

**STUDIES ON CONDUCTING POLYMERS AND
CONDUCTIVE ELASTOMER COMPOSITES**

Thesis submitted to the

**COCHIN UNIVERSITY OF
SCIENCE AND TECHNOLOGY**

by

PRINCY K. G.

*in partial fulfillment of the requirements
for the award of the degree of*

DOCTOR OF PHILOSOPHY

**DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI- 682 022**

JUNE 2002

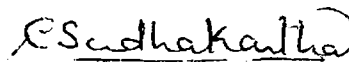
Certificate

This is to certify that this thesis entitled "Studies on Conducting Polymers and Conductive Elastomer Composites" is a report of the original work carried out by Smt. Princy K. G. under our supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.



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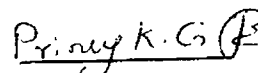
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DECLARATION

I hereby declare that the thesis entitled "Studies on Conducting Polymers and Conductive Elastomer Composites" is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, and Dr. C. Sudha Kartha, Reader, Department of Physics, Kochi 682 022, and no part of this thesis has been presented for any other degree from any other institution.


Princy K. G.

Kochi-22
22nd June 2002

to

my

family

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PREFACE

Conducting polymers, because of their unusual properties, have attracted great interest in recent years. Despite the short history, they have found a place in various applications. This thesis is about the development of conductive silicone rubber and nitrile rubber; and the synthesis, characterization and properties of novel conducting polymer –poly (p-phenylenediazomethine) and their blends with polyethylene, PVC and silica.

This thesis is divided into seven chapters as follows:

Chapter 1 presents a review of the literature in this field and the scope of the present investigation.

Chapter 2 deals with the materials used and the experimental procedures adopted for the study.

Chapter 3 is divided into three parts; Part-I reports the effect of different types of carbon blacks [e.g., acetylene black, lamp black, and ISAF (N-234) black], copper powder, and graphite on the electrical conductivity and mechanical properties of silicone rubber. Part –II reports the effect of different types of carbon blacks [e.g., N-220, N-347, and N-339 carbon blacks] on the electrical conductivity and mechanical properties of silicone rubber. The effect of temperature on the conductivity of silicone rubber vulcanizates is also studied. Part-III reports the effect of blending silicone rubber with high-density polyethylene on the conductivity and mechanical properties of the vulcanizates.

Chapter 4 is divided into two parts; Part I deals with the effect of concentration of acetylene black on the electrical conductivity and mechanical properties of nitrile rubber vulcanizates. Part II deals with the effect of blending of NBR with other polymers on the electrical conductivity and mechanical properties

of the vulcanizates at the same dosage of acetylene black. Preparation of nitrile rubber blends with NR, EPDM and PVC and the measurement of electrical conductivity and mechanical properties are reported. Part III deals with the variation in conductivity and mechanical properties of the vulcanizates with different composition of NBR/NR blends at the same dosage of acetylene black. Part –IV deals with the effect of temperature on the electrical conductivity of these vulcanizates.

Chapter 5 includes the synthesis and characterization of a new conducting polymer based on glyoxal and p-phenylene diamine. The synthesis of poly(p-phenylenediazomethine) was carried out in different solvents, like, methanol, toluene, m-cresol and DMF. D.C. conductivity, dielectric properties and thermal diffusivity of the polymer prepared in different solvents were determined. Effect of dopants on the d.c. conductivity and dielectric properties was also investigated.

Chapter 6 includes in-situ polymerization of glyoxal and p-phenylenediamine in different solvents containing different amounts of PE, PVC, and silica. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like HClO₄, HCl and I₂ on conductivity was also studied.

Summary and conclusions of the present investigation is described in the last chapter, **Chapter 7**.

At the end of each chapter a list of references has been given. A list of abbreviations used in this thesis is also cited.

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Chapter 1

INTRODUCTION

The possibility of improving the conductivity of polymers, which are conventionally insulators, to metallic levels has attracted not only chemists, but also physicists and even material scientists. Many researchers have tried to combine the processability and other attractive properties of polymers with the electronic properties of metals or semiconductors. Conducting polymers are different from electrically conductive polymers as they are conductive only if the individual conductive particles are in contact and form a coherent phase¹.

A major breakthrough in the search for conducting polymers occurred in 1977²⁻⁴ with the discovery that polyacetylene could be readily oxidized by electron acceptors such as iodine or arsenic pentafluoride or reduced by donors

such as lithium. The resulting material had a conductivity that was orders of magnitude greater than the original, untreated sample. The redox reaction can be carried out in the vapour phase, in solution, or electrochemically.

A significant development occurred in 1979 with the discovery⁵ that poly (p-phenylene) could also be doped with AsF₅ to high conductivity. It demonstrated that polyacetylene is not unique and this led to the development of a number of new poly aromatic-based conducting systems, including poly (p-phenylene sulphide)^{6,7}, polypyrrole⁸, polythiophene⁹, and polyaniline¹⁰.

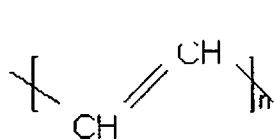
Another important development was the discovery of conducting polymer solutions. Films with high conductivity and mechanical integrity can be cast from these solutions. Composites and blends are also being investigated as means for processing and shaping conducting polymers for a wide spectrum of applications^{11,12}.

1.1 Synthesis of conducting polymers

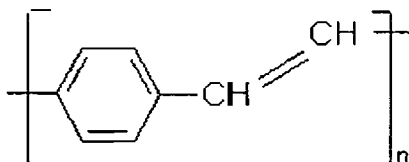
Since the conductivity of conducting polymers are known to depend on the method of synthesis, a large number of preparatory methods have been developed to improve the conductivity. Addition, condensation, electrochemical, ring opening, and plasma polymerisation are the most notable and widely used techniques in this regard. Other methods include Diels-Alder elimination, Wittig reaction, Ziegler-Natta catalysis, Friedel Crafts reaction and nucleophilic displacement reaction. In designing polymer synthesis, the incorporation of extended pi-electron conjugation is of foremost importance.

Polyacetylene films are prepared by exposure of acetylene gas to smooth surfaces wetted with solutions of the Ziegler-Natta polymerisation catalyst³. It exists predominantly as the cis isomer with a high degree of crystallinity. Isomerization to the more stable trans form can be induced by heat or dopants^{3, 13-16}. Polyacetylene

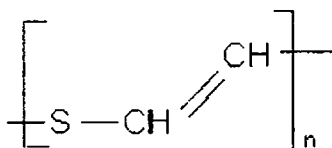
can also be synthesized by the retro Diels Alder reaction^{17,18}. Copolymers of acetylene units alternate with an electron rich unit include poly(vinylene)phenylene¹⁹, poly(vinylene)sulfide²⁰, and poly(vinylene)phenylene pyrrole²¹.



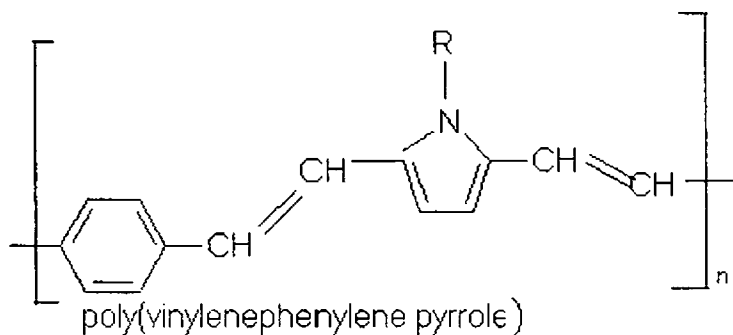
polyacetylene



poly(vinylene)phenylene)



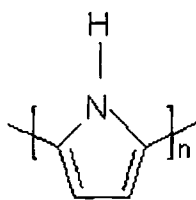
poly(vinylene sulfide)



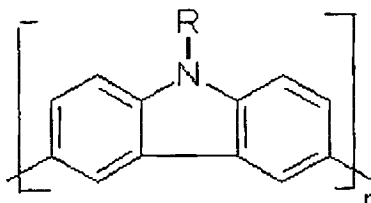
poly(vinylene)phenylene pyrrole)

Polymers of heterocycles such as pyrrole and thiophene can be viewed as derivatives of polyacetylene in which adjacent olefinic moieties have been bridged with nitrogen or sulphur. Pyrrole and its alkylated derivatives are usually polymerised electrochemically from a solution of the appropriate monomer²². Typically, application of a potential of 0.5 V between two electrodes in an acetonitrile solution containing AgClO_4 electrolyte and pyrrole monomer proceeds with the accumulation of an oxidized polypyrrole film on the anode. This film, as

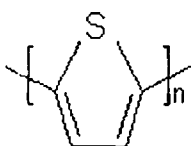
prepared, is conductive, since it incorporates inorganic counter ions (ClO_4^- ion) from the solution as it is oxidatively synthesized. In a similar manner other conducting polymers have been prepared electrochemically, including polythiophene^{23,24}, polycarbazole, polyazulene, and polyisothianaphthene²⁵. Electrochemical polymerisation offers the advantages of homogeneous incorporation of dopant counter ions into the polymer film as it is grown and control over the polymerisation parameters of current density and voltage. The method is limited, however, by the fact that the yield of polymer is restricted to the area of working electrode in the electrochemical apparatus.



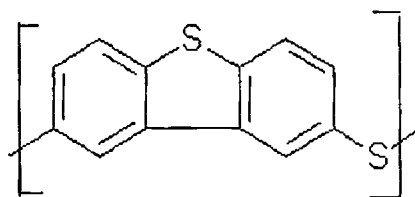
polypyrrole



polycarbazole



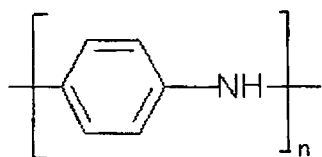
polythiophene



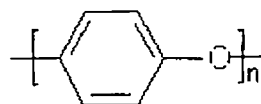
poly(dibenzothiophene sulfide)

Polymers containing phenyl group constitute a large class of conducting polymers, which are thermally, and oxidatively more stable than other polymers. Phenyl rings are there in the polymer backbone as repeat units in aniline (polyaniline), phenol (Poly(p-phenylene oxide)), thiophenol (poly(p-phenylene sulphide)), or simply as phenyl (poly(p-Phenylene)).

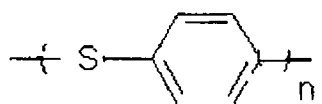
Poly(p-phenylene) is obtained when benzene is coupled by aluminium chloride/cupric chloride at 35 ° C in benzene solvent ²⁶ . Poly(p-phenylene oxide), which can be rendered conducting by doping has been prepared by an Ullman condensation of sodium p-bromophenolate ^{27,28} . Poly (p-phenylene sulphide) can be industrially prepared by the high temperature coupling of sodium sulphide and p-dihalobenzene²⁹. Polyaniline is an electro active organic polymer that displays good environmental stability. The acid doped polymer is the precipitated product from an aqueous solution containing ammonium per sulphate, hydrochloric acid and aniline ^{30,31}. Variations of the synthesis of polyaniline have included electrochemical techniques ^{10,32} and different solvent/acid media.



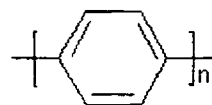
polyaniline



poly(p-phenylene oxide)



poly(p-phenylene sulphide)



poly(p-phenylene)

1.2 Doping

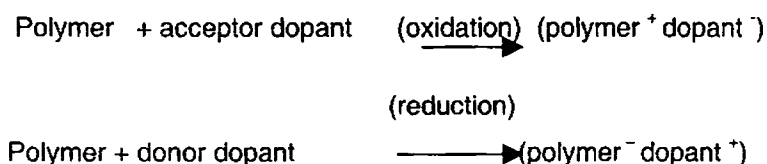
The conductivity ' σ ', of any conducting material is proportional to the product of the free-carrier concentration, n , and the carrier mobility, μ ,

$$\sigma = e n \mu$$

where ' e ' is the unit electronic charge. Since conjugated polymers have relatively large band gaps, the concentration of free carriers is very low at normal

temperatures. Therefore, even though conjugated polymers have high carrier mobility, the low carrier concentration results in low conductivity.

Doping is a process in which a virgin polymer is treated with a strong oxidizing or reducing agent that either abstracts electrons from the polymer or donates electrons to it through the formation of a charge carrier into the polymer for the enhancement of its conductivity.



The doping of conjugated polymers increases the carrier concentration. Doping in polymers is a redox process involving charge transfer with subsequent creation of charged species. With polymers, electronic excitations are accompanied by a disorder or relaxation of the lattice around the excitation, and thus structural and electronic excitation will result in structural defects along the polymer chain. Removal of an electron leaves an unpaired spin near the valence band (p- doping) and addition of an electron fills the corresponding state near the conduction band (n- doping)³³.

Oxidative dopants are usually electron-attracting substances. The common p-type dopants are Br₂, I₂, AsF₅, H₂SO₄, HClO₄, BCl₃, PF₅, SbF₆, CH₃F, NO₂F, NO₂, NO⁺SbCl₆⁻, SO₃, FeCl₃, etc. n-type dopants are electron donating substances like sodium naphthalide, Na/K alloy, molten potassium, LiI etc.. There are a number of ways by which doping can be carried out. Essentially, these different methods can be broadly summarized as being solution doping, vapour phase doping and electrochemical doping.

In conducting polymers the doping process can be reversed, i.e, the conducting polymer can be converted to insulator by neutralization back to the

uncharged state. This return to neutrality is called compensation. Exposure of oxidatively doped polymer to electron donors, or, conversely, of reductively doped polymers to electron acceptors effects compensation. This property is made use of in the construction of rechargeable batteries.

1.3 Temperature characteristics of conductors

The temperature characteristics are of importance when considering possible applications for conductors. Generally speaking, the conductivity of a metal falls as the temperature is raised because of the scattering of the carriers and this is recognized by an increase in resistance. In this case, the temperature coefficient of the resistance is positive (PTC). If the temperature of a semiconductor such as silicon is raised the conductivity increases because of the rise in the number of carriers. Such materials are said to have a negative temperature coefficient (NTC). The situation with a typical macromolecular conductor such as polyacetylene differs according to the doping concentration.

Even though many conducting polymers show metallic level of conductivity, the temperature dependence of conductivity is not like metal. In most of the cases, the dependence is like that of a semiconductor. The semiconductor like behaviour of conductivity can be explained on the basis of the existence of potential barriers between highly conducting regions. These barriers are due to conjugational defects or other inhomogeneities in the polymer chain. The charge carriers will have to hop or tunnel through the potential barriers. Since tunnelling by itself is a temperature independent process, the temperature dependence of conductivity must arise from other processes influencing the charge transfer between highly conducting regions. The models of Sheng³⁴, take into account the charging energy of conducting regions of the random thermal motion of charge carriers on both sides of the tunnel junction³⁵, and the derived transport characteristics have been the most successful ones in describing the conductivity of highly doped conjugated polymers.

When the size of highly conducting regions or islands are sufficiently small (less than 20nm), the energy required to move an electron from an electrically neutral island become significant. If the voltage between two adjacent islands is small compared to kT/e , charge carriers can be generated only by thermal activation, making conductivity temperature dependent and limited by only the charging energy. The charge carriers will then percolate along the path with least resistance. The conductivity varies with temperature as ³⁴,

$$\sigma(T) = \sigma_0 \exp \{(-T_0/T)^{1/2}\}$$

where σ_0 and T_0 are material constants.

If the size of the highly conducting regions is larger than about 20nm, charging energy becomes negligible. Sheng's second model for inhomogeneous conductors is based on fluctuation-induced tunneling of charge carriers between highly conducting islands. This model applies to larger conducting regions, typically of the order of a micrometer. The theory assumes that the random thermal motion of the charge carriers within the conducting islands induces a randomly alternating voltage across the gap between neighbouring islands. The temperature dependence of the conductivity arises from thermal fluctuation-induced tunnelling of charge carriers between highly conducting island ³⁵ and is expressed as follows:

$$\sigma(T) = \sigma_1 \exp \{-T_1/(T_2+T)\}$$

where T_1 and T_2 are material constants depending on the width and height of the tunnelling barrier³⁶.

Effects such as doping resulting in inhomogeneously distributed dopants, fibrillar morphology, interchain transport, transport through grain boundaries etc. can be well explained by the above mentioned models.

The values of the conductivity at zero temperature are a distinguishable difference between tunnelling and hopping conduction. Since tunnelling between localized electronic states is phonon assisted, the hopping conductivity vanishes as the temperature falls to zero. Since tunnelling process is temperature

independent, and depends only on the height and shape of the potential barrier separating the carriers, conductivity does not extrapolate to zero. As the temperature is decreased, fewer states fall within the allowed energy range and the average hopping distance increases. As a result, the hopping probability and thus, conductivity decrease.

1.4 Electrical conductivity and carrier transport

A great deal of work had been done for the characterization and understanding of electrical transport in conducting polymers. The factor limiting the conductivity is the carrier mobility, along with the carrier concentration. The doping process produces a generous supply of potential carriers, but to contribute to conductivity they must be mobile. There are at least three elements contributing to the carrier mobility: single chain or intramolecular transport, interchain transport, and interparticle contact. These three elements comprise a complicated resistive network (illustrated in the Fig. 1. 1), which determines the effective mobility of the carriers. Thus, the mobility and therefore the conductivity are determined on both a microscopic (intra- and interchain) and a macroscopic (interparticle) level ³⁷.

In conjugated polymers, ionisation results in substantial distortion of the lattice around the ionised states, similar to all organic materials. So, as a charge carrier moves through the polymer, due to this distortion of the lattices, mobility is reduced. Since disorder plays such a dominant role in conducting polymer systems, the mechanism of carrier transport is more akin to that in amorphous semiconductors (hopping transport) ³⁸.

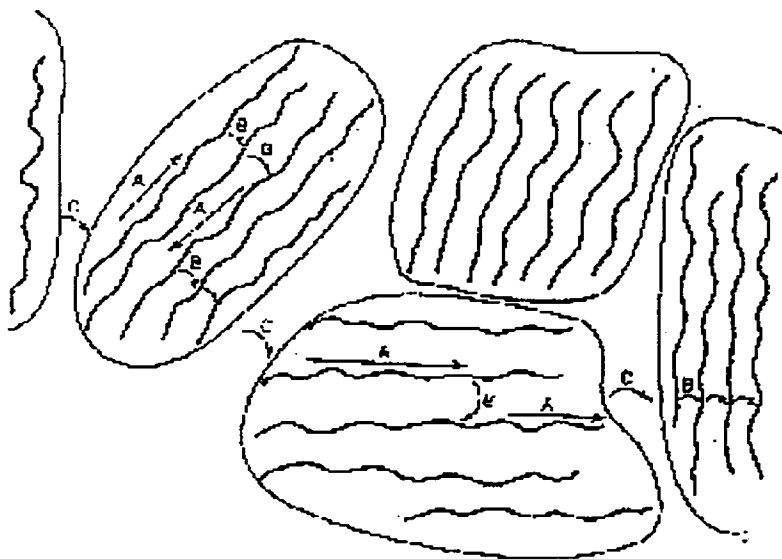


Fig.1.1 Conductivity network of a conducting polymer with A indicating intrachain transport of charge, B indicating interchain transport, C indicating interparticle transport, and arrows showing path of a charge carrier migrating through the material

1.5 Charged defects in conjugated polymers : Theory of conduction

The theoretical work on conducting polymers has been mainly concerned with radical and ionic sites, referred to as neutral and charged defects, respectively. The movement of the defect can be described mathematically as a solitary wave, or "soliton" in the language of field theory³⁹⁻⁴². The radical defect is referred to as a neutral soliton; the anion and cation defects are charged solitons. Charged solitons (anions or cations) can explain the spinless transport, since they carry charge but no spin.

The initial species formed on the ionisation of a conjugated polymer is a radical ion, which possess both spin and charge^{43,44}. In the language of solid-state physics, the radical ion is referred to as a polaron. A polaron is either a positively

charged hole site (radical cation) or a negatively charged electron site (radical anion), plus a lattice relaxation (distortion) around the charge. Theoretical models⁴³ demonstrate that two radical ions (polarons) on the same chain react exothermically to produce a dication or dianion (bipolaron) ,which are responsible for spin less conductivity in these polymers.

1.6 Microwave conductivity

All dielectric materials are characterized by their dielectric parameters such as dielectric constant, conductivity and polarization⁴⁵⁻⁴⁷. In conjugated polymers, ionisation results in substantial distortion of the lattice around the ionised states, similar to all organic materials. So, as a charge carrier moves through the polymer, due to this distortion of the lattices, mobility is reduced. Since disorder plays such a dominant role in conducting polymer systems, the mechanism of carrier transport is more akin to that in amorphous semiconductors (hopping transport)³⁸.

Microwave technology owes its origin to the design and development of Radar. In the earlier stages of development, phased array technique is used for the beam steering in Radar. It is a very complicated design and it needs mechanical work for the beam steering. Poly o-toluidine can easily undergo a dipolar polarization when the microwave frequency is applied⁴⁸. This property can be utilized for developing systems for electronic beam forming in Radar. The materials with low D.C. conductivity, but high microwave conductivity (poly o-toluidine) can be used to develop microwave communication link⁴⁸. It is also very useful in satellite communication, i.e, to prohibit stray signals and to allow the passage of microwave signals.

The determination of the complex permittivity and conductivity is based on the theory of perturbation. When a dielectric material is introduced in a cavity

resonator at the position of maximum electric field, the contribution of magnetic field for the perturbation is minimum.

In microwave studies the conductivity can be calculated using the equation,

$$\text{Conductivity, } \sigma = 2\pi f_s \epsilon_0 \epsilon_r''$$

where 'f' is the resonant frequency, ϵ_0 is the permittivity of vacuum and ϵ_r'' is the imaginary part of the complex permittivity, which is given by the equation,

$$\epsilon_r'' = (V_c / 4V_s) (Q_t - Q_s / Q_t Q_s)$$

where, 'V_c' is the volume of cavity, V_s is the volume of sample, Q_s is the quality factor of the cavity loaded with the sample and Q_t is the quality factor of the cavity with the empty sample holder. Quality factor 'Q' is given by

$$Q = f / \Delta f$$

where 'f' is the resonant frequency and 'Δf' is the corresponding 3dB bandwidth. The real part of the complex permittivity 'ε_r' is usually known as dielectric constant of the material. It can be calculated from the equation,

$$\epsilon_r' = 1 + (f_t - f_s) / 2f_s (V_c / V_s)$$

where 'f_t' is the resonant frequency of the unloaded cavity and 'f_s' is the resonant frequency of the cavity loaded with the sample. The imaginary part, ε_r'', of the complex permittivity is associated with dielectric loss of the material.

1.7 Poly (azomethine)s

Poly (azomethine)s, sometimes called poly(schiff bases), are a group of polymers which are catching more attention due to the following reasons. Fully aromatic poly (azomethine)s are highly thermo-stable in analogy to aromatic polyethers. Further more, fully aromatic poly (azomethine)s may possess a conjugated main chain and, after suitable doping, may show an attractive level of electric conductivity.

Most polycondensations of aromatic dialdehydes and diamines were conducted in solutions⁴⁹. Three kinds of solvents were used: benzene and toluene⁵⁰⁻⁵² to allow azeotropic removal of water, polar aprotic solvents, such as DMF, DMA, NMP or DMSO⁵³⁻⁵⁷ or, protic solvents such as acetic acid and m-cresol⁵⁸. Regardless of solvent most aromatic poly (azomethine)s are insoluble in common organic solvents and precipitate from the reaction medium, in particular if they are built up by para-substituted monomer units. Precipitation entails an almost complete stop of the chain growth process, and thus, strongly limits the resulting molecular weights. Azeotropic distillation of water with benzene or toluene accelerates the condensation and enhances the yields, but it does not significantly increase the degree of polymerisation, which is limited by the solubility of the polymers in the reaction medium. In this regard polar aprotic solvents, or the aforementioned protic solvents are advantageous, because poly (azomethine)s are better soluble in these polar reaction media. When the reaction is carried out in m-cresol at 200^oC, the polymers remained in solution over the whole course of the condensation and the molecular weight of the polymer is comparatively high.

Only a few poly (azomethine)s derived from aliphatic dialdehydes and aromatic diamines were described in literature, and most of them were prepared by solution condensation of diamines and glyoxal⁵⁹⁻⁶¹. High yields and satisfactory elemental analyses were reported, but no information on viscosity and molecular weights.

In the present study, the monomers, glyoxal and p-phenylene diamine was selected for the synthesis of a new conducting polymer. P-phenylene diamine introduces an aromatic ring in the polymer that helps to increase the thermal stability of the polymer. Solvents selected for carrying out the condensation reactions are methanol, DMF, m-cresol and toluene, which include all types of solvents mentioned above. This helps to compare the properties of the polymer formed under different conditions.

1.8 Conducting polymer blends

Conducting polymer composites have drawn considerable interest in recent years because of their numerous applications in a variety of areas of electrical and electronic industry⁶²⁻⁶⁴. Most of the conducting polymers are insoluble in common organic solvents and so the casting of it into film or other forms that are useful for different applications is very difficult. Similarly, conducting polymers like polyacetylene are unstable in air and their conductivity changes with time due to their interaction with air, oxygen, etc. The major drawbacks of conducting polymers like environmental instability and difficult processibility can be overcome by preparing their composites with other polymers. Incorporation of conducting polymers into a host polymer substrate, forming a blend, composite or interpenetrated bulk network has been used as an approach to combine electrical conductivities with desirable mechanical strength of polymers⁶⁵. Interpenetrating network conducting composites result through in situ polymerization of monomers of conducting polymers inside the matrices of the conventional linear polymers.

Conducting polymer blends with unusually low percolation threshold has been reported for polyaniline and styrene –butyl acrylate copolymer blends⁶⁶. Polyaniline – Epoxy Novolac Resin composite has been reported to be useful for antistatic applications⁶⁷. Interpenetrating networks of polypyrrole filaments in swellable insulating plastic matrices have been produced in electrochemical cells^{68,69}.

1.9 Electrically Conductive Elastomers

Elastomers and plastics are insulators to which conductivity is imparted by the addition of finely divided or colloidal filler of high intrinsic conductivity, such as carbon black. Conductive rubber compounds were first put to use for the prevention of corona discharge in cables. Large quantities of graphite or other

coarse carbon blacks or powdered metals were employed to produce conductivity in rubbers. Addition of acetylene black and other conductive blacks yielded conductive rubber with improved mechanical properties. Rubbers filled with furnace black showed antistatic properties. Non-insulating antistatic rubbers are now used in many situations where explosive (or inflammable) vapours, liquids, or powders are being handled. Effect of temperature on conductivity follows Arrhenius type of equation and estimation of activation energy for electrical conduction is possible. Conductive rubbers are used in various disciplines. E.g. sensors, electrochromic displays, EMI shielding, electrostatic discharge dissipation (ESDD), conductive pressure sensitive rubbers, fuel cells, circuit boards etc⁷⁰.

The basic and generally accepted concepts of conductivity are based on the fact that carbon black forms aggregates or network structures in the compositions⁷¹⁻⁷². The degree of conductivity depends on the nature of these chain structures. In recent years papers relating to the effect of various factors influencing the conductivity of polymer compositions containing carbon black have been published- like type of carbon black^{71, 72}, concentration of carbon black⁷², type of polymer^{73,74}, temperature^{72,75} and degree of dispersion of carbon black in the polymer matrix^{76,77}. The effect of mixing time on electrical and mechanical properties on SBR vulcanizates has been reported⁷⁸.

Bulgin⁷⁹ has critically analyzed the importance of cure conditions with reference to the electrical properties. The effect of processing parameters on resistivity of NR vulcanizates is also reported⁸⁰. Jana⁸¹ reports electrical conduction in short carbon fibre filled polychloroprene composites. Abo-Hashem et al.⁸² reports the effect of concentration and temperature dependence of butyl rubber mixed with SRF carbon black.

1.10 Conductive fillers

For many years, finely divided carbon black has been a valuable addition to electrically conductive polymers, including rubber compounds and the resulting

composite materials exhibit a wide spectrum of conductivity depending on the loading of the carbon black. It is used to enhance their conductivity and cost effectiveness. Many grades like channel black, thermal black, furnace black, acetylene black etc. are available from the combustion of hydrocarbon feed stocks. The high structure and surface area of conducting carbon blacks facilitate the contact probability of aggregated carbon black by decreasing the particle –to-particle distance. Sometimes carbon black can be hybridised with carbon fibre in compounding so as to reach the optimum electrical conductivity, enhanced mechanical properties, and improved processability.

Acetylene blacks have been attractive to compounders desiring high electrical conductivity. X-ray spectrographic analysis shows acetylene black to have, in part, a graphite structure with a lace-like acicular or fibrous aggregate of carbon particles. About 70% of the particles occur in the 25 to 60 nanometer size range. ‘Vulcan’ XC-72 carbon black also appears to fall in this range of good electrically conductive carbon black. ‘ketjen’ carbon black is also well recommended. Furnace blacks produced by thermal decomposition of oil fed stocks, and channel blacks produced by natural gas flames on water-cooled channel iron have prominent roles in materials used by the plastics and the rubber industry⁸³⁻⁸⁴.

Other conductive additives are:- polyacrylonitrile (PAN) carbon fiber, metal-coated carbon fiber and in particular nickel-coated graphite fiber, stainless steel fibers, aluminium fibers, metallized glass fibers, aluminium flakes, metal powders, metal-coated glass beads, metal-coated mica and graphite powder.

1.11 Electrical conduction in carbon black loaded rubber vulcanizates

The particles of carbon black are not discrete but are fused ‘clusters’ of individual particles^{84,85}. These aggregates are the working unit in vulcanized rubber. At low loadings of carbon black, the conductivity of the composite is very

