Defence Science Journal, Vol 46, No 2, April 1996, pp 91-104

Conducting Polymers : Emerging Commercial Materials

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ABSTRACT

Conducting polymers are materials of recent origin. They are obtained by polymerisation of simple organic monomers and doping with electron acceptor or donor species and show conductivity ranging from that of a semiconductor to that of metal. These materials are now available with unique electronic and optical properties of metals and semiconductors in combination with the attractive mechanical and processable advantages of polymers. The field has progressed to a level of maturity consistent with a new set of opportunities to develop wide range of applications based upon conducting polymers as materials for industrial products. Examples include: static charge dissipation, EMI shielding, flexible light emitting diodes, transparent electrodes, batteries, gas sensors, gas separators, etc. Many of the conducting polymers and devices based on them are now available commercially.

1. INTRODUCTION

The earlier concept that the name polymers is synonymous with an electrically insulating material is no longer true in all the cases. There now exist certain polymers whose conductivities range from that of a semiconductor to that of a metal (Fig. 1) and such materials are classified as conducting polymers. The first conducting polymer was obtained by a group of American Scientists[1] in 1977 from the common gas acetylene used for welding purposes. This report led to the synthesis of large number of conducting polymers derived from a variety of organic monomers, such as acetylene[1], heterocyclic[2,3] and aromatic[4-7] compounds (Fig. 2). One of the most important criteria for the selection of these monomers is the formation of alternate single and double bonds (conjugation) in the backbone of their polymer chain.

The conductivity in these polymers arises on their doping with electron donor or electron acceptor species. The important criteria for the doping of these polymers are low values of ionisation potentials (<6 eV) and high values of electron affinities (>2 eV). The important dopant species are:

Electron donors :

Li^+, Na^+, K^+, Ag^+, etc.

Electron acceptors:

Cl^-, ClO_4^-, BF_4^-, AsF_6^-, $Sb6^-$ *etc.*

The combination of metal-like or semiconducting conductivities and other properties, such as low density, flexibility, processability, transparency, optical changes (linear and nonlinear), film/fibre formation, low environmental contamination, redox behaviour and above all modulation/tuning of many of the properties via Organic Chemistry, have generated great commercial interest in these materials[8]. In fact, at present a number of commercially viable products based on conducting polymers have been demonstrated (Table 1)[9-13]

In addition to the products mentioned in Table 1, some of the conducting polymers, e.g. polyaniline powder (trade name Versicon) and polyaniline blend with PVC (trade name Incoblend) from Zipperling Kessler, Germany, polypyrrole powder (trade name Basotronic) and polypyrrole film (trade name Lutamer) from BASF, Germany and polyphenylene vinylene from UNIAX Corporation, USA, are available commercially. Projections are that a billion dollar industry based on conducting polymers and their products will be in existence by the turn of the century. In India, a number of laboratories, including Defence Laboratory (DL),

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Received 10 October 1994, revised 29 May 1995

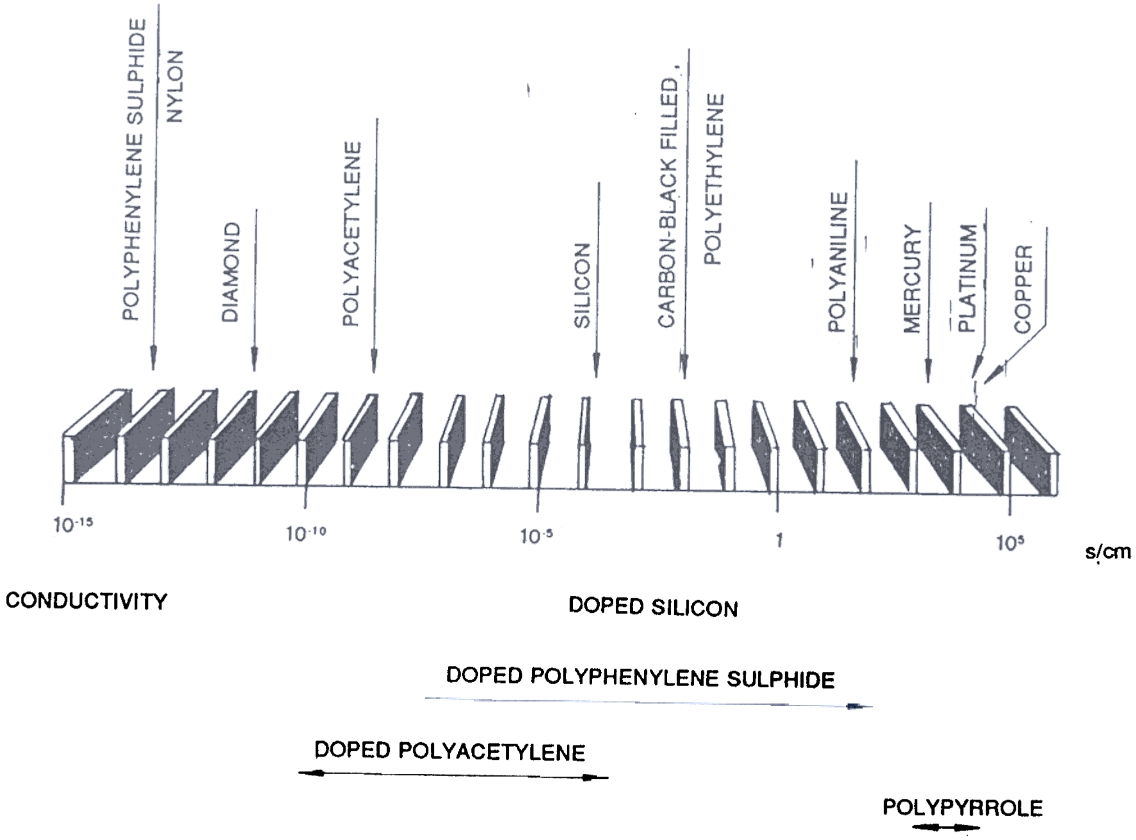

Figure 1. Electrical conductivities for common materials and conducting polymers.

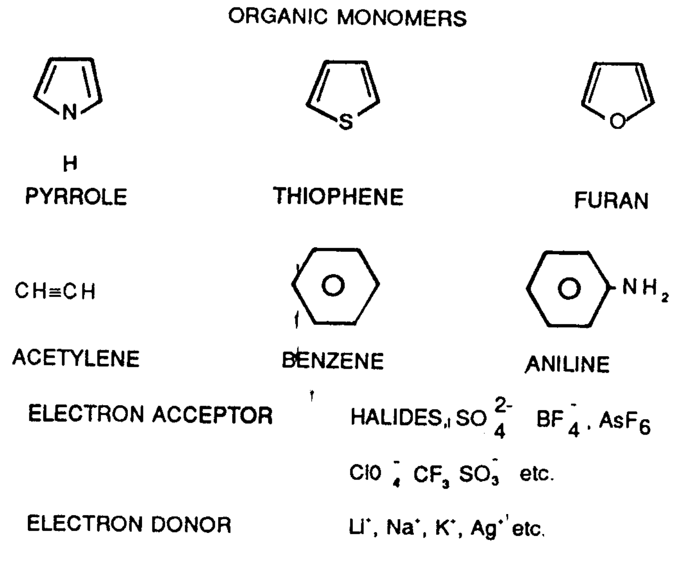

Figure 2. Common organic monomers and dopants forming conducting polymers.

Jodhpur, are involved in R&D work on conducting polymers. Defence Laboratory, Jodhpur, has been successful in indigenous development of the technical know-how for making some of the known as well as new conducting polyanilines in kilogram quantities.

2. SYNTHESIS OF CONDUCTING POLYMERS

There is no singular method for synthesising polymers that can be transformed into conductors. In designing polymer synthesis the incorporation of the extended π-electron conjugation is of the foremost importance. In general, both chemical and electrochemical polymerisation procedures have been used[14].

In the chemical procedures for the synthesis of the neutral conducting polymer precursors, the commonly used methods are adopted, e.g. polymerisation methods of Ziggler-Natta, Freidel-Crafts, and nucleophilic displacement generate polyacetylene[15], poly (paraphenylene)[1], and poly (*P*-phenylene sulphide)[16], respectively. Other methods include sulphonium polyelectrolyte precursor method[17] and dehydrohalogenation method[18] for the synthesis of poly (para phenylene vinylene) (PPV). The pristine polymers thus obtained are subsequently doped by their reaction with electron donor or electron acceptor species.

Table 1. Commercially available conducting polymer-based products

Product	Corporation	Conducting polymer (Trade name)
Electrolytic capacitor	Matsushita/Panasonic (Japan)	Polypyrrole (SP cap series)
Rechargeable battery	Bridgestone-Seiko (Japan) Vatra Batterie, BASF (Germany)	Polyaniline (AL920, AL2016, AL2032) Polypyrrole (Knopfzelle 2025)
High capacity (4MB) magnetic disk for IBM & Toshiba drives	Hitachi-Maxell (Japan)	Polyaniline (MF2-ED)
Conducting polymer coated disk electrode	Elchema (USA)	Polypyrrole & polyaniline (E-101-104)
Conducting coatings for textiles	Milliken & Co. (USA)	Polypyrrole (Contex)
Plating bath for *Cu* deposition on PCBs	Blasberg (Germany)	Polypyrrole (DMS-2, 4 process)
Conducting polymer powder	Allied-Signal (USA) Neste (Finland) Hexcel (USA)	Polyaniline (Versicon) (CP-EX-1)
Conducting powder	Polaroid (USA)	Polypyrrole (ICP-117)
Transparent coatings	Zipperling-Kessler (Germany) and Americhem (USA)	Polyaniline (Incoblend)
Themoplastic polymer blends	Americhem (USA) and Zipperling-Kessler (Germany)	Polyanilline
Antistatic electronic component carriers	IBM (USA)	Polyaniline

Electrochemical procedure has mainly been used in the synthesis of polymers of heterocyclic compounds, such as pyrrole[19], thiophene[20], furan[21], carbazoles[22], azulene[22] and isothiaphnaphthene[23]. This method offers the advantages of homogeneous incorporation of dopant counterions into the polymer film as it is grown and of close control over the polymerisation parameters, viz., current density and voltage. The method is limited, however, by the fact that the yield of polymer is restricted to the area of the working electrode. For this reason (among others), chemical syntheses are used when large quantities are required. Some of the conducting polymers are now available commercially (Table 2)[12].

In the Laboratory, both electrochemical and chemical methods have been employed to synthesise a number of conducting polymers derived from the organic monomers, such as aniline, pyrrole, thiophene, methylthiophene, furan and doped with common electron acceptors, such as Cl^-, BF_4^-, ClO_4^-, $CF_3SO_3^-$ etc. Further, a new concept of doping of polyaniline with complex metal[24] and mixed metal ions was developed which led to the formation of conducting polyanilines showing thermal stability up to 150°C and electrical conductivity ranging from 10^{-6} to 10^3 S/m.

Table 2. Commercially available conducting polymer

Materials	Maximum conductivity (S/m)	Structure	Available from
Polyacetylene	1.5×10^7	Alternating single and double carbon-carbon bonds	Not commercially available
Polypyrrole	2.0×10^5	Five-membered ring containing nitrogen and alternating signal and double carbon-carbon bonds	BASF Group, Ludwigshafen, Germany; Neste Oy, Espoo, Finland; Polaroid Corp., Cambridge, mass.
Polyphenylene vinylene	1.0×10^5	A combination of polyacetylene and polyphenylene	Uniax Corp., Santa Barbara, California, USA
Polyphenylene sulphide	1.0×10^4	Benzene rings linked by sulphur atoms	Hoechst-Celanese, Summit N.J.; Phillips 66, Bartlesville, Okla.
Polythiophene	1.0×10^4	Five-membered ring containing sulphur and alternating single and double carbon-carbon bonds	Allied-Signal Inc., Morristown, N.J.; BASF Group, Neste Oy
Polyaniline	1.0×10^3	Benzene rings linked by nitrogen atom	Allied-Signal, Americhem, Inc. Cuyahoga Falls, Ohio; Hexcel Corp., Dublin, Calif.; Lockheed Corp., Calabasas, Calif.; Neste Oy; Zipperling Kessler & Co., Ahrensburg, Germany.
Polyaniline	3.0×10^3	Benezene rings linked by N_2 atoms	Defence Lab, Jodhpur.

3. CHARACTERISTICS OF CONDUCTING POLYMERS

Determination of chemical and physical properties of these materials is of both scientific and technological interest. The standard techniques used for the characterisation of conducting polymers are given in Table 3.

Table 3. Known techniques for characterisation of conducting polymers

Properties	Techniques
Electrical conductivity	Four-point resistivity probe
Magnetic	Vibrating sample magnetometer, B-H curve, AC-susceptibility, EPR
Optical*	UV-, VIS-, IR-spectroscopy
Morphology, surface	Scanning electron microscopy
Structural	XRD, IR, NMR-spectroscopy
Thermal & glass transition	DTA, TGA, Calorimetry
Electrochemical	Potentiostat/Galvanostat, Polarography
Microwave	Waveguide, Network analyser
Chemical	*C,H,N* analysis, Atomic Absorption spectrophotometer, ASCI, X-ray, IR-, UV-, VIS-spectroscopy
Molecular weight	GPC, Osmometry Light Scattering

* ESR and optical studies provide very useful information about the nature and concentration of charge carriers.

3.1 Electrical Properties

Conjugated organic polymers in their pure (undoped) state are described as electrical insulators. Electrical conductivity in most of these polymers is not intrinsic and arises due to doping with electron acceptor or donor species. The coductivity, (σ) is proportional to the product of the free carrier concentration, n, and the carrier mobility, μ .

$$\sigma = n\, e\, \mu$$

Due to relatively large bandgaps, the concentration of free carriers in these materials is very low at normal temperatures. Therefore, even though conjugated polymers have backbone structures well suited to conduction (i.e. high carrier mobilities) the low carrier concentration results in negligible conductivity.

The doping of conducting polymers, accomplished by oxidation or reduction with electron acceptors or donors respectively, results in increase in carrier concentrations and hence higher conductivities. Description of this process as doping is somewhat misleading since dopant concentrations are extremely high as compared to those commonly encountered in doped inorganic semicohductors (typically in parts per million range). In some cases, the dopant constitutes

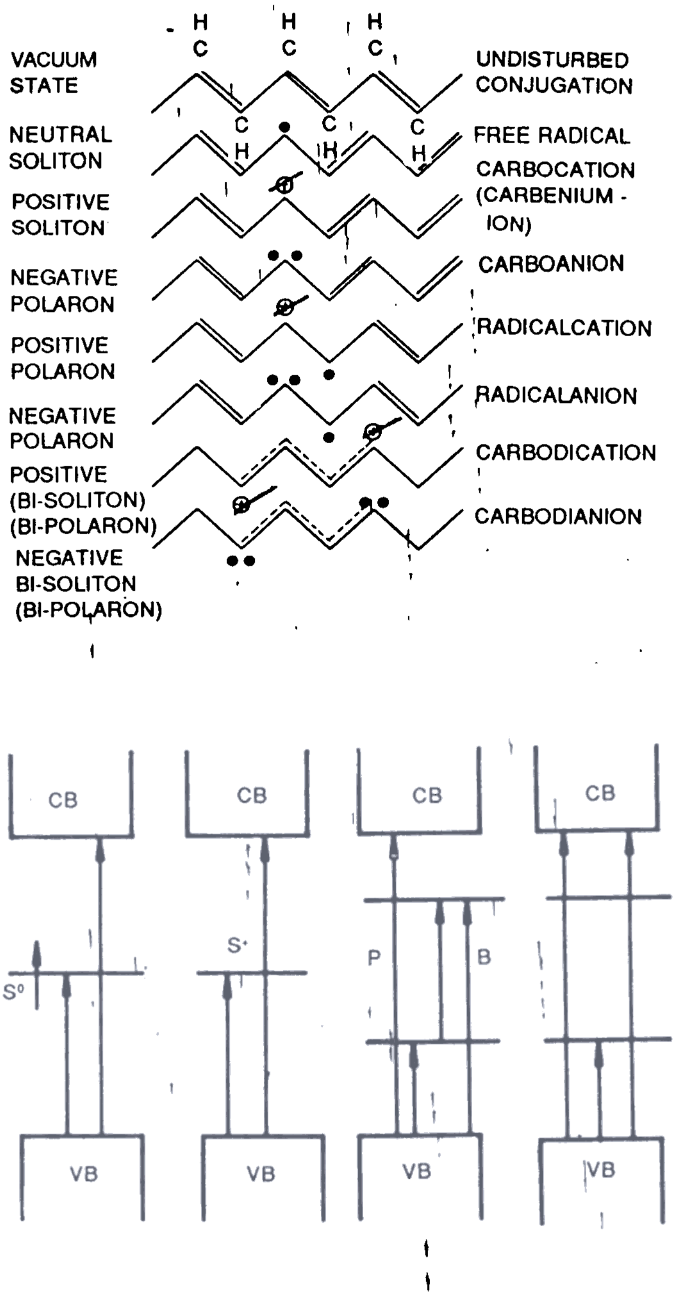

Figure 3. Formation of charge carriers and their energy levels.

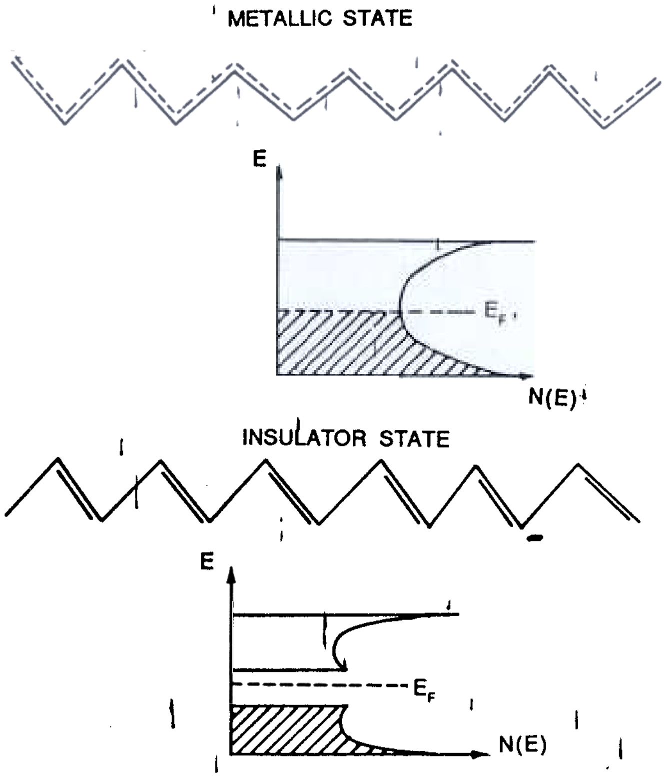

Figure 4. Peierls transition in polyacetylene (Ref. 26).

about 50 per cent of the final weight of the conducting polymer composition[25]. However, the doping terminology is so ingrained in the literature that it has been accepted for common use.

3.1.1. Charge Carriers

In traditional three-dimensional semiconductors, the four-fold (or six-fold, etc.) coordination of each atom to its neighbours through covalent bonds leads to a rigid structure. In such systems, therefore, the electronic excitations can usually be considered in the context of this rigid structure leading to the conventional concept of electrons and holes as the dominant excitations. The situation in conducting polymers is quite different; the two-fold coordination makes these systems generally more susceptible to structural distortion. As a result, the dominant 'electronic' excitations are inherently coupled to chain distortions. Thus, in this class of materials the solitons, polarons and bipolarons (Fig. 3)[26] are the important excitations leading to the change in geometry of the polymers due to electron-photon coupling.

The ground state of trans-acetylene is a two-fold degenerate Peierls insulator which allows for the possibility of nonlinear excitations in the form of soliton-like bond alteration domain walls, each with an associated electronic state at the centre of the energy gap (Fig. 3). These solitons are believed to be responsible for many interesting properties of the system, including doping mechanism.

Because of the Peierls instability [27,28] adjacent (CH) groups move towards each other, forming alternatively short (or double) bonds and long (or single) bonds, thereby lowering the electronic energy by opening an energy gap at Fermi level (Fig. 4). The existence of bond alteration in trans-$(CH)_x$ is fundamental to the concept of soliton and it has been verified in its ground state structure through X-ray scattering[29] and by observation of appropriate dipolar splitting in NMR studies.[30].

The soliton in $(CH)_x$ is a topological kink in the electron-lattice system, a bond alteration domain wall connecting the two phases with opposite bond alteration. Since, there is a translational asymmetry (the kink can be anywhere) and since the mass is small, the soliton should be mobile. Associated with the structural kink is a localised energy state in the mid-gap. This electronic state is a solution of the Schrödinger equation in the presence of structural domain wall and therefore can accommodate 0,1,2 electrons. The neutral soliton has one electron in the mid-gap state; the positive and negative charged soliton's have zero and two electrons, respectively, in the mid-gap state. The unique reversed spin-charge relation's for solitons are summarised in Table 4.

Table 4. Reverse spin-charge property of solitons

Charge		Spin
	$Q = 0$	
Positive,	$Q = +e$	S
Negative,	$Q = -e$	$S = 0$

Change in electronic structure due to charge injection provokes a local modification in geometry which, in turn, induces new electronic states in the band-gap. The net result is the formation of polarons and bipolarons as the charge excitations.

Formation of polaron, i.e. radical ion is associated with local distortion of the lattice (of the chain geometry) and presence of two localised electronic states in the gap (Fig. 3). It is to be noted that polaron formation is generally favoured in a conjugated polymer because the gain in ionisation energy more than compensates for the increase in elastic energy required by the local appearance of a geometric structure of higher energy. Polaron formation leads to the possibility of at least three new optical transitions below the gap[31].

When a second charge is injected into the chain, it is usually the case that the two charges combine to form a diionic defect species known as bipolaron (Fig.3). The bipolaron is spinless since the two localised electronic states in the gap either fully occupied (*n*-type doping) or empty (*p*-type doping). Only two optical transitions can be obtained below the gap since the transition between the two gap levels is no longer possible. Further, the formation of bipolaron on doping in certain polymer chains is responsible for the very unusual spinless conductivity regime and/or electrochromic effects which are experimentally observed in such materials[32].

3.1.2 Charge Transport

In designing models for carrier transport in doped conjugated polymers, analogies to doped inorganic semiconductors are very useful. In both cases, doping introduces new electronic states within the bandgap of the material which can be thermally populated and depopulated with electrons leading to increased (extrinsic) carrier concentrations. At high dopant concentrations, these states interact strongly with each other and, as a result, the overlap of their electronic wavefunctions yields a band of electronic states within the gap instead of discrete levels[33,34]. The temperature dependence of conductivity is, however, dependent on the dopant concentration in the case of conducting polymers[34]. Further, the mobility of charge carriers in conducting polymers is lower as compared to those in inorganic semiconductors due to the influence of the lattice structure of the material on transport. Another feature of conducting polymers is the observation of spinless conductivity-an effect first observed for doped polyacetylene.

Further study of carrier transport with both ac and dc conductivity measurement techniques[32] has generated a model based on variable range hopping of the carriers (Fig. 5); this model takes into account the inherent disorder of the material and the additional disorder induced by doping[35]. In doing so, it explains the conductivity data but fails to account for the low-spin concentration quantitatively. Another explanation of conductivity in doped polymers, particularly in polyaniline, is based on a picture of metallic islands in an insulating matrix[36], a model commonly applied to metal-filled plastics. In this case, carriers tunnel through the neutral, undoped regions of the polymers which constitute the insulating matrix separating the conducting regions. Conductivity *vs* dopant concentration curve (Fig. 6) has been taken as evidence for a 'percolation' phenomenon[37]. Though this model also fails to explain spinless conductivity, some support for percolation phenomenon is found in dielectric measurements on doped polyacetylene[38].

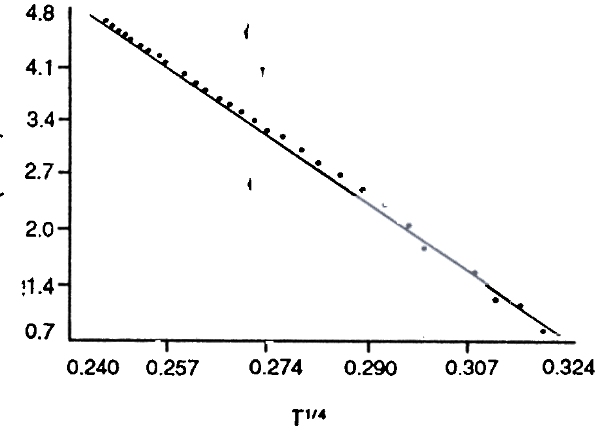

Figure 5. Variable-range hopping plot for $FeCl_4^-$ doped polyaniline.

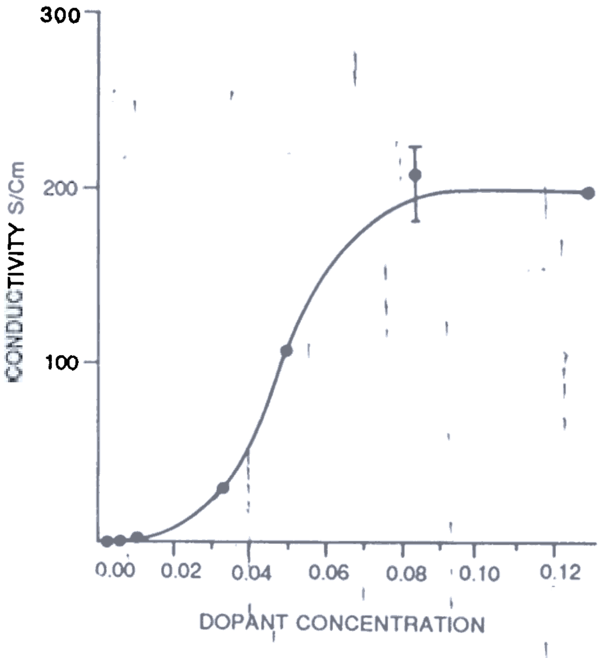

Figure 6. Conductivity of trans-polyacetylene *vs* AsF_5 dopant concentration; *y* given by the formula $(CH(AsF_5))_x$.

Though the mechanism of carrier transport in doped conjugated polymers has not been fully established, it is clear that disorder plays an important role. For that reason variable range hopping is an attractive concept for further exploration in doped conjugated polymers. Further, the metallic islands could also be important, particularly at high dopant concentrations. Their existence is likely to be controlled by disorder in the starting material and homogeneity of the doping process. Finally, theoretical explanations for spinless conductivity are still qualitative and require further theoretical and more detailed experimental studies of the broad spectrum of the doped conjugated polymers which are now available.

3.2 Optical Properties

Optical properties of conducting polymers are important to the development of an understanding of the basic electronic structure of materials. The *in situ* techniques[39] used for studying the charge-transfer doping reactions in conducting polymers have made it possible to determine the nature of the charge storage state as well as to monitor the kinetics of the charge transfer reactions. Further, these studies have played an important role in clarifying the chemistry and physics of conducting polymers. The existence of π-conjugation in conducting polymers is implied by their colours and their electronic spectra. The electronic spectra of certain key conducting polymers in their film form or solution form have been studied and the bandgap energies derived from these results are given in Table 5.

Table 5. Bandgap energies of key conducting polymers

Polymer	Bandgap energy (eV)
Trans-polyacetylene	1.4
Poly(*p*-phenylene)	3.2
Polydiacetylene	2.1
Poly(*p*-phenylene sulphide)	4.0
Polypyrrole	3.0
Polyaniline	1.9

It has been observed[40-42] that the spectral characteristics of solution-cast films are nearly identical with those of synthesised films, wherein the π-π * absorption edges neither shifted nor significantly broadened. In addition, the residual absorption below the interband transition is extremely weak for the solution cast films, indicating the absence of impurity or disorder-induced states in the gap.

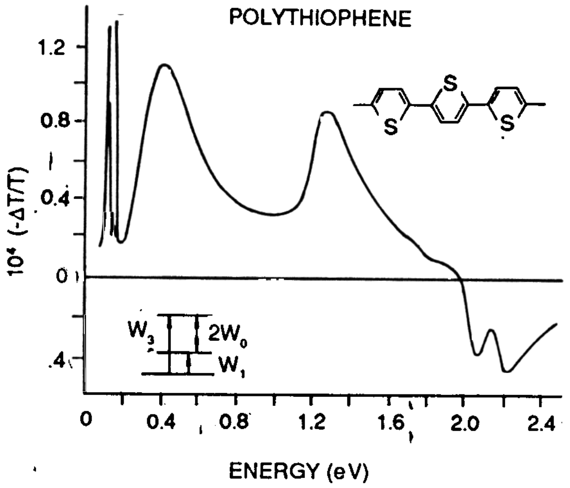

Figure 7. Photo-induced absorption difference spe trum of neutral

Absorption studies of neutral and doped polymers at different doping levels lead to the information about the nature of charge carriers in the species. Photo-induced absorption measurements[43] have demonstrated that charged solitons and bipolarons are stable species on conjugated polymer chains, even in the absence of dopants (Fig. 7). This is the essential connection between electrical conductivity aspects and nonlinear optics aspects; they demonstrate that conjugated polymers inherently possess very high nonlinear optical responses since upon illumination there occur major shifts in oscillator strength's. Thus, the very same defect species, i.e. solitons, polarons and bipolarons, which play a major role in the transport properties upon doping, are also the source of the nonlinear optical properties.

3.3 Magnetic Properties

In the case of organic polymers the magnetic properties depend strongly whether or not unsaturated sequences exist in the carbon backbone[44]. While saturated systems, like polyethylene or polyvinylchloride exhibit only the expected diamagnetism, polymers containing sequence of polyvinyl type, the category to which the conducting polymers also belong, are strongly paramagnetic. Table 6 presents some typical values of the magnetic susceptibility of characteristic systems. The origin of paramagnetism in organic conducting polymers is due to a carbon

π-electron system. In terms of an energy band description, the π-bond lead to a partially-filled energy band structure which is responsible for the important electronic properties of these systems. Paramagnetism appears when unpaired π-electrons are stabilised on macromolecules of sufficient size.

Table 6. Typical values of the magnetic susceptibility for various materials

System	Susceptibility (emu/mol)
Li (metal)	χ_p ~ 2×10^{-6}
Polyethylene (insulator)	χ_{dia} ~ -8×10^{-7}
Irradiated (semiconductor)	χ_{para} ~ 10^{-7}
Polyvinyl chloride	
Benzene (insulator)	χ_{dia} ~ -55×10^{-6}
Si (semiconductor)	χ_{dia} ~ -3×10^{-6}
Trans-$(CH)_x$ (semiconductor)	χ_{para} ~ 10^{-6}
Cis-$(CH)_x$ (semiconductor)*	χ_{para} ~ 3×10^{-8}

Absolute value in emu/mol of π-bonded carbon.

Measurement of magnetic susceptibility is, in principle, easy to perform using a Faraday balance[45]. In fact, the measured susceptibility is generally the sum of two or more components of different signs and magnitudes. It is often possible to use the different temperature dependence of each component to recognise each contribution; nevertheless it is generally difficult to deduce their absolute values.

Electron spin resonance (ESR) has largely been used as a complimentary technique[46] to study the magnetic properties of polymers. The good resolution of the technique allows discrimination between unpaired electrons belonging to different atoms or molecules. The spectrum parameters, such as multiplicity, position, shape, linewidth, intensity and symmetry can be analysed in terms of static and dynamic characteristics of the paramagnetic species.

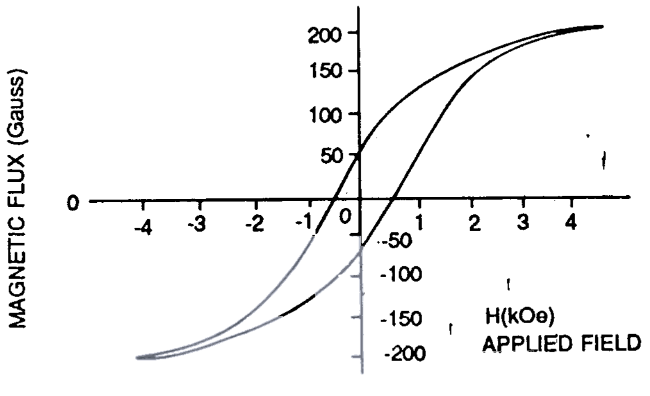

Figure 8. B-H curve of complex metal ion-doped copolymer of anilineformaldehyde.

Recently, ESR technique has been used to measure magnetic susceptibility of PANI-CSA and PANI-DBSA, both in their blend and solution forms[47]. In both the cases the magnetic susceptibility was reported to be temperature independent which implies a metallic state[48] with Pauli spin susceptibility, χ_P, resulting from a density of states at the Fermi level, of about one state per eV per two rings. Presence of Pauli susceptibility (which is related to the metallic state) indicates that these complexes are the first of metallic polymers in solutions, i.e. stable liquid metals.

Recently, an organic polymer, poly BIPO[49], has been reported to show ferromagnetism with a Curie temperature of 150 °C; however, the reproducibility of material could not be achieved by other groups. Other systems, like quasi one-dimensional charge transfer salts[50], polynuclear complexes[51], and Schiff bases[52] have also been reported to show ferromagnetic coupling at very low temperature (below 20 K). The fact that conducting polymers have a particular type of charge carriers, viz., polarons which have spin, generated great interest to obtain these materials with long range order of spins but so far there is no such report in the literature. Recently, we have observed that a synthesised copolymer of anilineformaldehyde doped with complex oxide of iron and cobalt is attracted towards a simple bar magnet. This observation made us curious to investigate the magnetic character of this material as well as the origin of the phenonmenon causing it. Some of our findings are discussed in the following.

For determining the bulk magnetic properties, the material has been studied using vibrating sample magnetometer, and a *B-H* loop (Fig. 8) has been obtained with saturation magnetisation value of 194 gauss, coercivity 560 kOe and squareness ratio of the loop 0.32. The study clearly indicates the presence of magnetic ordering in the material.

The material has further been examined microscopically at room temperature by using ^{57}Fe Mössbauer spectroscopy and X-ray diffraction techniques. The ^{57}Fe Mössbauer studies show a pure six-line spectrum (Fig. 9) indicating that the iron ions are in magnetically ordered environment. On making computer analysis[53], it is observed that the six-line pattern consists of two sextets which are due to iron ions in two different environments with effective magnetic field values of 476 kOe and 440 kOe. Further, the isomer shift values (0.32 mm/s and 0.42 mm/s) show that the iron is in +3 oxidation state[54] at both the sites while zero quadrupole splitting values indicate that there exists charge symmetry around the iron nuclei at both the sites. The presence of two sextets and high symmetry around iron nuclei may point towards the presence of a cobalt ferrite phase; however, the values of effective magnetic fields at both the sites are different from those of cobalt ferrite[55].

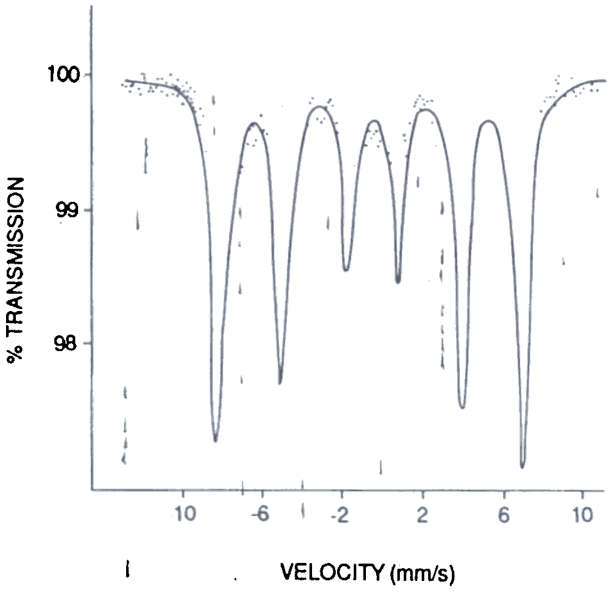

Figure 9. Room temperature ^{57}Fe Mössbauer spectrum of complex metal ion-doped copolymer of anilineformaldehyde.

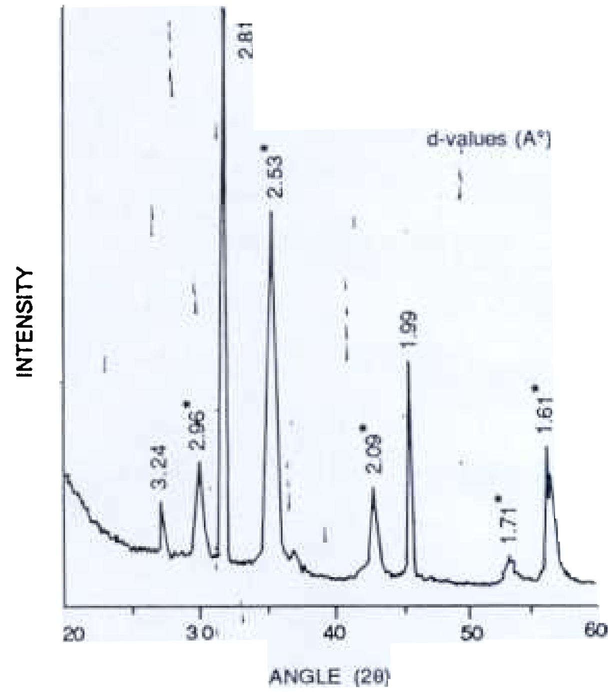

Figure 10. X-ray diffraction pattern of complex metal ion-doped copolymer of anilineformaldehyde.

The X-ray diffraction studies on the material indicate crystalline nature of the material. From the X-ray diffraction pattern (Fig. 10), it is observed that some of the *d*-values could not be correlated with any known oxide, hydroxides or mixed oxides of iron or cobalt. From these studies it is difficult to conclude whether the magnetism in the material is intrinsic or extrinsic in nature. Further, the investigations are in progress to resolve the issue. Nevertheless, the low density (1.5 g/cc) and non-separation of phases by any chemical or physical means make this a unique magnetic material which may be termed as a 'composite magnetic polymer'.

4. APPLICATIONS

Conducting polymers have from the outset inspired interest in possible commercial applications. The projected commercial applications of conducting polymers are based on the promise of novel combination of light weight, processability and electronic conductivity. Foremost amongst the current commercialisation ventures is their applications in rechargeable batteries, circuitry elements functioning as passive elements (conducting transducers) or active elements (Schottky or *p-n* junction devices), EMI shielding, electrolytic capacitors, antistatic films and bags, etc. Further, the electrical conductivity is not the only application of conjugated polymers. Certain materials can change their optical properties on application of current/voltage resulting in two very interesting applications, viz., heat shutters and light emitting diodes. Medical scientists are also interested in these materials as a way of releasing controlled quantities of drugs. Recent reports[9,10] indicate that more than 15 products have already been commercialised. Some of the important applications of these materials are discussed here.

4.1 Batteries

The light weight characteristic of conducting polymers is expected to satisfy the low weight requirement of batteries for portable devices and vehicles. The main problems, however, are retention of processability at high conducting levels and environmental stability. However, neither of these two is a serious impediment to the development of commercial batteries employing conducting polymer electrode since these typically operate under sealed conditions.

A 3-V, coin-sized primary battery manufactured by the Bridgestone-Seiko[12] was the first commercial product reported in 1987 utilising the conducting polymer. Its anode is made of *Li-Al* alloy, its cathode is polyaniline and the electrolyte is an organic liquid. More recently, a German joint Venture Varta-BASF has also introduced a 3-V button cell with a *Li-Al* alloy anode, polypyrrole cathode and an organic liquid electrolyte. Both these batteries are excellent wherever low power, long life and reliable operations are required. Their main use to date has been for computer power backup but they have also shown up in wrist watches, telephones, timer for video cassettes, and TV remote controls.

Interest in the applications of conducting polymers in rechargeable batteries began with the discovery of the electrochemical doping of polyacetylene[56]. The electrochemical doping process constitutes the basic electrochemistry of the batteries. The reversibility of the electrochemical doping provides a rechargeable (or secondary) battery system. A typical example of small plastic or 'double polymer'[56-59] is illustrated in Fig. 11. In this case, the conducting polymer functions as both cathode and anode. The redox reactions at the two electrodes are:

$$\text{Anode}: \quad p^{-} \quad D^{+} \quad \xrightleftharpoons[\bar{e}\ \text{charge}]{e\ \text{discharge}} \quad P^{o} + D_s^{+}$$

$$\text{Cathode}: P^{+} \quad {}^{-}A^{-} \quad \xrightleftharpoons[+e\ \text{charge}]{+e\ \text{discharge}} \quad p^{o} + A_s^{-}$$

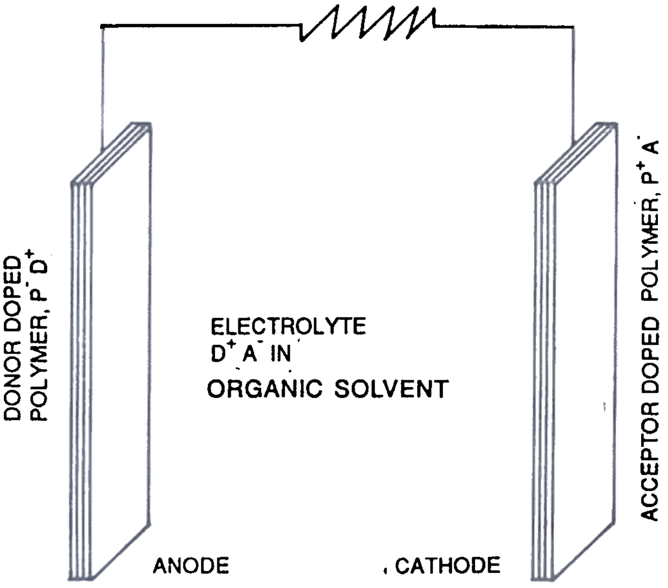

Figure 11. Schematic diagram of rechargeable battery with conducting polymeric electrodes.

While a small market is being established for primary cells, the big payoff for polymer batteries lies ahead due to rechargeable, high power, high rate, and light weight characteristics of conducting polymers, particularly for electric vehicles. Much work remains to be done in that desirable combination of high power density (400 W/kg), high every density (72,000 J/kg) and rapid recharge (three to six hours) as well as long life and low cost are needed. Because of huge commercial potential of electric vehicles worldwide, many companies, national laboratories, and universities are deeply involved in the development of conducting polymer-based batteries.

4.2 Gas Sensor

The recent advancement in the field of conducting polymers has shown that these materials offer new possibilities for using them as sensing elements for the detection of different gases[60-64]. The underlying principle for the detection is the change in their electrical conductivity due to change in their chemical or physical character. Recent studies have shown that the sensitivity of conducting polymers can be controlled by modification of the polymer backbone or by bringing changes in dopant species.

At the Defence Laboratory, Jodhpur, a copolymer of anilineformaldehyde doped with complex ions of iron, synthesised here, has been found to show the change in its electrical conductivity on exposure to different polar toxic gases, like NH_3, HCl, CO, NO, Cl_2, etc. at ppm levels[65]. The concentration of *HCl vs* change in current graph is shown in Fig. 12. The effect has been found to be reversible. Further, an audio-visual alarm device has also been developed. The schematic diagram of the device is shown in Fig. 13.

4.3 EMI Shielding

A ramification of the electronic conductivity of these materials is their ability to absorb energy at low frequencies[66]. This absorption of low frequency electromagnetic radiation constitutes the basis for the use of conducting polymers as shielding barriers against

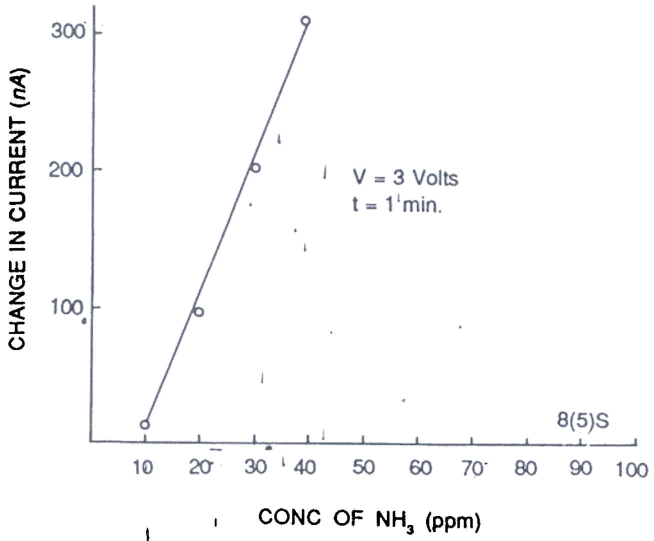

Figure 12. Plot of change in electrical current versus concentration of NH_3 in copolymer of aniline-formaldehyde.

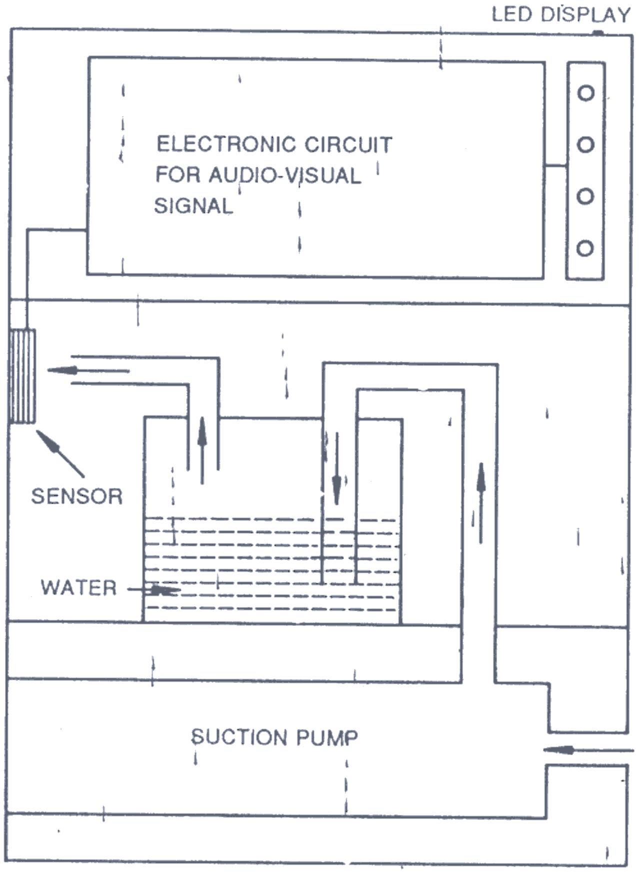

Figure 13. Schematic diagram of the gas sensor device developed at the Defence Laboratory, Jodhpur.

electromagnetic interference (EMI). The EMI shielding for computers and many of the other sophisticated equipment is a very important requirement. Currently, metal filled- or metal coated plastics are used as EMI shielding materials. Replacement of these components with conducting polymers offers the possibility of higher conductivity and better processability and the advantage that both structural and electroactive properties are embodied in the single material.

The EMI shielding measurements have been reported on poly(3-octylthiophene) (P-3OT) blends with polystyrene, polyvinyl chloride (PVC) and ethylvinyl acetate as matrix materials[67]. Shielding efficacy values of up to 45 dB have been reported in the frequency range 0.1-10 MHz which decrease sharply at higher frequencies. At the Defence Laboratory, Jodhpur, the blends of conducting polyanilines were developed with three different conventional polymers, viz., polyethylene, PVC and silicone rubber. The blend of conducting polyaniline with PVC gives maximum shielding efficacy value of 16 dB over a frequency range of 1-100 MHz.

4.4 Light Emitting Diodes

Normally, the electron releases its energy in the form of heat, but it can return to the ground state by releasing a photon which we see as light. The possibility that conducting polymers can show such a behaviour has generated great interest in developing light emitting diodes (LEDs) by using these materials [68]. For this application, the high level of conductivity is not required. In theory, producing a rainbow of LEDs appears a relatively simple job. The wavelength of the light produced by an LED, and hence its colour, varies with the energy of photon, which in turn is exactly equal to the energy that kicks the polymer up to an excited state[69]. By adjusting the structure of the polymer backbone it should be possible to tune the amount of energy the polymer requires to reach the desired excited state. During the last 3-4 years, fabrication of LEDs by using conducting polymers has been a very hot subject[70-72]. The underlying reason for this is the dream of building ultra slim screens, made entirely of plastics, for TVs and computers.

Recently, Gustafsson *et al*[70], have reported a flexible light emitting diode using conjugated polymers. The diode was fabricated by using poly(ethylene tetraphthalate) as the substrate, soluble polyaniline as the hole-injecting electrode, a substituted poly(1,4-phenylene-vinylene) as the electroluminescent layer and calcium as the electron-injecting top contact. This mechanically robust LED has been reported to have external quantum efficiency of 1 per cent and turn on voltage of 2-3 V to make it clearly visible under room light conditions.

4.5 Solar Cells

Currently, organic semiconductors are of great interest as an alternative to inorganic semiconductor photovoltaic devices. In a recent report[73] photovoltaic properties of *Al*/PPY/ITO sandwich devices were investigated by measuring steady-state photocurrents resulting from illumination through the *Al*-electrode. Open circuit voltage of 1.2 V and short circuit current 6.7 x 10^{-7} A/cm^2 has been reported at 1 mW/cm^2 of incident illumination. The device showed photovoltaic conversion efficiency of 0.07 per cent.

Schottky barriers by using organic semiconductors, i.e. *Mg* phthalocyanine (*Al*/*Mg* phthalocyanine/*Ag*)[74], merocyanine (*Al*/merocyanine/*Ag*)[75] and conducting polyaniline (*Al*/polyaniline/ITO)[76] have been reported to show conversion efficiency up to 1 per cent. It has been observed that in the case of conducting polymers the conversion efficiency can be tuned by the variation of dopant species, e.g. undoped PANI (0.04 per cent) polyacrylic acid-doped PANI (0.6 per cent) and toluene sulphonic acid-doped (TSA) PANI (0.9 per cent). The low conversion efficiency of the undoped PANI solar cell can be attributed to a high recombination rate of carriers which can limit the collection efficiency of the electron-hole pairs. The cell with TSA-doped PANI is comparable with that of *HCl*-doped $(CH)_x$ (1 per cent at 7 W/cm^2).

ACKNOWLEDGEMENTS

Authors are grateful to Dr A.R. Reddy, Director and Shri T.V.R. Sarma, Joint Director of Defence Laboratory, Jodhpur, for their constant encouragement and keen interest in the work. Further, the authors wish to express their gratitude to Dr B.B. Sharma of Solidstate Physics Laboratory, Delhi and Prof M.S. Multani of Tata Institute of Fundamental Research, Bombay, for useful discussions.

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