Recently nonconjugated conductive polymer was used to demonstrate its energy storage capacity as rechargeable batteries and super capacitors [1, 9-11]. With the advent of nonconjugated conducting polymers many new polymers with nonconjugated backbone like 1, 4 polybutadiene [1], polyalloocimine [12] and poly(β-pinene) were studied for its electrical and optical properties.

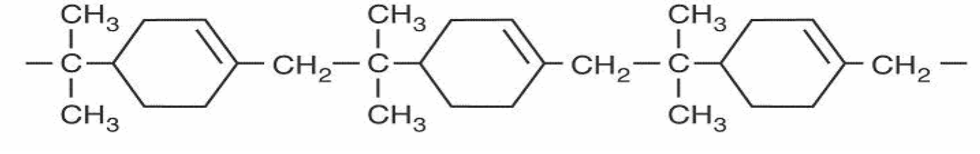

Figure 2.1 Molecular structure of undoped poly beta pinene

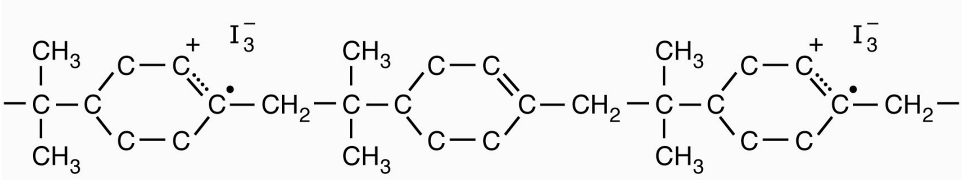

Figure 2.2 Radical cations formed upon doping and charge-transfer in poly(β-pinene)

2.4 RECHARGEBALE BATTERIES

Batteries that can be restored even after discharging completely are called rechargeable batteries. Initially the energy storing capacity of these rechargeable batteries was lower than the alkaline counterpart. The invention of Li-ion and Ni-MH brought in a new set of rechargeable batteries with almost the same energy storage capacity as that of the primary alkaline cell [13].

Ni-Cd batteries were first to be introduced in the market. These batteries had a better energy storing capacity and high performance compared to lead-acid batteries. These Ni-Cd batteries withstand high current surges and were robust to tolerate any adverse condition without any damage. The disadvantage in this being the negative electrode cadmium which is a toxic material caused problem in its disposal.

Ni-MH was developed as a replacement for Ni-Cd, which replaced the toxic negative electrode of Ni-Cd with hydrogen absorbing alloy negative electrode. The invention of hydrogen absorbing metals in 1970’s lead to the design of Ni-MH cell. The cell reaction is given by the following equation [14].

$$MH + 2NiOOH = Ni(OH)_2 + M + 1/2H_2 \qquad 2.30$$

These Ni-MH batteries were introduced in 1990's as a replacement for Ni-Cd cells in portable electronics and automated electric vehicle applications as a high performance rechargeable batteries [14]. These Ni-MH cells had a better energy storing capacity and current characteristics for the same size as of Ni-Cd batteries [14].

Lithium ion batteries are the most common rechargeable batteries found in the electronics recently. They have a low self-discharge, energy-to-weight ratio and no memory loss. The lithium based batteries are found to be lighter and small; also they are flexible to take any form to fill the space of the devices in which they are used. The life of the battery depends not just on the number of charging and recharging but also on the shelf life. These set of batteries should never be discharged below a predefined threshold to avoid damage and abnormal behavior from the battery.

2.5 CONDUCTIVE POLYMERS AS ENERGY STORAGE DEVICE

The polymers were found to be electrically conductive and posses energy storage capacity. These set of polymers fall under two broad classification one that follows the property of conductivity and the other which follows its electroactivity. The conductive polymers that follow the electroactivity property are utilized for preparing rechargeable light weight batteries and supercapacitors [15]. These rechargeable batteries and supercapacitors act as potential power sources of electric vehicles, mobile phones, laptops, pulsed light generators [16, 17] .

Some prototype models of rechargeable batteries were made using polyacetlyene, polypyrrole-lithium combination which were comparable with the commercially available rechargeable batteries in the industry like nickel cadmium (Ni-Cd) and nickel metal hydride (Ni-MH).These conducting polymers represent a unique set of synthetic metals due to high doping level and a fast electrochemical switching [18]. Conducting polymers that are electrically active like polyaniline(PAN), polypyyrole(PPy), poly-(3,4-ethylenedioxythiophene) (PEDOT) and others were tested to be used as supercapacitors [18].

Lithium polymer batteries are based on the same principles as of Li-ion batteries except that the electrolyte is not held in an organic solvent but by a polymer compound which is not flammable. The energy density of Li-polymer batteries is found to be higher than the Li-ion cell and other rechargeable batteries like Ni-Cd and Ni-MH. The battery has a charging voltage of 4.235 V, which should not be exceeded and care must be taken to remove the load as soon as the voltage drops below 3 V while discharging. These batteries have slightly higher internal resistance which restricts their high-rate capability but their rate of self discharge is found to be much less when compared with Ni-Cd and Ni-MH batteries [14]. The first of its kind was developed by *Bellcore*. They used PVdF-HPF, (poly (vinylidene fluoride)-hexafluoropropylene) polymer as the binder in the active materials and for the electrolyte of the battery.

The development in research has lead to invention of new rechargeable batteries using conjugated and nonconjugated conducting polymers as electrodes. These polymer materials are doped by specific dopant material to convert it to act as a semiconductor. These conjugated systems of polymers are also used along with lithium as one of the electrode in rechargeable batteries. Lithium based polymer rechargeable batteries use *polybithiophene*, a conjugated polymer as the cathode material. The polymer, *polybithiophene-hexafluorophosphate* was subjected to various conductivity and electrochemical impedance spectroscopy studies which proved that; it is a potential material for lithium based polymer batteries [19].

Similar studies and measurements were also reported by *Thakur et.al* on nonconjugated polymer cis-1,4-polyisoprene. This battery upon fabrication showed an open circuit voltage of 1.2 V and current of 2 mA . The current was found to drop and saturate at about 300-400 μA. The battery capacity was found to be around 25 mAh after recharging for about 5 minutes at 4 V by a DC voltage supply.

2.6 EPR MEASUREMENTS ON NONCONJUGATED POLYMER

Electrical conductivity, FTIR spectroscopy and electro-optic effect in a novel nonconjugated conductive polymer, *cis*-1,4-polyisoprene have been recently reported [11]. Electron Paramagnetic Resonance (EPR) spectroscopic measurements of *cis*-1,4-polyisoprene before and after iodine doping were studied and reported. The presence of cation radical species due to doping was confirmed by magnetic measurements and their concentration was found to increase with dopant concentration. The optical measurements showed peak at 3.3 eV attributed to the charge transfer between the localized states and a peak at 4.27 eV due to the excitation of cation radicals.

2.7 MAXWELL'S EQUATION

The field of optics and all the electromagnetic phenomena are being governed by the Maxwell's equations [20]. A set of four equations explaining the behavior of electric and magnetic fields and their interaction with matter can be represented by the Maxwell's equations.

$$\nabla . \mathbf{D} = \rho \qquad 2.1$$

$$\nabla .\mathbf{B} = 0 \qquad 2.2$$

$$\nabla \times \mathbf{E} = -\frac{\partial B}{\partial t} \qquad 2.3$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \qquad 2.4$$

The above equations explaining the relation between electric field strength **E**, magnetic field strength **H**, electrical displacement **D** and magnetic displacement **B** are the differential form of Gauss's law, Gauss' law of magnetism (absence of magnetic monopoles), Faraday's law and Amphere's law in that order. In dielectric the electric charge **ρ** and current density **J** can be considered as zero as there is no free charge and no current flows.

2.8 ISOTROPIC MEDIUM

A medium in which the characteristics of the light wave remain unaltered irrespective of the direction of its propagation is called Isotropic medium. In linear materials the relation for the polarization density **P** and magnetization density **M** is given by,

$$\mathbf{P} = \chi\varepsilon_o\mathbf{E} \qquad 2.5$$

$$\mathbf{M} = \chi_m\mathbf{H} \qquad 2.6$$

E and **H** are electric and magnetic field strength respectively. The relation between **E** and **D** is given as,

$$\mathbf{D} = \varepsilon_o\mathbf{E}+\mathbf{P} = \varepsilon_o\mathbf{E}+ \chi\varepsilon_o\mathbf{E} = (1+\chi)\varepsilon_o\mathbf{E} = \varepsilon\mathbf{E} \qquad 2.7$$

$$\varepsilon = (1+\chi)\, \varepsilon_o \qquad 2.8$$

where χ is the electrical susceptibility, χ_m is the magnetic susceptibility, ε_o is the permittivity of free space and ε is the dielectric constant of the medium. The polarization **P** field is proportional and parallel to the electric field **E** [21]**.**

The value $\sqrt{(1+\chi)}$ is called the relative permittivity of the medium and its relation with the refractive index ***n*** of magnetic media is given by,

$$n = \sqrt{(1+\chi)} \qquad 2.9$$

$$n = N+iK \qquad 2.10$$

where **N** is the real part of the refractive index which is refraction and **K** is the imaginary part describing absorption of light in dielectric medium. It is found that for a linear optical medium the refractive index ***n*** is independent of the electric field strength **E** [21].

In a isotropic medium the $\boldsymbol{\varepsilon}$ and $\boldsymbol{\mu}$ are time-independent scalars which reduces the Maxwell's equation to,

$$\nabla .\varepsilon\mathbf{E} = \rho \qquad 2.11$$

$$\nabla .\boldsymbol{\mu}\mathbf{H} = 0 \qquad 2.12$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{H}}{\partial t} \qquad 2.13$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \boldsymbol{\varepsilon}\frac{\partial \mathbf{D}}{\partial t} \qquad 2.14$$

2.9 NONLINEAR OPTICAL PHENOMENON

The emergence of nonlinear optical effects in material medium is due to its dependence on the polarization of electrons caused by the field associated with the propagating light wave. Each particle in the medium will be disturbed from its original position creating a dipole in the medium. The resulting dipole moment per unit volume is given as,

$$\mathrm{P} = \varepsilon_o\left(\chi^{(1)}\mathrm{E} + \chi^{(2)}\mathrm{E}^{(2)} + \chi^{(3)}\mathrm{E}^{(3)} + \ldots\right) \qquad 2.15$$

$$\mathrm{P} = \mathrm{P}^{(1)} + \mathrm{P}^{(2)} + \mathrm{P}^{(3)} + \ldots \qquad 2.16$$

where $\chi^{(1)}$ is the linear susceptibility while $\chi^{(2)}$ and $\chi^{(3)}$ are second and third order nonlinear optical susceptibilities. The induced dipole moments in the medium were found to react instantaneously to the applied electric field and hence the above expression for dielectric polarization **P** was expressed as a power series in electrical field **E** [21].

The equation for polarization can be divided into linear P^{L} and nonlinear P^{NL} terms as,

$$\mathrm{P} = \mathrm{P}^{\mathrm{L}} + \mathrm{P}^{\mathrm{NL}} \qquad 2.17$$

$$\mathrm{P}^{\mathrm{L}} = \varepsilon_o\chi^{(1)}\mathrm{E} \qquad 2.18$$

$$\mathrm{P}^{\mathrm{NL}} = \varepsilon_o\left(\chi^{(2)}\mathrm{E}^{(2)} + \chi^{(3)}\mathrm{E}^{(3)} + \ldots\right) \qquad 2.19$$

The optical wave equation for a nonlinear material medium is expressed as,

$$\nabla^2\mathrm{E} - \frac{n^2}{c^2}\frac{\partial^2\mathrm{E}}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2\mathrm{P}^{NL}}{\partial t^2} \qquad 2.20$$

The second and third order nonlinear optical susceptibilities give rise to many interesting phenomena like second-harmonic generation (frequency doubling), sum and difference frequency generation, third harmonic generation, phase matching, self-focusing and optical phase conjugation.

2.10 EFFECTS DUE TO SECOND $\chi^{(2)}$ AND THIRD $\chi^{(3)}$ ORDER SUSCEPTIBILITY

The combination of two angular frequencies ω_1, ω_2 of waves in a nonlinear medium gives rise to second order polarization $\varepsilon_o \chi^2 \mathrm{E}^2$, which includes the frequencies $|\omega_1 \pm \omega_2|, 2\omega_1, 2\omega_2$ and dc [22]. The electric field can be represented as

$$\mathrm{E}(t) = \mathrm{E}_1 e^{-i\omega_1 t} + \mathrm{E}_2 e^{-i\omega_2 t} + c.c \qquad 2.21$$

where *c.c* is complex conjugate.

For a second order process the nonlinear susceptibility tensor for sum-frequency generation is given by the relation

$$\mathrm{P}^{\omega_3}(t) = \varepsilon_o \overset{=}{\chi}^{(2)}(-\omega_3, \omega_1, \omega_2)\mathrm{E}^{\omega_1}(t)\mathrm{E}^{\omega_2}(t) \qquad 2.22$$

The sum frequency is $\omega_3 = \omega_1 + \omega_2$ which is represented by $\overset{=}{\chi}^{(2)}(-\omega_3, \omega_1, \omega_2)$. The various nonlinear processes due to $\chi^{(2)}$ are Second harmonic generation (SHG), Sum and Differential frequency mixing and Optical rectification.

Second harmonic generation (SHG) is a nonlinear process, in which new photons with twice the energy, and frequency and half the wavelength of the initial photons are formed due the interaction of the photons with the nonlinear medium.

$$\mathrm{P}(2\omega)=\frac{1}{2}\,\varepsilon_o\chi^{(2)}\mathrm{E}_1\mathrm{E}_2 \qquad 2.23$$

Sum frequency generation (SFG) is an example of a second order non-linear optical process, in which two beams of light of different frequencies ω1 and ω2 interact, creating light with frequency ω3 = ω1 + ω2.

$$\mathrm{P}(\omega_1+\omega_2)=\frac{1}{2}\,\varepsilon_o\chi^{(2)}\mathrm{E}_1\mathrm{E}_2 \qquad 2.24$$

When ω3 = ω1 - ω2 the above equation describes the differential frequency mixing given by

$$\mathrm{P}(\omega_1-\omega_2)=\frac{1}{2}\,\varepsilon_o\chi^{(2)}\mathrm{E}_1\mathrm{E}_2^* \qquad 2.25$$

Optical rectification, also known as differential frequency mixing effect occurs in media with large second order susceptibility.

$$\mathrm{P}(0)=\frac{1}{2}\,\varepsilon_o\chi^{(2)}\left(\mathrm{E}_1\mathrm{E}_2^*+\mathrm{E}_1^*\mathrm{E}_2\right) \qquad 2.26$$

The electro-optic effect is a change in the optical properties of a material in presence of a dc (or low frequency) electric field which depends linearly on the strength of the applied electric field is known as linear electro-optic effect or ***Pockels effect***.

The linear electro-optics effect can be expressed in terms of second order susceptibility as

$$\mathrm{P}^2(\omega) = \varepsilon_o \chi^{(2)}(-\omega, 0, \omega)\mathrm{E}^0\mathrm{E}^\omega \qquad 2.27$$

This effect is seen only in noncentrosymmetric materials, for a centrosymmetric material the $\chi^{(2)}$ effect vanishes.

In a similar manner when the frequency component of polarization was examined for the effect of χ^3, third order susceptibility the nonlinear optical process such as two photon absorption, quadratic **Kerr effect** and third harmonic generation were obtained.

The third order susceptibility contribution to the nonlinear polarization is given by [23]

$$\mathrm{P}^3(t) = \varepsilon_o \chi^{(3)}(\mathrm{E}(t))^3 = \sum_n P(\omega_n)e^{-i\omega_n t} \qquad 2.28$$

The **Kerr effect** or the **quadratic electro-optic effect** (**QEO effect**) is a change in the refractive index of a material in response to an electric field. It is different from the Pockels effect, in which the change in the refractive index of centrosymmetric material is directly proportional to the *square* of the electric field. For non-symmetric media this induced change of nonlinear susceptibility produces a change in refractive index in the direction of the electric field. The difference in refractive index, Δn, is given by

$$\Delta n = \lambda \mathrm{K}\mathrm{E}^2 \qquad 2.29$$

where λ is the wavelength of light and *K* is the *Kerr constant* for the medium. The applied field induces birefringence in the medium in the direction of the field. These effects are found to be prominent only when the optical intensity is very high.

2.11 NONLINEAR OPTICAL MATERIALS

Nonlinear optical (NLO) materials are found to be the backbone of nonlinear optics and have a great impact on many industrial applications. There has been an increased interest in the characterization and fabrication techniques of these nonlinear materials since its evolution. The introduction of high power laser systems added importance to explore these nonlinear materials as they had the required energy density to produce nonlinear effects. There are a wide range of nonlinear materials available typically with crystalline structures which are anisotropic compared to the incident light. These materials include wide range of organic crystals to semiconductors and thin film of polymers.

These studies were started from the inorganic materials like quartz, potassium dihydrogen phosphate (KDP), potassium dideuterium phosphate (DKDP), lithium niobate ($LiNbO_3$) which were widely used as second, third and fourth harmonic generators for Nd: YAG lasers. These crystals were capable of being grown in to any size by a solution growth method. High nonlinearities were found in semiconductors like gallium arsenide (GaAs) and these crystals were shown to be fabricated in periodically poled form for quasi-phase matching [24]. These inorganic materials had many inherent shortcomings like large dielectric constant, low electro-optic coefficient, and larger poling voltage. The technical advancement and advantages like design flexibility, low dielectric constant, thermal stability, low cost, etc., lead to the development of new organic crystals which made these materials more suitable for nonlinear optical applications compared to the inorganic materials [25].

The first organic material to be studied for its electro-optics effect was hexamethylenetetramine (HMT) and 2-methyl-4-Nitroaniline (MNA) [26]. This lead to the development of a host of organic materials with nonlinear optical properties. Following the growth of bulk single crystals, thin-film NLO materials found their way in many opto-electronic applications. The materials like potassium titanyl phosphate (KTP) and their derivatives were found to have wide working ranges of wavelength and temperature, high thermal and chemical stability and were readily available in crystalline form. These materials posses high nonlinearities and are found to be suitable for periodic poling.

It is important to consider certain properties of the nonlinear crystals before choosing them. They are,

- The available operating range of wavelength.
- The magnitude of nonlinear coefficients.
- Optical response time.
- Thermal and chemical stability.
- Ease of fabrication.

Materials with exceptional nonlinear qualities were found to be the backbone in the development of many photonic and electro-optical devices used in communication, networking and storage equipments.

From the available nonlinear materials DAST, 4-dimethylamino-N-methyl-4-stilbazolium-tosylate was found to exhibit high nonlinearity, high second-order nonlinear optical coefficient and was also suitable for high speed modulation [27]. Single crystal films of such nonlinear material had many interesting applications in photonics. Many techniques have been adopted to grow a thin film of this organic crystal DAST like melt shear or solution shear method and recently Thakur *et al* [28-30] proposed a method for the growth of single crystal thin-films of DAST by modified shear method which was used for Electro-optic, Electroabsortion and Fabry-Perot interferometry studies based on field induced birefringence method [31, 32].

Thakur *et.al* have reported previously the electro-optic modulator at 633 nm based on single crystal thin-film of DAST with a modulation depth of 20% on a $3\mu m$ thick film with a ac field of $1V/\mu m$ and a frequency of $4\ KHz$. The modulation depth at such low field was improved using a multi pass electro-optics modulator which uses a Fabry-Perot interferometry technique. The DAST sample was held between 2 parallel mirrors coated with aluminum, of which one mirror which contained the sample was fixed and the other aluminum coated mirror was free to move to control the cavity length between them. The entire setup was mounted on a motion control stage [33]. With such a setup the modulation depth was found to be as high as 80% for a low field of $0.5\ V/\mu m$ [33].

2.12 QUADRATIC ELECTRO-OPTIC EFFECT ON NONCONJUGATED CONDUCTIVE POLYMER

Nonconjugated conductive polymer gained its importance recently, due to the electrical and optical properties the polymer has when doped with proper dopant [1, 2, 10-12]. These set of polymers exhibit huge nonlinearities, especially high χ^3 effect. Recently the third order susceptibility or quadratic electro-optic effect of nonconjugated polymer *cis*-1,4-polyisoprene and poly(β-pinene) were reported [34]. These polymers showed a large quadratic electro-optic effect and this large magnitude was due to the loosely bound hole created at the isolated double bonds formed upon doping and charge-transfer. The other factor attributed to the huge quadratic effect was the confinement of charge in a small volume. A modulation of 0.8% for a field of 2.0 V/μm and 0.12% for a field of 1.25 V/μm was observed for *cis*-1, 4-polyisoprene and poly(β-pinene) respectively [34].

CHAPTER 3

OBJECTIVES

The objectives of this research are i) to study specific nonconjugated conducting polymers for use as electrodes in rechargeable batteries, ii) to study their internal structures after doping and iii) to measure quadratic electro-optic effect of a nonconjugated polymer at low temperature.

1. The polymer *cis*-1,4-polyisoprene will be studied in detail to determine the capacities of the rechargeable batteries made with the doped polymer used as electrodes. The other nonconjugated polymer, poly(β-pinene) will be used as the electrode in a rechargeable battery with similar configuration. The discharge capacity and their recharge cycle will be measured.
2. The presence of radical cations will be confirmed by the spectroscopic measurement, EPR(electron paramagnetic resonance). Samples of the nonconjugated conductive polymer, poly(β-pinene) will be prepared on a glass slide and doped with iodine for different doping levels. The molar concentrations will be calculated by measuring the weight uptake of iodine in the film. Then EPR measurements will be performed on the undoped and doped samples.

3. Quadratic electro-optic effect measurements on nonconjugated conductive polymer poly(β-pinene) will be made at low temperature. The measurements will be made using field induced birefringence at specific wavelengths.

CHAPTER 4

RECHARGEABLE BATTERY WITH POLYISOPRENE AS CATHODE MATERIAL

4.1 INTRODUCTION

A battery is a device which is used to convert the stored chemical energy to electrical energy. Rechargeable batteries are one of its types which can be re-charged by applying external power supply even after the battery is completely drained. The conception of using rechargeable battery started with the introduction of lead acid battery. Since the introduction of rechargeable battery, there has been constant research and development towards finding a suitable electrode material and electrolyte for better characteristics of current and voltage. Polymer rechargeable battery is the latest in the market which is found to be a substitiute for alkaline batteries. These are environmentally friendly, light weight, inexpensive for the same amount of capacity rating. Researchers have come up with many polymer based rechargeable battery with either one or both its electrode and the electrolyte as the polymer which has conjugated backbone. Besides conjugated conductive polymer, it was proven by *Mrinal Thakur* that the nonconjugated polymer like cis-1, 4-polyisoperene could be made conductive by doping with iodine at room temperature [1]. This conductive polymer was used to prove their energy storage capacity as rechargeable battery and supercapacitors [35]. This chapter studies in detail about the battery capacity and various combinations of electrode and their pros and cons.

4.2 EXPERIMENT

4.2.1 CHOICE OF ELECTRODES AND ELECTROLYTE

It was shown that *cis*-1, 4-polyisoperene becomes electrically conductive when doped with iodine [2]. The nonconjugated polymer was also used to demonstrate its potential as energy storage device in rechargeable batteries and supercapacitors [35]. In the present work this nonconjugated conductive polymer was used as the cathode material and the other electrode of the battery was chosen between Zinc and Steel with certain compromise over voltage and capacity rating. Three different combinations of electrolyte were tested. One is a solution of potassium iodide dissolved in water and the other two is a mixture of aqueous solution of potassium iodide and poly(vinyl alcohol), with a difference in the molecular weight of polyvinyl alcohol added to the potassium iodide solution.

4.2.1.1 CATHODE MATERIAL

The electrical conductivity was less than 10^{-13} S/cm for undoped polymer and its conductivity increased when doped with iodine. The conductivity of the doped film was in the range of 10^{-2} - 10^{-1} S/cm, which is an increase of 10 orders of magnitude in conductivity upon doping [1]. The electrical conductivity of *cis*-1, 4-polyisoperene as a function of molar concentration of iodine is shown in figure. The *cis*-1, 4-polyisoperene film can be made using latex or dissolving a dry film of natural rubber in toluene solution. In the first method a thin film of latex is allowed to dry which is then doped with iodine at room temperature to make it conductive. In the second method a dry film of latex or natural rubber is formed initially which is then dissolved in toluene. A thin film of about 5 to 6 microns thickness is formed on a glass slide which is then doped with iodine. The resistance of the film was in the range of 60-70 kilo ohms. The *cis*-1, 4-polyisoperene film formed out of doped natural rubber could be made in any dimensions. The bigger the area of the film better will be its performance as an electrode of the battery, since it has large contact space available. The capacity of the battery is found to increase with the size of the electrode.

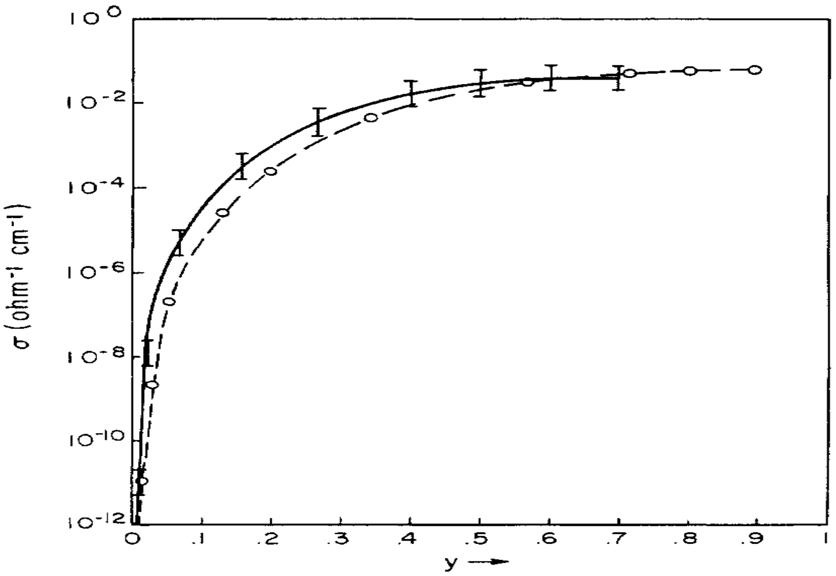

Figure 4.1 Electrical conductivities of doped cis-polyisoprene, trans-polyisoprene, and poly(dimethy1butadiene) as a function of molar concentration (y) of iodine. The data of cis- and trans-polyisoprene lie on the curve shown with the error bars. The other curve (dashed) corresponds to poly (dimethy1butadiene) [1].

4.2.1.2 ANODE MATERIALS

The other electrode was chosen between a thin strip of zinc and steel. The zinc was coated with latex to prevent it from corrosion when it reacts with electrolyte and iodine from the polymer electrode. The other anode material steel did not corrode when it reacts with electrolyte or the iodine. There is a difference in the electrode potentials of zinc and steel which shows up in the open circuit voltage available. The open circuit voltage is more for zinc-polymer combination compared to steel-polymer. In contrast the steel-polymer combination was found to show better current rating and capacity.

4.2.1.3 ELECTROLYTES

As mentioned before three different combinations of electrolyte were tested. The addition of poly(vinyl alcohol) makes the potassium iodide solution thicker and makes it like a gel. The resistance of the electrolyte depends on the type of solution formed. The potassium iodide solution by itself has the least resistance followed by the solution with PVA. The resistance of such an electrolyte depends on the ratio of PVA to KI present in the solution.

4.2.2 PACKAGING

Two different types of packaging were tried. The first method used a polyethylene pouch like bag similar to lithium polymer battery which holds the entire assembly of electrodes and electrolyte inside it. The electrolyte is sandwiched between the electrodes and the pouch is vacuum sealed. The packaging in a pouch helps to make a battery in any size and thickness needed according to the application. The second method uses a plastic box which can hold the glass slide which has the polymer film deposited on it. This type of packing is more compact and acts as better sealant to prevent water from evaporating. The traditional metallic cylinder packaging is avoided which reduces the weight and the cost involved.

4.2.3 CURRENT AND VOLTAGE RATING

The open circuit voltage and current ratings vary with the combinations of electrode used. For a *cis*-1, 4-polyisoperene-zinc combination the open circuit voltage was around 1.2V and current was about 4-5 mA. When the zinc is replaced by steel as anode material the open circuit voltage dropped down a bit to 0.75V and a current of around 2-3 mA. This rechargeable battery with zinc electrode when charged at 5V for about 5 minutes using a DC voltage supply current increases to 100-105 mA and the voltage is found to be around 1.9V. Some batteries were found to show about 2V when charged. Recharging helps to regain its charge completely every time after its complete discharge. When the steel electrode was used in place of zinc, for the same amount of recharge time and supply voltage it showed an open circuit voltage of 1.4V and the current rating depended on the size of the steel and electrolyte used.

4.2.4 MEASUREMENT

The current readings with time are recorded in real time for a set period directly by the computer. The multi-meter which reads the current value of the battery is interfaced with the computer so that the value read by the multi-meter is recorded in the computer. The multi-meter is interfaced with the computer using software which plots a graph of measured value with respect to the sample number or time.

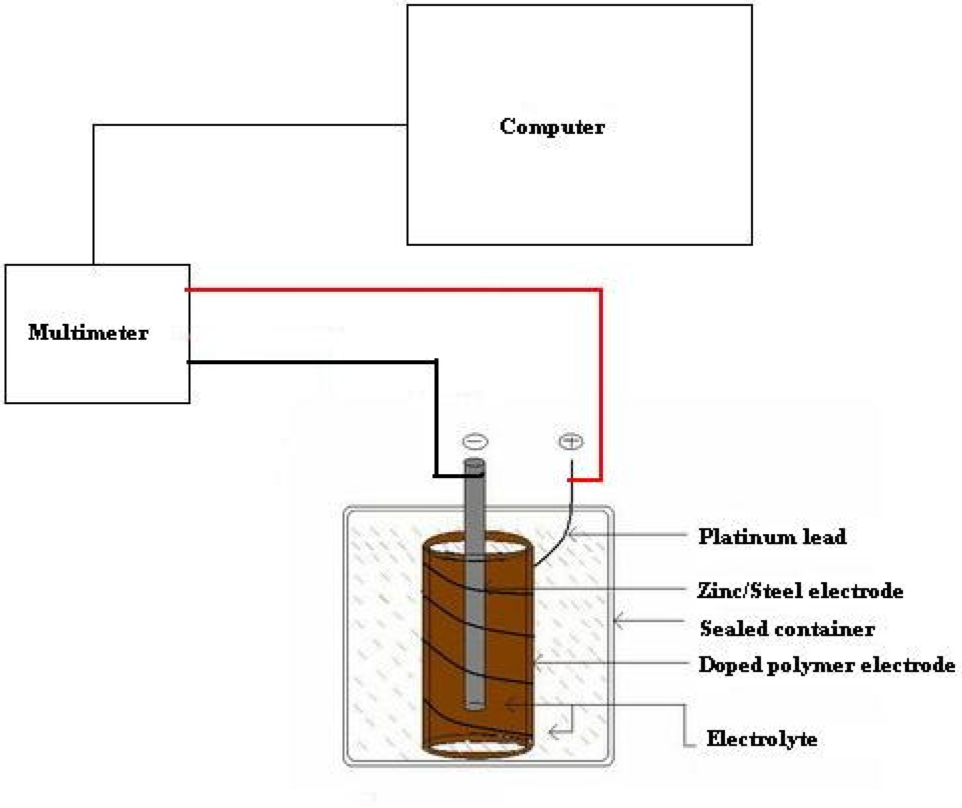

Figure 4.2 Schematic of the battery assembly and the measurement setup.

4.3 DISCUSSION

Graphs were plotted for current characteristics with time and capacity measurements were made. Capacity measurements were made to decide the ampere hour rating. It was found that a *cis*-1, 4-polyisoperene-zinc combination battery showed high capacity rating of about 45.33 mAh. A plot of current vs. time characteristics of the battery is shown in Figure 4.3 which gives the capacity rating. The polymer electrode used was made out of natural rubber for a dimension of 3 cm by 3 cm. A plot of two cycles of charge and discharge of a battery is shown in the Figure 4.4. The graph shows the response of current with respect to time over a period.

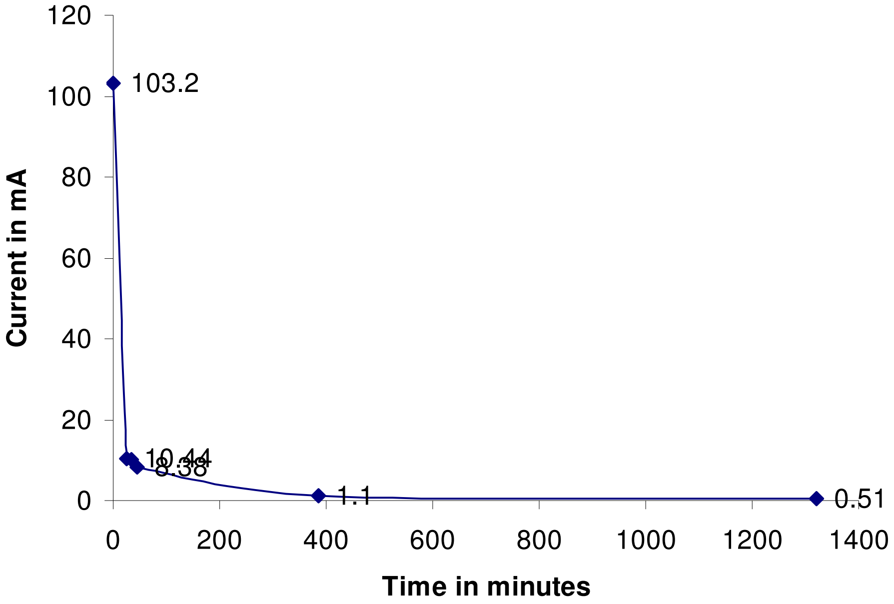

Figure 4.3 A plot showing the current vs. time characteristics of a polyisoprene battery

The batteries can be connected in series or parallel or as a combination of both. In a series connection the positive terminal of one battery is connected to negative terminal of the other. The series connection of batteries increases the voltage rating. A stack of 10 batteries each measuring 1.2 V was connected in series to measure 12 V. The Figure 4.5 shows 11.9 V which is close to 12 V that was expected.

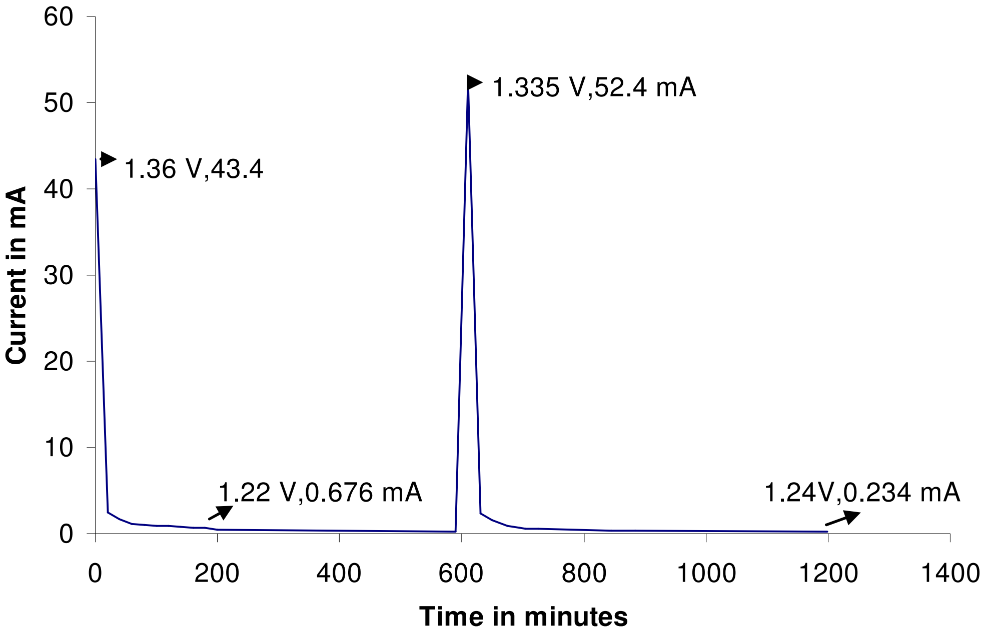

Figure 4.4 Graph showing 2 discharge cycles of current curve of the battery.

Figure 4.5 A stack of 10 batteries connected in series

The above graphs show the battery current characteristics with the use of zinc electrode. The zinc electrode was replaced by steel to compensate for the corrosion of zinc with time. The battery assembly with polymer-steel electrode combination was tested with the three different types of electrolytes. The polymer film was formed on a glass slide which was later doped to form the electrode. The current characteristic vs. time graph of the battery in three different electrolytes was plotted. The plot of current with time for a battery assembly with KI electrolyte is shown in Figure 4.6.

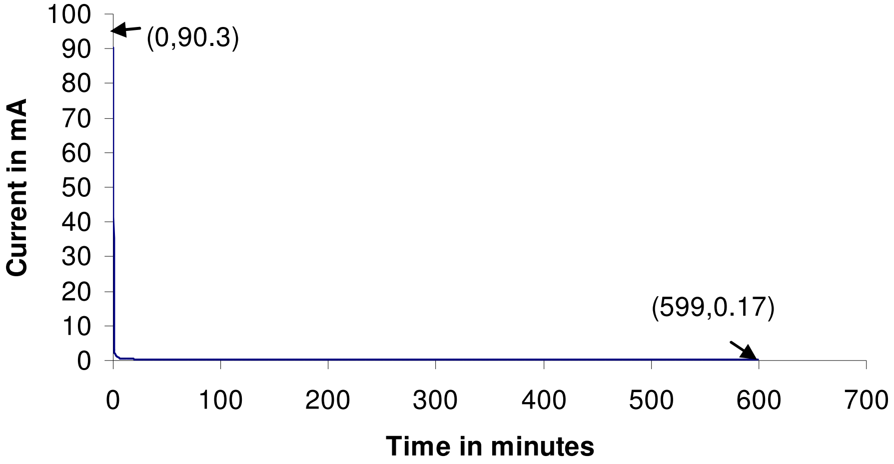

Figure 4.6 A plot showing the current characteristics vs. time of a polyisoprene battery with KI electrolyte.

The battery characteristic with time for a battery assembly with PVA in the electrolyte along with KI is given in Figure 4.7 and Figure 4.8. It could be seen that the current characteristics with time is not appreciable when compared to the battery assembly which used the polymer electrode made from latex. This explains the role of the polymer size in the battery capacity.

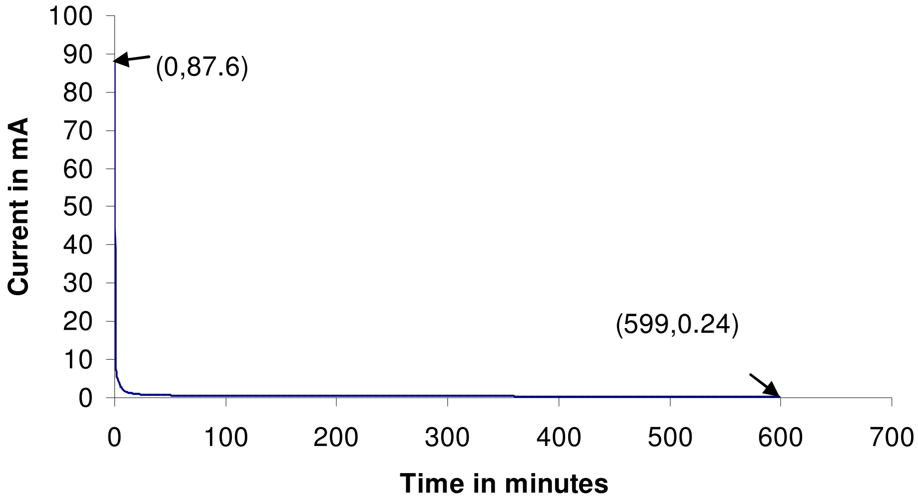

Figure 4.7 A plot showing current characteristics vs. time of a battery with (2PVA-5KI) ratio and mW of PVA >85,000.

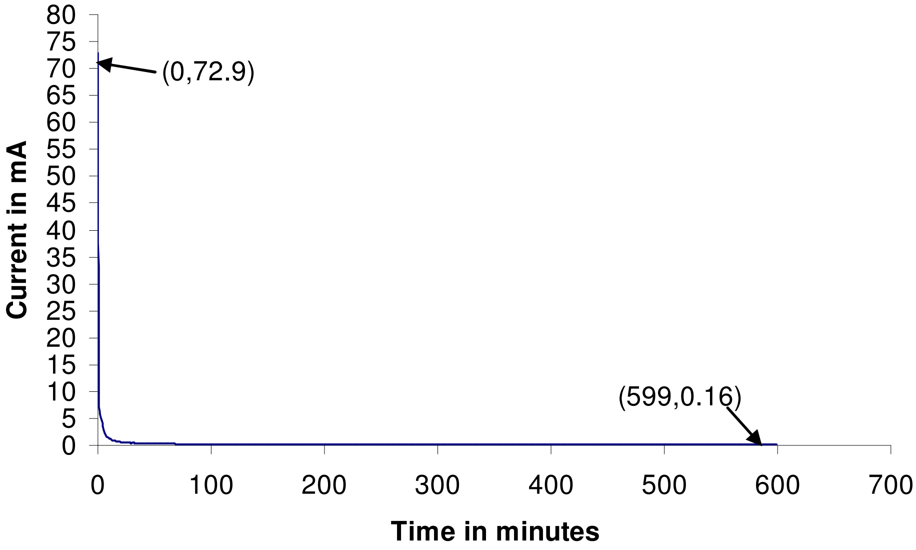

Figure 4.8 A plot showing current characteristics vs. time of a battery with (PVA-KI) ratio 1:1 and mW of PVA <10,000.

4.4 CONCLUSION

The polymer *cis*-1, 4-polyisoperene was used in the development of a rechargeable battery and studied for its capacity and characteristics in different types of electrolytes. Steel electrode was used as a replacement for zinc to avoid corrosion and reduction in the battery capacity with time. As the capacity was found to increase with the size of the polymer electrode, the electrode made out of the latex was found to be ideal.

CHAPTER 5

RECHARGEABLE BATTERY WITH POLY(β-PINENE) AS CATHODE MATERIAL

5.1 INTRODUCTION

Different combinations of electrode and electrolytes need to be tried to obtain the optimum configuration. As stated earlier specific polymers with nonconjugated backbones become electrically conductive when doped with iodine [1]. The first of its kind was *cis*-1, 4-polyisoperene followed by many others. Recently another nonconjugated polymer, poly (β-pinene) has been shown to become electrically conductive upon doping with iodine at room temperature. The conductivity of a doped poly(β-pinene) film was found to be 10 orders of magnitude greater than the undoped film with a maximum value of ~ 8 x 10^{-3} S/cm [36]. The conductivity is less than *cis*-1, 4-polyisoperene for the same amount of doping since the double bond number fraction of poly(β-pinene) is less than polyisoprene. Molecular structure and schematic of formation of radical cation upon doping of poly(β-pinene) is shown in Figure5.1 and Figure 5.2 respectively. The hole or the positive charge created upon doping and charge transfer is responsible for the electrical conductivity.

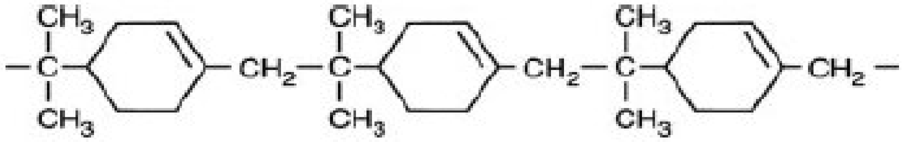

Figure5.1Molecular structure of undoped poly (β-pinene)

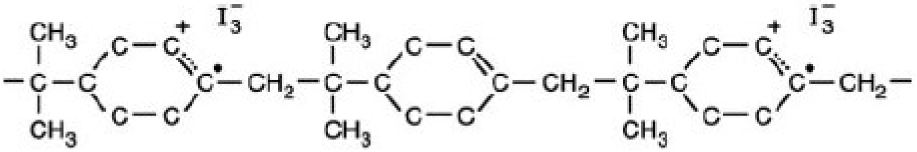

Figure 5.2 Schematic of radical cation formed upon doping with iodine

5.2 EXPERIMENT

5.2.1 CHOICE OF ELECTRODES AND ELECTROLYTE

It was shown that the electrical properties of doped *cis*-1, 4-polyisoperene could be used in demonstrating its purpose as a rechargeable battery in Chapter 4. The other nonconjugated polymer poly(β-pinene) which was also found to be conductive when doped with iodine was tried here to be used as an electrode in a rechargeable battery. This nonconjugated conductive polymer was used as the cathode material and the other electrode of the battery was chosen to be Steel with certain compromise over voltage and capacity rating which would be obtainable. The major reason for avoiding zinc as the anode was due to its corrosion problem when it reacts with electrolyte and iodine. This corrosion leads to gradual decrease of the battery capacity with time. The same set of three combinations of electrolyte was tested with this new battery assembly.

5.2.1.1 CATHODE MATERIAL

The electrical conductivity for an undoped polymer was less than 10^{-12} S/cm [36]. The conductivity of the doped film increased upon doping with iodine and saturated at a value of ~ 8 x 10^{-3} S/cm for a dopant molar concentration of 0.85 [36]. The electrical conductivity of poly(β-pinene) as a function of molar concentration of iodine is shown in Figure 5.3. The poly (*β* pinene) was dissolved in toluene and a thin film was deposited on a glass slide which was doped with iodine later. These film were thicker than *cis*-1, 4-polyisoperene films formed using the toluene solution and the resistance was also on the higher side, about 1-2 M-ohms for the same amount of doping as that of other polymer. The thicknesses of the films were in the range of 20-40 microns.

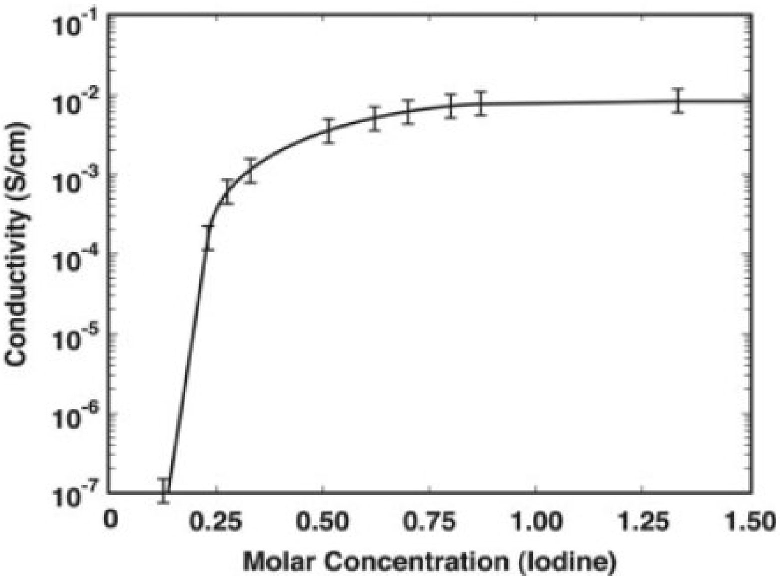

Figure 5.3 Electrical conductivity of poly(β-pinene) as a function of molar concentration of iodine [36].

5.2.1.2 ANODE MATERIAL

The other electrode of the battery was steel. Steel has less reaction to iodine than compared to zinc. There is a difference in the electrode potential of zinc and steel because of which there is a difference in the open circuit voltage available. The open circuit voltage for zinc-polymer combination was higher compared to battery which had steel-polymer combination of electrodes. But the steel-polymer combination of battery was found to show better current rating, capacity and stability.

5.2.1.3 ELECTROLYTE

The same three combinations of electrolyte were tested. The electrolyte made no difference in the performance of the battery due to the change in the polymer electrode. It had the same effect as with the polyisoprene. Based on the resistance of the electrolyte needed PVA was added in the KI solution. The KI solution by itself has the least resistance in the range of 3-5 kilo-ohm. The addition of poly vinyl alcohol makes the potassium iodide solution thicker and makes it like a gel. The resistance of the electrolyte depends on the type of solution formed.

5.2.2 PACKAGING

Since the poly(β-pinene) cannot be formed as a free standing film, the film was deposited on a glass slide. Two of these slides were used in the battery assembly. These slides were placed in a slide holder facing each other. The slide holder is a plastic box which is compact to hold the glass slides with a grove for holding.

5.2.3 CURRENT AND VOLTAGE RATING

The open circuit voltage and current ratings vary with the size of electrodes used. For a poly (β pinene)-steel electrode combination the open circuit voltage was around 0.75V and current was around 2-3 mA. This setup was charged for the same amount of time and DC supply voltage as that other battery with polysioprene electrode. After charging the peak voltage and current measured depends on the size of the electrodes used. Since the size of the polymer electrode is restricted by the size of the glass slide available the voltage and current rating depends on the size of the steel electrode used. The voltage and current rating was found to increase with the size of the steel used. Accordingly the peak voltage was in the range of 1.4-1.6 V and the peak current was in the range of 45-250 mA. The increase in the peak current and discharge also depends on the type of electrolyte used.

5.2.4 MEASUREMENT

The current and voltage of the battery was measured as before. The battery terminals were connected to the multi-meter through a probe which is then interfaced with the computer to record real time values of the measured quantity. The schematic of the battery assembly together with the multi-meter and computer is shown in Figure 4.2 of Chapter 4.

5.3 DISCUSSION

A plot of current vs. time was plotted for different type of electrolyte used. Capacity measurements were made from the current vs. time plot to decide the ampere hour rating. Graphs were also plotted for three recharge cycle for all the electrolytes used in the battery assembly to show the regaining capability of the system. A plot showing the current vs. time characteristics is shown in Figure 5.4 for a system of polymer-steel electrode combination with KI electrolyte.

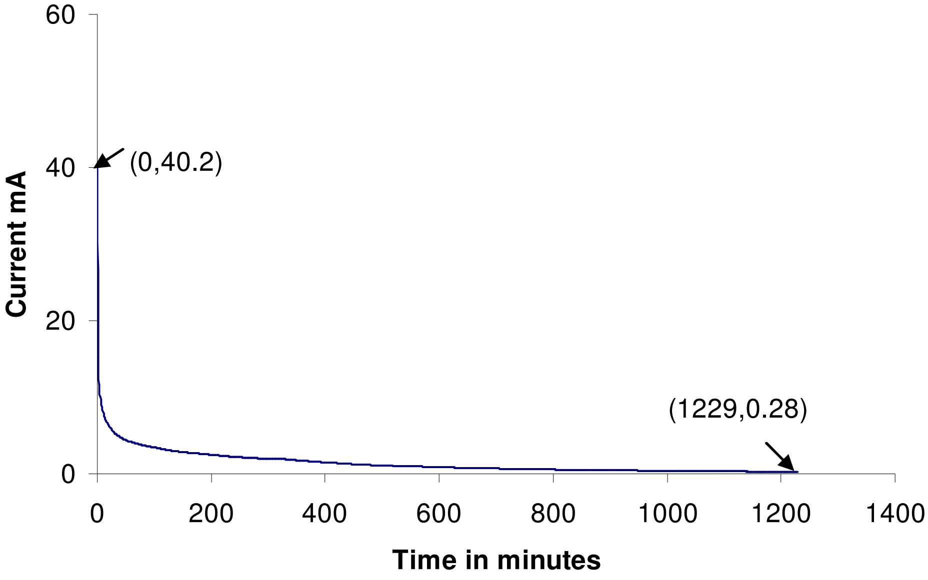

Figure 5.4 A plot showing the current vs. time characteristics for a KI electrolyte setup.

The capacity of the battery with an electrolyte solution of KI was about 33.33 mAh. It measured a peak current of 40.2 mA and an open circuit voltage of 1.3 V. The measurement was done for about 20 hrs after which the open circuit voltage and current were 0.72 V and 0.28 mA respectively. Initially the capacity of this battery with KI electrolyte was found to be greater than the other two batteries with an electrolyte of KI and PVA solution. The plot showing three recharge cycle of the battery is shown in Figure 5.5 which shows the repeatability.

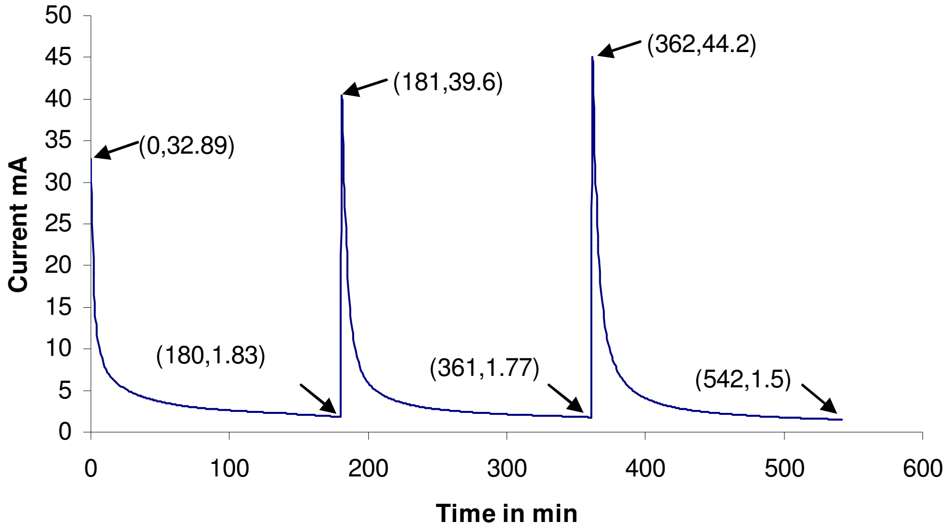

Figure 5.5 A plot showing 3 recharge cycles of a battery with KI electrolyte.

For few recharge cycles the capacity rating of the battery with PVA in electrolyte was not comparable with that of KI electrolyte battery. The capacity rating of the battery with KI electrolyte was found to decrease due to evaporation of water with time and continuous charge and discharge. There was a difference in molecular weight of the PVA added to the KI solution. A plot showing the current characteristics with time for a battery with PVA in electrolyte in ratio 2:5 to KI is shown in Figure 5.6 .The molecular weight of the PVA added to the KI solution was about 85,000. The peak value of current and voltage was found to be 244.3 mA and 1.4 V. After 25 hrs of discharge the current and voltage ratings were 0.15 mA and 0.75 V respectively. Another plot showing 3 cycles of recharge is shown in Figure 5.7 which proves its repeatability.

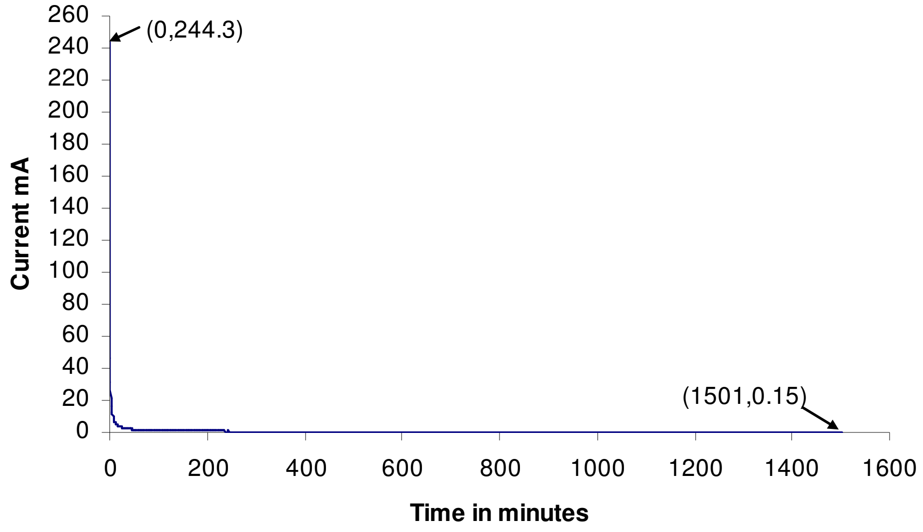

Figure 5.6 A plot showing current vs. time characteristics of a battery with (2PVA-5KI) ratio and mW of PVA >85,000.

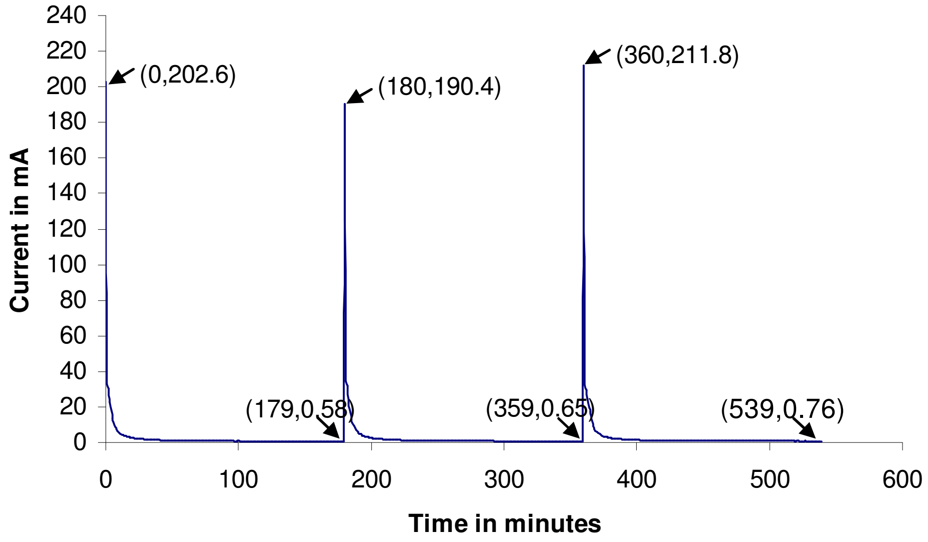

Figure 5.7 A plot showing 3 recharge cycles of a battery with (2PVA-5KI) in electrolyte and mW of PVA >85,000.

A plot of current vs. time characteristics of a battery with PVA in electrolyte in the ratio of 1:1 to KI in the solution in shown in Figure 5.8. The molecular weight of

PVA added was less than 10,000. The electrolyte so formed was viscous in nature unlike the other electrolyte solution which had PVA that forms a gel. There wasn't any significant change in battery capacity between these two electrolytes that had PVA, except for a large peak current noticeable in case of electrolyte that had PVA in ratio of 2:5 to KI. There was no change in the open circuit voltage measured.

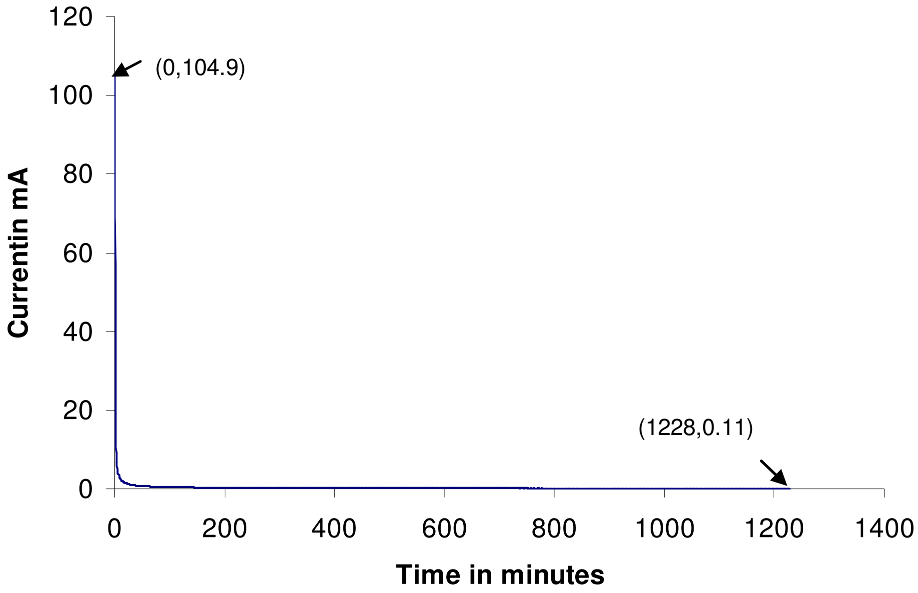

Figure 5.8 A plot showing current characteristics vs. time of a battery with (PVA-KI) ratio 1:1 and mW of PVA <10,000.

The Figure 5.9 shows the recharge cycle of a poly(β-pinene) battery with an electrolyte combination of KI and PVA with molecular weight of PVA< 10,000. The recharge cycle of the battery with the other electrolyte combination was better in terms of current stability and in its repeatability.

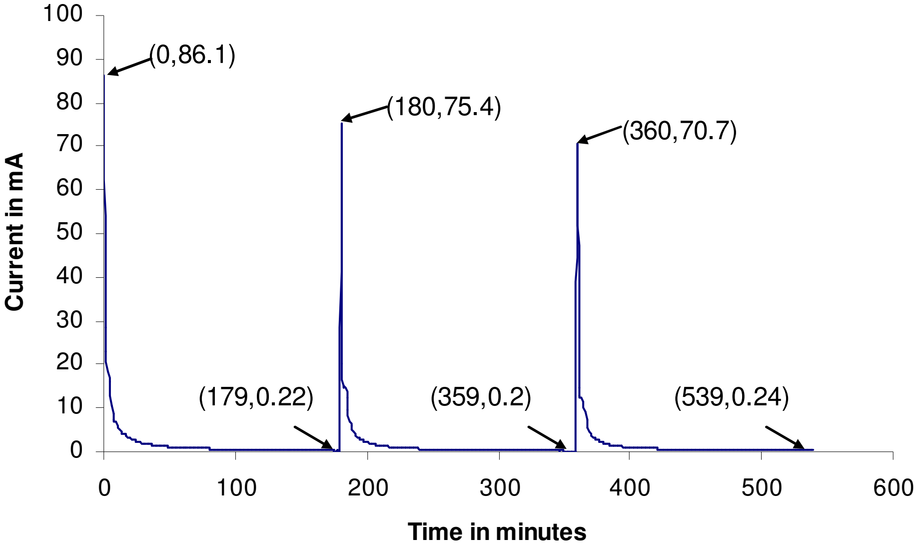

Figure 5.9 A plot showing 3 recharge cycles of a battery with (PVA-KI) ratio 1:1 and mW of PVA <10,000.

5.4 CONCLUSION

The nonconjugated conducting polymer, poly(β-pinene) was used to develop a rechargeable battery. The polymer was used as an electrode in the battery assembly and tested with different combinations of electrolytes. The polymer was found to show better stability and high rating on voltage and current when used with steel, the other electrode.

CHAPTER 6

A COMPARATIVE STUDY ON RECHARGEABLE BATTERIES

6.1 INTRODUCTION

Research has been continued to bring out the best possible combinations in the field of batteries since the day of its evolution. At present the focus is on the rechargeable batteries and the corresponding cost involved. The growing technology demands lightweight and higher capacity batteries. The choice of electrodes plays an important role in deciding the cost. Conductive polymers are candidate materials for various battery related applications. Besides conjugated conductive polymer, it was proven by *Mrinal Thakur* that nonconjugated polymer like cis-1, 4-polyisoperene and poly(β-pinene) could be made conductive by doping with iodine at room temperature [1, 36]. Many conjugated polymers were used individually and along with Lithium as one of the electrode in designing a polymer rechargeable battery. Lithium polymer rechargeable battery is gaining ground in today's electronics world, manufacturers of mobile phones; PDA's and Laptops are in the look out for batteries with less weight and a high discharge capacity. Lithium polymer batteries are found to be flexible as far as the size is concerned. The thickness of these batteries is around 3mm with a capacity starting from 110mAh. The energy storing capacity of nonconjugated conductive polymers like cis 1,4-polyisoprene and poly(β-pinene) have been used to demonstrate their ability as electrodes in rechargeable batteries in Chapter 4 and Chapter 5 respectively. This chapter talks about the contemporary rechargeable batteries and looks on to certain comparisons between these nonconjugated polymers based batteries and the batteries from modern day.

6.2 RECHARGEABLE BATTERIES

There has been tremendous growth in battery industry in recent years with an emergence of several high-capacity batteries to rechargeable light weight batteries. In early 90's the rechargeable cell system gained popularity. Lead-acid batteries were the first rechargeable system developed which opened up the market for other cells like, Ni-Cd, Ni-MH and Li-ion cells in quick succession.

Lead-acid cells are the oldest of the known rechargeable batteries till date. They provide huge surge currents which made them suitable for automobile motors. A single lead-acid cell could develop a potential difference of about of 2V under load and 1.75 V when completely discharged.

Ni-Cd batteries are popular rechargeable batteries used in consumer electronic goods. They were perfect replacement for alkaline batteries and primary cells. The Ni-Cd cell has a potential of 1.2 V which is lower than the lead-acid batteries but sufficient enough for the applications which used these batteries. These batteries have a better energy density compared to lead-acid batteries but lower than the other cells like Ni-MH and lithium-ion batteries. The toxic nature of the cadmium electrode also paved way to the design of new battery with hydrogen replacing the cadmium electrode in Ni-Cd batteries to form Ni-MH cells [37].

Ni-MH batteries were designed as a replacement to Ni-Cd batteries. They are designed in the same principle as Ni-Cd batteries except for the cadmium electrode which is replaced by hydrogen due to its toxic nature. They possess twice the capacity for the same size of a Ni-Cd battery and the memory effect is also negligent. They are used in application like digital cameras, electronic toys and even in some high current drain applications like power tools [37, 38].

Lithium-ion battery was released in 1990, relatively most common battery used in all the electronic goods today. This battery offers a very high charge density compared to all other contemporary rechargeable batteries. The batteries find applications in all the modern day electronic goods like laptops, MP3 players, and digital equipments. These batteries are free from memory effect and have a very low rate of self discharge. The battery life depends both on the charge-discharge cycle and the shelf life. A stand-alone Li-ion battery should never be discharged below a certain threshold value to avoid some irreversible damage. The open circuit voltage of a typical Li-ion battery is 3.6 V and the charging voltage is about 4.2 V. Care must be taken to store these batteries in a cooler environment failure could cause degradation of the battery [39].

6.3 POLYMER RECHARGEABLE BATTERIES

Lithium polymer batteries are based on the same principles as of Li-ion batteries except that the electrolyte is not held in an organic solvent but by a polymer compound which is not flammable. The energy density of Li-polymer batteries is found to be higher than the Li-ion cell and other rechargeable batteries like Ni-Cd and Ni-MH. The battery has a charging voltage of 4.235 V, which should not be exceeded and care must be taken to remove the load as soon as the voltage drops below 3 V while discharging. These batteries have slightly higher internal resistance which restricts their high-rate capability but their rate of self discharge is found to be much less when compared with Ni-Cd and Ni-MH batteries. The first of its kind was developed by *Bellcore*. They used PVdF-HPF, (*poly(vinylidenefluoride)-hexafluoropropylene*) polymer as the binder in the active materials and for the electrolyte of the battery [14].

The development in research has lead to invention of new rechargeable batteries using conjugated conducting polymers. These polymer materials are doped by specific dopant material to convert it to a semiconductor. These conjugated systems of polymers are also used along with lithium as one of the electrode in rechargeable batteries. Lithium based polymer rechargeable batteries use *polybithiophene*, a conjugated polymer as the cathode material. The polymer, *polybithiophene-hexafluorophosphate* was subjected to various conductivity and electrochemical impedance spectroscopy studies which proved that; it is a potential material for lithium based polymer batteries. The discharge capacity of these batteries was found to be 81.67 $m\text{Ahg}^{-1}$ [19].

New assemblies of batteries with polymer as both the electrodes were developed. *Polypyrrole* and *styryl-substituted dialkoxyterthiophene* (poly (OC10DASTT) are used the cathode and anode material of a cell. The batteries of these combinations showed as high as 94% discharge efficiency and a discharge capacity of 39.1 $m\text{Ahg}^{-1}$ [40]. Killian *et.al* fabricated an all-polymer battery based on *polypyyrole*. The battery used the redox properties of the conducting polymer for the electrodes in conjunction with polymer gel electrolyte based on polyacrylonitrile The discharge capacity of the battery was found to be 22 $m\text{Ahg}^{-1}$ [41]. Gofer *et.al* reported an all polymer battery system using *polythiphenes* electropolymerized onto a polymer support coated with graphite. The setup delivered a discharge voltage of 2.4 V and a discharge capacity of 9.5-11.5 *m*Ahg^{-1} [42].

6.4 COMPARISON BETWEEN THESE NONCONJUGATED POLYMER BASED BATTERY AND THE CONTEMPORARIES.

The nonconjugated polymer based rechargeable batteries are quite comparable with the contemporary batteries and actually it was found to be better when looked upon for certain characteristics. Both the nonconjugated polymer based batteries provided the open circuit voltage comparable to other available batteries. When Zinc was used as the anode material the open circuit voltage was around 1.2 V which was same as many other batteries in the market. Even the current ratings for these batteries were similar to those available in the market which is based on conjugated polymer. Though the capacity of these batteries was not as good as the Li-polymer battery available in today's battery world, they were comparable with certain batteries which were made out of conjugated polymers.

These nonconjugated polymer based battery had its own advantages like light weight, inexpensive except for the use of platinum, flexible design, free from memory effect which is common in certain rechargeable batteries, long life, comparable discharge capacity.

6.5 COMPARISON BETWEEN THE ELECTROLYTES USED

Three different types of electrolytes were studied and tested in the development of the nonconjugated conductive polymer based rechargeable battery. The KI electrolyte showed good current and voltage rating and even had a higher capacity rating initially for few recharge cycles. The capacity decreased with time with repeated charge and discharge due to the evaporation of water from the electrolyte. On the other hand the electrolyte which had PVA in the solution of KI was holding better and the rate of evaporation of water was less compared to the electrolyte with KI. There was a difference in the battery characteristics even in the electrolyte with PVA. The electrolyte with PVA of higher molecular weight showed better battery current, voltage and capacity rating compared to the PVA with lower molecular weight.

There was case where the KI electrolyte dissolved the polymer completely and evaporated with time. The electrolyte with PVA had no such problems. The polymer in the battery with PVA-KI electrolyte was intact even after several recharge cycles.

6.6 FTIR MEASUREMENTS ON POLY (β-PINENE) ELECTRODE AFTER SEVERAL RECHARGE CYCLES

FTIR spectroscopy studies were made on the polymer electrode used in the rechargeable battery after several recharge cycles. The data showed that there was no change in the polymer structure due to charge and discharge. As observed in the doped polymer poly(β-pinene), the decrease in the intensity of C=C stretching at 1610 cm^{-1} and =C-H at 728 cm^{-1} was retained. There were some peaks due to water molecules found around 1610 cm^{-1} which could be from the electrolyte. The comparison the FTIR plots for undoped polymer, doped polymer and the electrode is shown in Figure 6.1 and Figure 6.2.

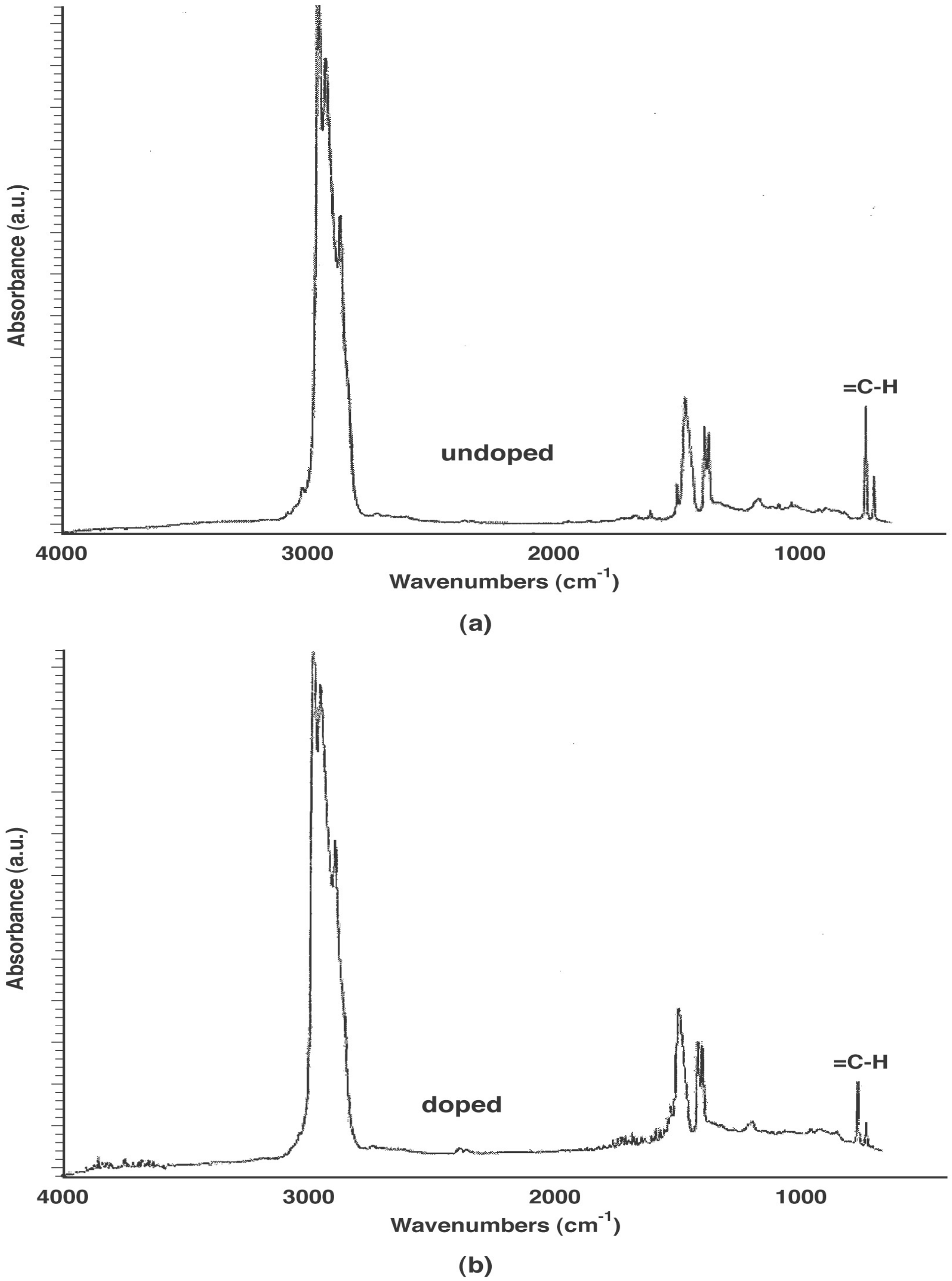

Figure 6.1 FTIR spectra of poly(β-pinene): a) undoped, b) iodine doped [36].

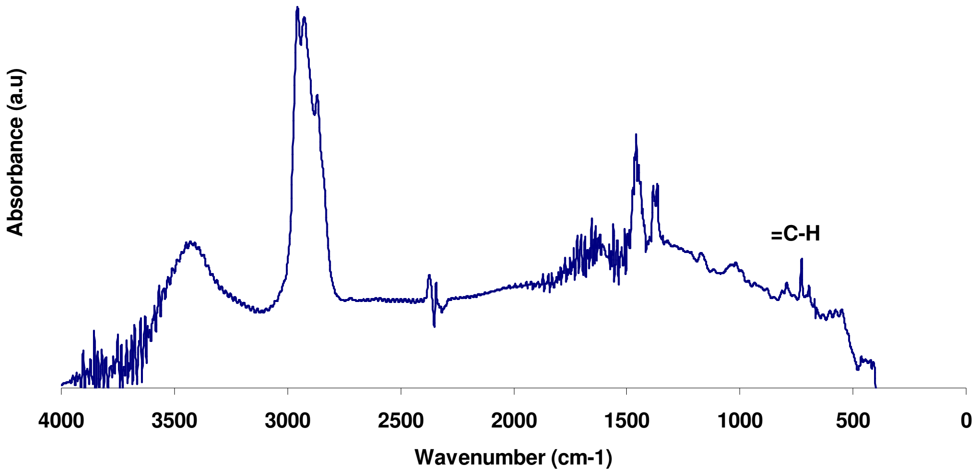

Figure 6.2 FTIR spectra of poly(β-pinene) electrode after several charge-discharge cycle.

6.7 CONCLUSION

In summary it can be seen that most of the commercially available rechargeable batteries and those based on polymers had similar characteristics as that of our model. The voltage and current rating of our model is comparable with some of the available rechargeable batteries. The capacity was also found to be higher than some of the batteries based on conjugated polymer.

6.8 FUTURE WORK

The capacity is found to be on the lower side, when compared to Li-polymer based batteries which could be improved by altering the composition of the electrolyte and ways to prevent evaporation of water. The weight of the battery could be reduced further to about 5-10gms. The expensive platinum needs to be replaced either by a platinum coated material or any other material which does not corrode in presence of iodine. As the area of the polymer increases the capacity is found to increase, work is on, to monitor the increase in the capacity with area of the polymer film doped with iodine.

CHAPTER 7

EPR SPECTROSCOPIC STUDIES OF INTERNAL STRUCTURE OF DOPED THE NONCONJUGATED CONDUCTIVE POLYMER, POLY (B-PINENE)

7.1 INTRODUCTION

Electronic and optical polymers have attracted significant research attention because of the fundamentally interesting characteristics and a wide range of potential applications. Nonlinear optical properties of organic and polymeric materials have various applications in photonics. Detailed studies of nonconjugated conductive polymers have been made using various spectroscopic methods including optical absorption, FTIR, Raman, ^{13}C-NMR, Mossbauer and EPR. Various applications of these polymers have been demonstrated. Nonconjugated conductive polymers such as doped polyisoprene are important materials having confined electronic or nano-optical structures [34]. Exceptionally large quadratic electro-optic effect (third order optical susceptibility) has been reported for iodine-doped polyisoprene [34]. Electrical conductivity, FTIR spectroscopic and photoluminescence characteristics of a novel nonconjugated conductive polymer, poly(β-pinene) have been recently reported [36]. Large quadratic electro-optic effect in iodine-doped poly(β-pinene) due to formation of nano-optical domains has been recently reported. The molecular structures of poly(β-pinene) before and after doping with iodine are shown in Figure 4.1 and Figure 4.2 respectively. The doping leads to a charge-transfer from the isolated double bond to iodine forming radical cations. In this chapter, the results of electron paramagnetic resonance (EPR) measurements of poly(β-pinene) for different doping levels to confirm formation of radicals are discussed.

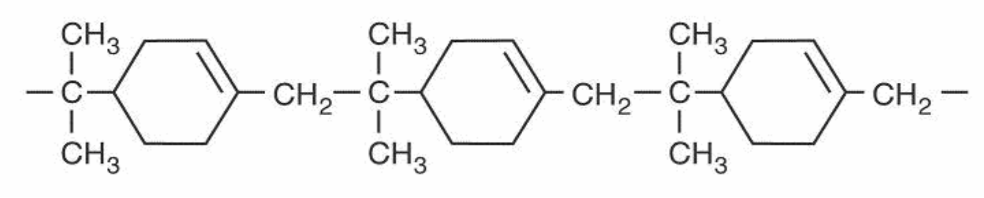

Figure 7.1 Molecular structure of undoped poly(β-pinene)

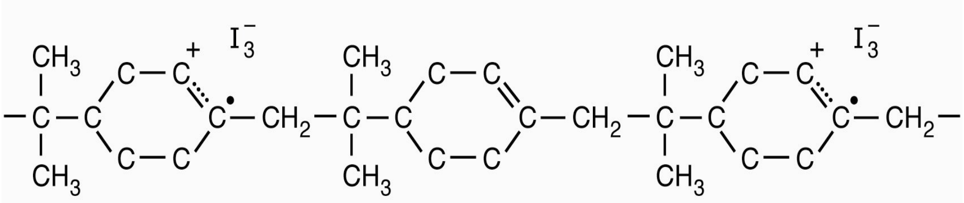

Figure 7.2 Radical cations formed upon doping and charge-transfer in poly(β-pinene)

The electrical conductivity of poly(β-pinene) increases by more than ten orders of magnitude upon doping with iodine. Undoped poly(β-pinene) has conductivity less than 10^{-12} S/cm. Upon doping with iodine the conductivity increases rapidly. When the molar concentration of iodine reaches about 0.85 the conductivity saturates at ~ $8x10^{-3}$ S/cm [36].

7.2 OPTICAL ABSORPTION AND FTIR SPECTROSCOPIC STUDIES

Optical absorption and FTIR spectroscopic results of poly(β-pinene) have been reported [36]. The optical absorption spectra for different dopant concentrations are shown in Figure 7.3. Two major optical absorption peaks have been observed for lightly doped samples: one at 4 eV corresponding to cation radicals and the other at 3.1eV due to the charge transfer between the donor and the acceptor. The lower energy peak undergoes a red shift when the dopant concentration increases. This is due to the reduction of the average distance separating the radical cation and the iodine anion [11, 36].

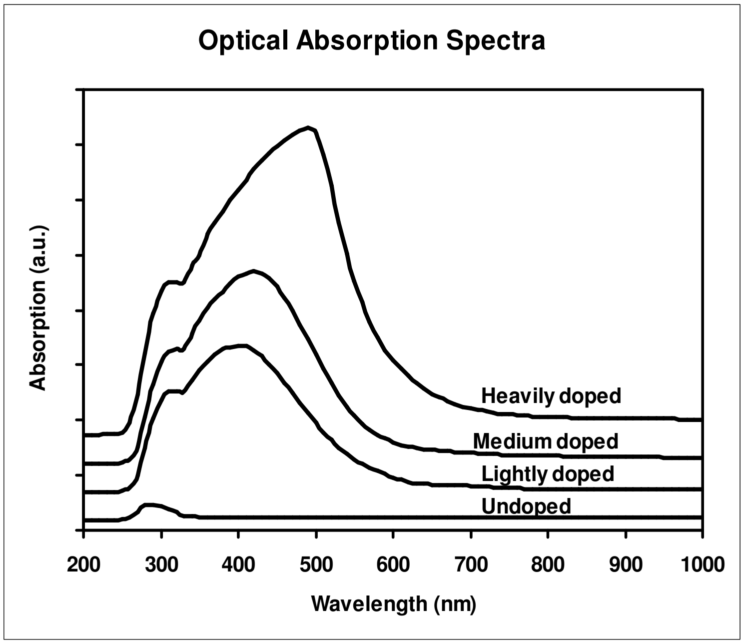

Figure 7.3 Optical absorption spectrum of poly(β-pinene) at different dopant concentrations[36].

FTIR spectra of the polymer before and after doping are shown in Figure 7.4. Upon doping, there is a decrease in the FTIR peaks at 1610 cm^{-1} and 728 cm^{-1} corresponding to C=C stretching vibration and =C-H bending vibration respectively. This decrease is due to charge-transfer from the isolated double-bond to the dopant and formation of radical cations (Figure 5.2). We discuss results of EPR measurements to show that cation radicals are formed upon doping of poly(β-pinene).

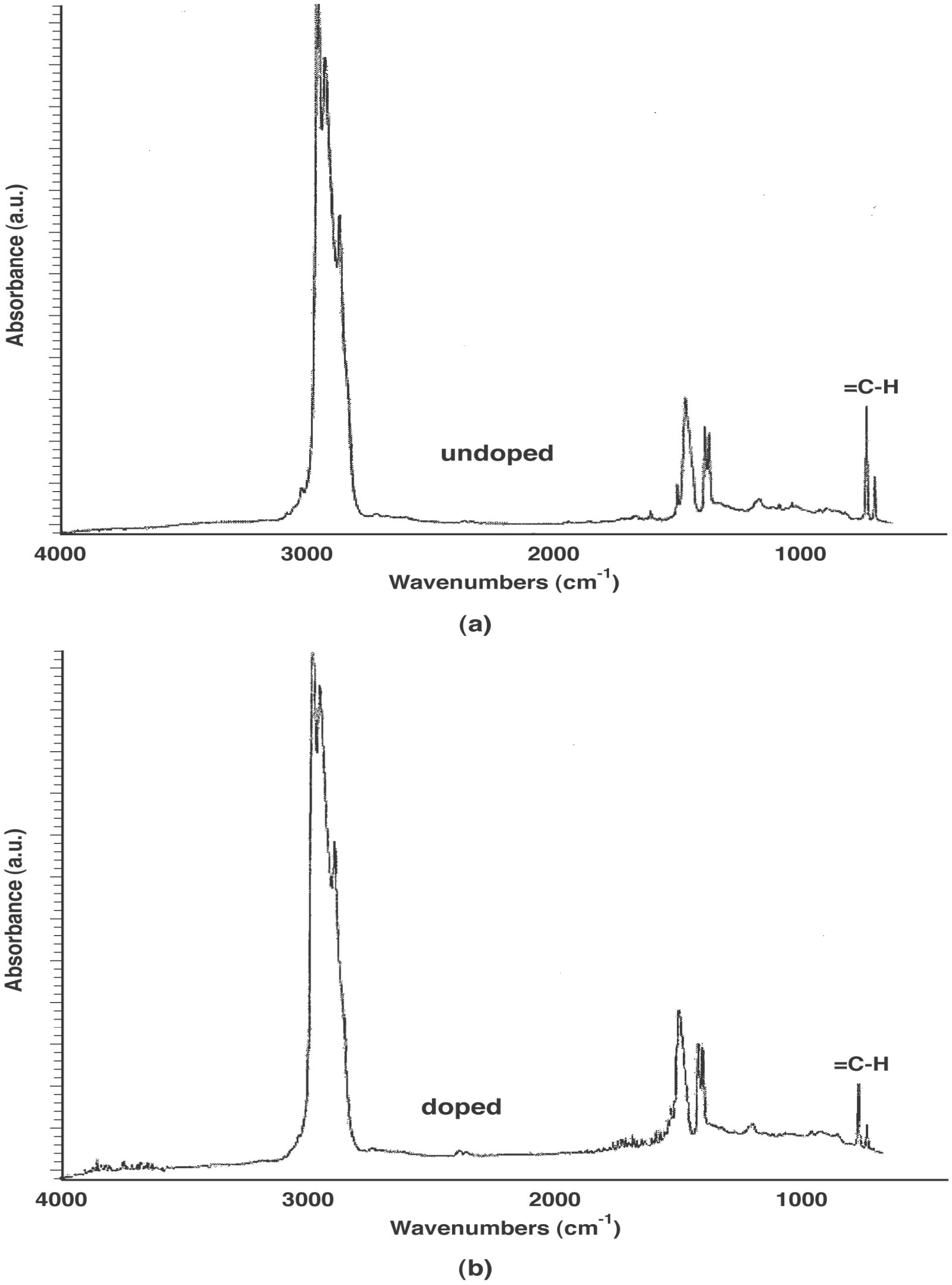

Figure 7.4 FTIR spectra of poly(β-pinene): a) undoped, b) iodine doped [36].

7.3 EXPERIMENTAL SETUP

7.3.1 PREPARATION OF SAMPLE

The EPR measurements were performed on poly(β-pinene) at different doping levels of iodine. The poly(β-pinene) samples used in this work were purchased from Aldrich Chemicals Corp. Films of poly(β-pinene) were prepared on a glass substrate from a toluene solution. The films were then doped with iodine at different concentrations. The molar concentrations were calculated by measuring the weight uptake of iodine in the film. The powder samples obtained from the doped films were used to perform the EPR measurements. Undoped poly(β-pinene) samples were also prepared as a powder and weighed to perform the EPR measurement.

7.3.2 EPR MEASUREMENT

EPR is a spectroscopic measurement which gives the details of species under study, its identity and the molecular structure. Spectroscopic measurements are in general a study of energy difference between the different atomic and molecular states. The energy difference in EPR measurements are from the interactions between the unpaired electrons in the sample and the magnetic field around it produced by a magnet. The electrons are supposed to have magnetic moment and they are found to act like a bar magnet when placed inside a magnetic field. These electrons posses a highest or lowest energy state according to their alignment in the magnetic field. The energy difference between the two unpaired electrons or spin states could be obtained either by varying the electromagnetic radiation frequency and keeping the magnetic field constant or vice versa. The EPR measurement is made using a constant electromagnetic radiation frequency and a varying magnetic field as in Figure 7.5, where a peak is observed in the absorption spectrum when the energy difference between the two spin states is tuned to match the electromagnetic radiation by the magnetic field. This is the field of resonance and this technique is used in all Bruker EPR spectrometers. The EPR experiment was conducted at X-band (9 GHz) using a Bruker EMX spectrometer at room temperature and

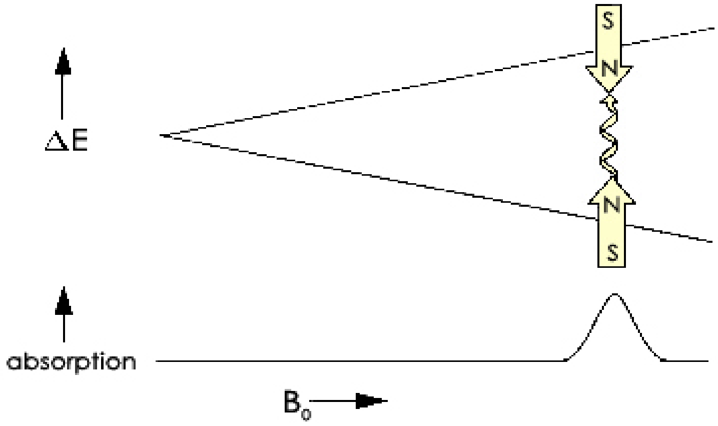

Figure 7.5 Variation of the spin state energies as a function of the applied magnetic field [43]

at a lower temperature (100 °K). Cooling of the sample was performed with an Oxford Instruments ESR 900 flow cryostat with an ITC4 temperature controller. Consider the following two basic equations of EPR from quantum mechanics.

$$E = g\mu_B B_0 M_S = \pm\tfrac{1}{2} g\mu_B B_0 \qquad 7.1$$

$$\Delta E = h\nu = g\mu_B B_0 \qquad 7.2$$

Where g is the Zeeman splitting factor, M_S is the magnetic spin moment and μB is the Bohr magneton, a natural unit of electronic magnetic moment [43].

7.4 DISCUSSION

The undoped poly(β-pinene) sample showed a very weak EPR signal due to the methyl radicals. Significant EPR signals increasing in proportion to the dopant concentration have been observed and the results are shown in Figure 7.6.

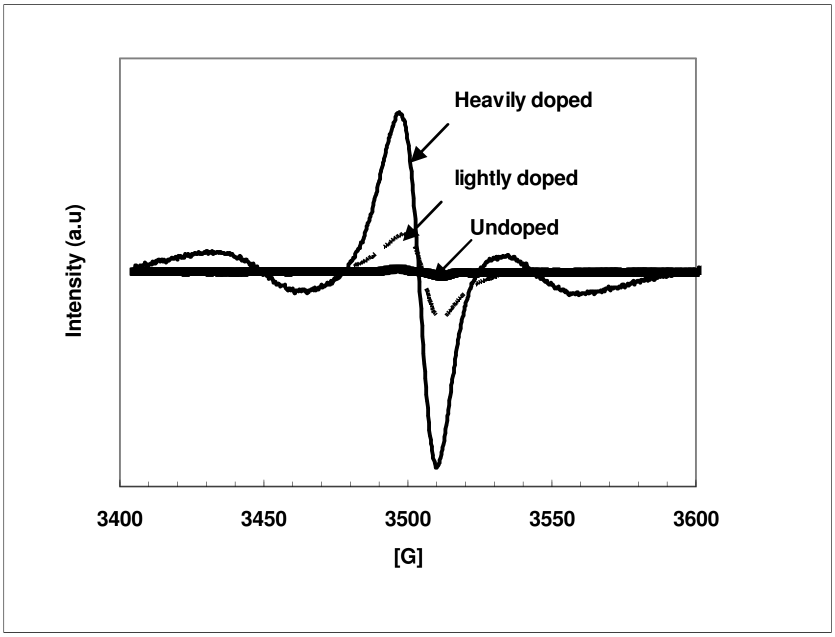

Figure 7.6 EPR signals of poly(β-pinene) at different dopant concentrations.

Clearly, the EPR signal of the heavily doped sample is large. As these results have shown, g = 2.0042 and the EPR line-width (ΔH_{pp}) of the doped samples is about 13 G. These values compare well with those of doped cis-polyisoprene reported earlier [11]. The line-width is larger compared to that in conjugated conductive polymers because the radical is less mobile (confined) in the case of the nonconjugated conductive polymer [3].

7.5 RESULTS

EPR measurements have been performed on poly(β-pinene) at different concentrations of iodine. The signal was found to increase proportionally with the iodine concentration due to the formation of cation radicals upon doping and charge-transfer. The results are consistent with the FTIR and optical absorption data. The g-value and the EPR line-width (ΔH_{pp}) compares well with that of another nonconjugated conductive polymer, doped 1,4-*cis*-polyisoprene [11].

CHAPTER 8

QUADRATIC ELECTRO-OPTICS STUDIES OF PBP AT A LOWER TEMPERATURE

8.1 INTRODUCTION

There is a tremendous growth in the research area involving the studies of optical nonlinearities in organic molecules and polymers due to their possible commercial applications. Large and ultra fast optical nonlinearities have been measured in various organic, inorganic materials and nanostructures. It was shown by Thakur *et al* that nonconjugated polymers such as *cis* 1,4 polyisoprene could be made to conduct electricity when doped with iodine [1]. Electro-optic measurements have been recently made on these nonconjugated conductive polymers which showed exceptionally large quadratic electro-optic effects (third order nonlinearity). Quadratic measurements on nonconjugated conducting polymers like *cis* 1, 4 polyisoprene and poly(β-pinene) were reported at 633nm (He-Ne laser) using field-induced birefringence method with an ac field of 4 kHz. In this chapter quadratic electro-optic measurements were made on poly(β-pinene) at a lower temperature. The modulation depth obtained with such an arrangement was found to be high. Such large nonlinearities have been attributed to the confinement of this electronic system within a sub nanometer domain.

8.2 QUADRATIC ELECTRO-OPTIC EFFECT

The application of external electric field results in change of optical impermeability tensor due to the redistribution of charges in the crystals and possible deformation of the ion lattice. This is known as electro-optic effect and the coefficients are defined as

$$\eta_{ij}(E) - \eta_{ij}(0) \equiv \Delta\eta_{ij} = r_{ijk}E_k + s_{ijkl}E_kE_l \qquad 8.1$$

$$= f_{ijk}P_k + g_{ijkl}P_kP_l \qquad 8.2$$

where **E** is the applied electric field, **P** is the polarization filed vector, r_{ijk} and f_{ijk} are linear electro-optic coefficients and s_{ijkl} and g_{ijkl} are quadratic electro-optic coefficients. Quadratic effect is seen in materials with any molecular orientation. For a material placed in an electric field **E**, a beam of light passed through it perpendicularly displays birefringence proportional to $\mathbf{E}^2$. The rays emerging out of the material was found to have different refractive index which is related to the Kerr constant '**K**' by the following expression, where **Δn** is the change in refractive index of the ordinary ray **($\mathbf{n_o}$)** and the extraordinary ray **($\mathbf{n_e}$)**.

$$\Delta n = n_o - n_e = \lambda KE^2 \qquad 8.3$$

The **'λ'** is the wavelength of the light passed through the material. This Kerr effect is a third order effect and is also called as quadratic electro-optic effect. These Kerr effects are used to construct wave plates and ultra fast optical shutters ($< 10^{-10}$ s) by placing the material between two polarizer in a cross polarized geometry [44].

8.3 QUADRATIC ELECTRO-OPTIC EFFECT ON POLY (β-PINENE)

Quadratic electro-optic effect has been measured and reported in a nonconjugated conductive polymer, poly(β-pinene) doped with iodine. A large quadratic effect has been observed at 633 nm and this large value was attributed to the quartic term in the potential energy of a spring-mass system which is a model of a loosely bound hole to the dopant in the polymer and due to the charge confinement in a small volume (nano-domain) [45]. A Kerr constant of 1.2×10^{-10} m/V^2 and modulation depth of 0.118% was reported for a sample doped with iodine of molar concentration equal to 0.86 [45].

8.4 EXPERIMENTAL SETUP

A thin film of poly(β-pinene) was formed on a glass slide and doped with iodine at room temperature. When the film was sufficiently doped copper electrodes were placed. The experiment was conducted at room temperature initially and at a lower temperature by reducing the temperature of the sample locally. A strip of copper dipped in liquid nitrogen was wrapped around the sample to reduce its temperature. The experimental setup is shown in Figure 8.1. The experiment was performed in a cross polarized geometry using field induced birefringence method at low temperature. The incident laser beam was polarized at an angle of 45 degrees by a polarizer. A 4 kHz supply was applied across the slit in the sample which was maintained at low temperature. The laser beam passes through the slit in the sample in presence of the applied field and the resulting beam is passed through an analyzer before being collected by a photo detector. The analyzer was cross polarized with respect to the polarizer.

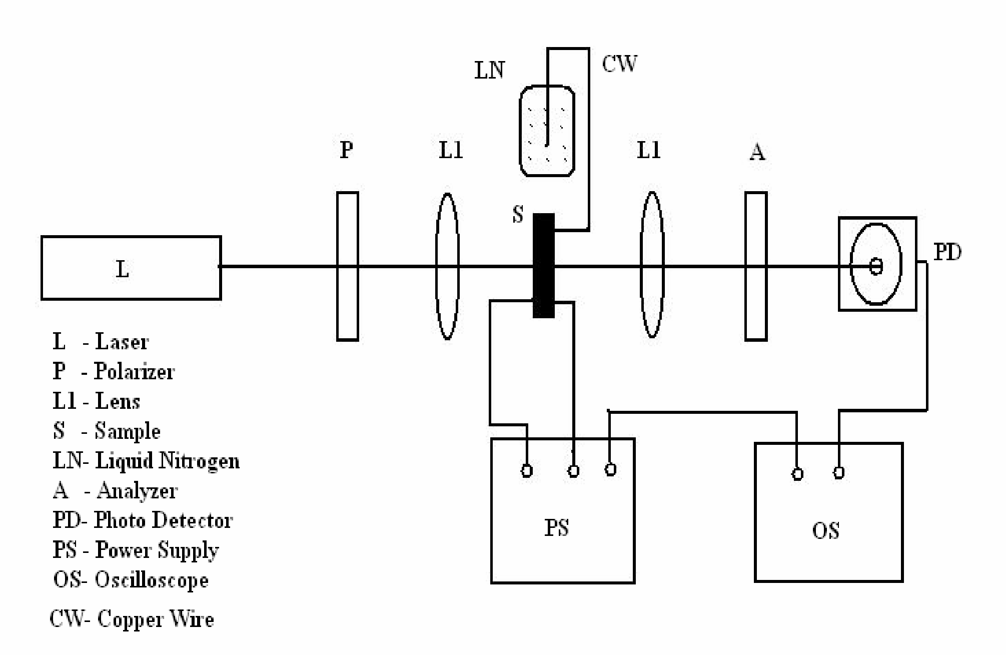

Figure 8.1 Quadratic Electro-optic setup

8.4.1 RESULT & DISCUSSION

A quadratic electro-optic effect was observed in presence of an applied ac field. The experiment was conducted at room temperature to begin with, which showed a modulation of 0.1%. Then the temperature of the sample was reduced and the experiment was repeated which showed a modulation depth of 0.5% for an applied ac field of 200 V and 0.3% for a field of 150 V. The obtained modulation depth was found to be large compared to previous results [45]. The observed quadratic effect is due to the loosely bound hole to the dopant iodine molecule I_3^- , in the doped film. It is known that the loosely bound hole can be modeled as a spring-mass system with a quartic term in the potential energy [45]. The quadratic and the cubic term in the harmonic oscillator potential energy lead to the first and second order optical susceptibilities. Likewise the quartic term is responsible for the third-order susceptibility or the quadratic electro-optic effect.

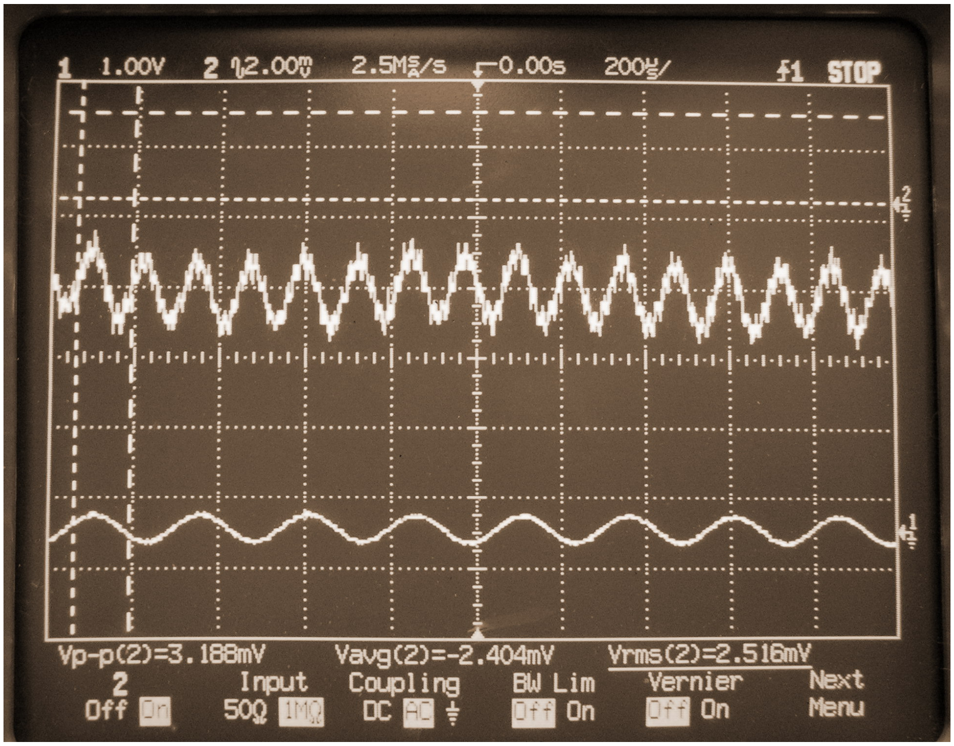

Figure 8.2 Oscilloscope trace of the signal modulation at room temperature

At low temperature the sample was found to be more stable and the contribution of the higher magnitude quartic term was significant to give a large third-order optical or quadratic electro-optic effect. The temperature measurement of the sample was made using a point and shoot thermocouple. The oscilloscope trace of the modulation of the signal for both room temperature and a low temperature measurement is shown in Figure 8.2 and Figure 8.3 respectively.

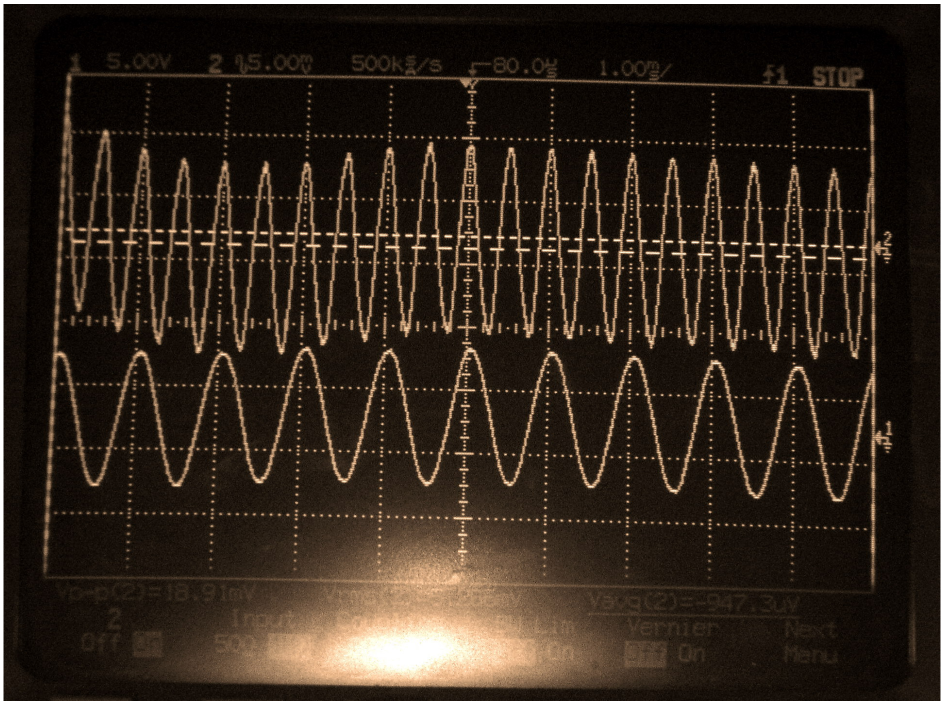

Figure 8.3 Oscilloscope trace of the signal modulation at low temperature.

8.5 CONCLUSION

Quadratic electro-optic effect has been measured in a sample of poly(β-pinene), a nonconjugated conductive polymer at a lower temperature and the modulation depth has been found to be higher. The increase in modulation depth could be due to several reasons including higher stability of structure, a different linear absorption spectrum at a lower temperature and others. The exceptionally large quadratic electro-optic effect as observed has been attributed to the confinement of this electronic system within a subnano meter domain (nano metallic).

CHAPTER 9

SUMMARY

Specific nonconjugated conductive polymers have been studied for its electrical properties and their use as electrodes in rechargeable batteries. Different combinations of electrode pairs and different types of electrolytes were tested for optimal condition. Capacity measurements were made to determine the ampere-hour rating of the battery that showed promising results which forms a foundation for further improvement in the electrode combination and fabrication to improve the battery's stability. The capacity of these battery were found to vary with the size of the polymer electrode used which brings in the adaptability and comfort of design of such batteries in any dimension using these polymers.

Electron Paramagnetic Measurements (EPR) was made to study the internal structure of the nonconjugated conductive polymers after doping. The doping leads to a charge-transfer to the dopant from the double bond in the molecule forming radical cation. EPR measurements were made for different doping level and these signals were found to increase with doping concentration due to the formation of cation radicals and charge transfer.

Quadratic electro-optic effect of nonconjugated conductive polymer, poly(β-pinene) have been performed at low temperature. The experiment was performed using the field induced birefringence method at 633 nm. The measurement has shown an exceptionally large electro-optic coefficient (Kerr constant) at a lower temperature. This large effect is due to the confined structure (nano mettalic) of the doped polymer.

In conclusion, these nonconjugated conductive polymers have been studied to measure its capacity as electrodes in rechargeable batteries, internal structure (radicals) and nonlinear optical properties upon doping. These experiments and studies have shown that these polymers have significant potential for applications in the electronics and photonics industry. Their electrically conductive nature could be employed in energy storage devices and their large optical nonlinearities can be used in various applications in photonics.

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