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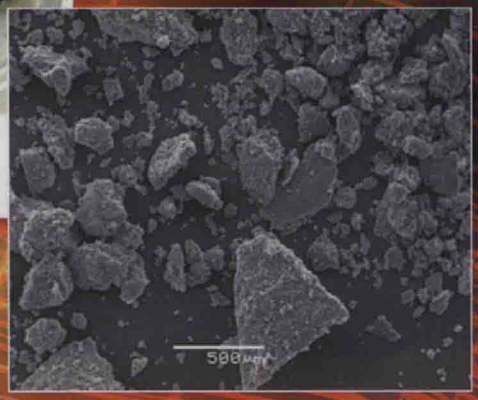
Ed

TRENDS IN POLYANILINE RESEARCH



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TRENDS IN POLYANILINE RESEARCH

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PREFACE

This book presents an overview on recent "Trends in Polyaniline (PAni) Research" covering synthesis, properties and applications such as capacitors, electronics, sensors, composites, adsorption, biomedical and membrane technology. Scientists and researchers from various disciplines including Physics, Chemistry, Materials, Nanoscience and Engineering contributed chapters for the book based on their expertise in these fields. PAni, an interesting conducting polymer (CP), has attracted great attention over the last decades owing to its tunable properties and potential applications in multidisciplinary areas. PAni is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties, wide range of application possibilities and higher thermal stability compared to other CPs. Therefore, it is the appropriate time to comply a book with a comprehensive review of the recent trends on PAni synthesis, properties and application. This book presents the latest research on PAni from around the world.

Chapter 1 describes the synthesis, characterization and gas sensing applications of PAni. The sensor films prepared by spin coating technique are characterized for structural, morphological, optical and electrical properties. The room temperature gas sensing properties of PAni sensor films are tested for volatile and non-volatile gases. Chapter 2 discusses the synthesis of PAni using electrochemical methods. Electrochemical syntheses by galvanostatic, potentiostatic or potentiodynamic methods are adopted, most often on inert metal and carbon-based electrodes, to produce films directly adherent on the electrode surface. PAni is electrochemically synthesized on aluminium and its alloys through the electrochemical polymerization. The antibacterial and antifouling properties and corrosion resistance behavior of the PAni films are also described. In chapter 3 sonochemical synthesis and application of functional hybrid nanomaterials containing PAni are presented. Besides, ultrasound assisted mini-emulsion synthesis of functional conducting latex (PAni latex) and various applications such as anticorrosion, coatings, photoelectrochemical cell and sensor are also reported.

The structure control synthesis of PAni is very interesting. Chapters 4 and 5 provide an introduction and examples of structure control syntheses of PAni using electrochemical and chemical polymerizations in unique reaction fields and media. Ionic liquids and supercritical fluids are now used as electrolytic media for controlling the physical structure of the materials.

Chapter 6 describes the recent advances of PAni as an electrode material for supercapacitor. Literature data on historical background of capacitor, classification of

supercapacitors and status of PAni and its composites with carbon and/or metal oxide for supercapacitor work are summarized in this part.

Chapter 7 provides a comprehensive review on the PAni based composite materials and addresses the perspective of the use of PAni in composites with variety of materials, characterization techniques, and multi-facet applications in different areas. Chapter 8 describes the fabrication and electrical behaviour of electrospun PAni-carbon black composite nanofibers. The role of carbon black in PAni matrix, which can be beneficial as conductive electrode applications in electronic and photovoltaic storage devices is discussed. In chapter 9, the designing of conducting ferromagnetic PAni composites for EMI shielding is described. It also focuses on synthesis, conduction mechanism, magnetic and dielectric properties of conducting ferromagnetic PAni nanocomposites and associated phenomenon to EMI attenuation.

In chapter 10, electrochemical synthesis of PAni nanocomposite is described with a novel biphasic electro-polymerization technique. Multiwalled carbon nanotube/PAni nanocomposite formation based on biphasic electro-polymerization technique provides a general method for the formation of uniform nanocomposites for other polymers and fillers.

PAni has also played a significant role in membrane technology and applications. Chapter 11 deals with the PAni based membranes field and focuses on their gas/vapor separation applications.

Chapter 12 focuses the gas sensing ability of PAni. In this chapter, the fabrication of various morphological PAni gas sensors, PAni/metal nanocomposite gas sensors, other PAni nanocomposite gas sensors and PAni based hetero-junction type gas sensors are discussed.

Chapter 13 furnishes the anticorrosive properties of PAni and focuses the mechanism of corrosion protection of coatings based on PAni. Here, a short review of application of nanomaterials to improve the anticorrosive property of PAni coating is also reported.

Chapter 14 describes the application of PAni nanocomposites as a potential material for the removal of pollutant metal ions and dye molecules from wastewater. The mechanism of removal of pollutants by using PAni and its composites and nanocomposites are elucidated.

Chapter 15 accumulates the biomedical application of PAni in tissue engineering, biosensors and drug delivery devices and also several modification manners of PAni in order to improve its technological usage.

The book "Trends in Polyaniline Research" is a sincere attempt to make available the recent developments in PAni synthesis, properties and its application in a single issue which we believe to bring comfort to the readers worldwide. We hope, this book would be a piece of latest information on PAni researches.

Finally, we would like to thank all of our family members for their understanding, strong support and encouragement. If, any technical errors exist in this book, all editors and chapter contributors would deeply appreciate the reader's comments for further improvement.

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CONTENTS

In: Trends in Polyaniline Research
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Chapter 1

POLYANILINE: SYNTHESIS, CHARACTERIZATION AND GAS SENSING APPLICATIONS

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This chapter describes the synthesis of polyaniline (PAni) by oxidative chemical polymerization method. The characterization concerning structural, morphological, optical and electrical properties of the sensor films prepared by spin coating technique have been discussed. The room temperature gas sensing properties of PAni sensor films that have been tested for volatile and non-volatile gases are described with examples. Gas sensing mechanism for PAni films is also described. The research work describing the detailed study of selective PAni based sensors to ammonia gas is also presented.

1. INTRODUCTION

Polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh) and their derivatives, conducting polymers, have been widely investigated for the development of room temperature (RT) gas sensors. The sensors made of conducting polymers shows improved characteristics such as high sensitivities and short response time at room temperature. However, a major disadvantage of conducting polymers is their lack in specificity towards the target gas molecules since they may sense all the gases present in the system. The selectivity and enhance sensitivity of a particular gas sensor obviously depends on the characteristics of sensors with conductive polymers. As a result, a lot of attention has been paid to fabricate smart gas sensors with conducting polymers [1]. This chapter represents the summary of works that have been carried out on the synthesis and characterization of PAni films used as gas sensors operating at room temperature.

1.1. Conducting Polymers

Conducting polymers are polymers with conjugated structures [1]. Chemical structures of some of the commonly known conducting polymers are shown in Figure 1.1.

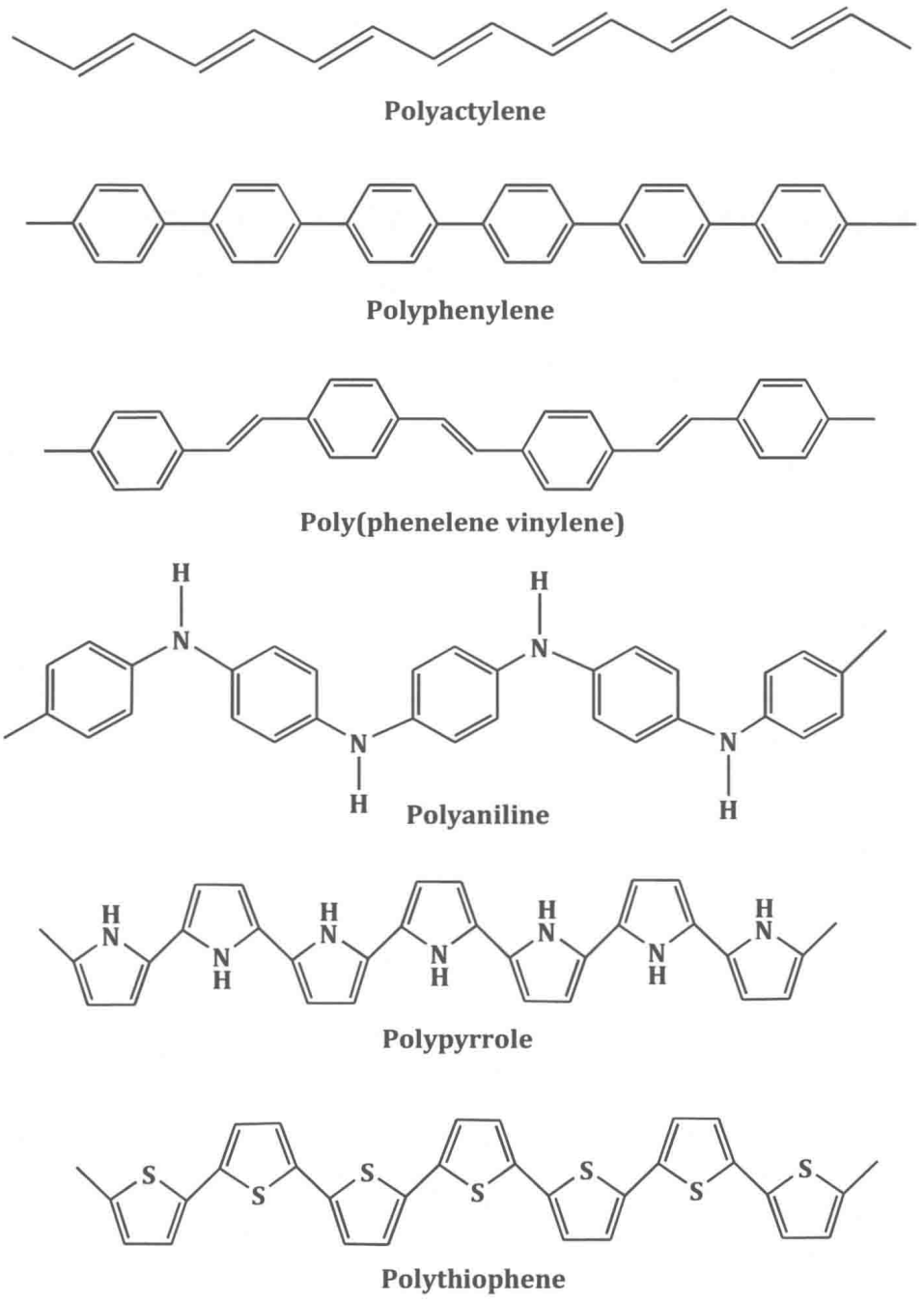

Figure 1.1. Chemical structures of some of the most significant conjugated organic conducting polymers.

In the structure of the polymers, a common feature, i.e., the occurrence of double bonds alternating with single bonds along the polymer chain known as conjugated bonds can be

seen. In fact, such an arrangement of conjugated bonds in the organic polymers is the origin of conduction that can be understood as follows. In each repeated unit of polymers, three of the four electrons in the outer shell of every carbon atom occupy hybridized states formed from one 's' and two 'p' states (sp^2 hybridization) [2]. These electrons form three strong 'σ bonds' that play a key role in forming the polymer structure. In polyacetylene each carbon atom forms these σ bonds with one hydrogen and two neighboring carbon that leaves one valence electron left over (the π-electron), which occupies a p orbital. The π-electron wave functions from different carbon atoms overlap to form a π -bond. π-electrons are delocalized over large segments of the polymer chain, which is responsible for the electronic properties of the conjugated polymers. The addition of heteroatoms (atoms other than carbon and hydrogen) and side chains allows fabricating a larger variety in this class of materials.

Conducting polymers in their neutral states are insulators and exhibit a strong UV-visible absorption characteristic. Neutral conjugated polymers with a small conductivity, typically in the range 10^{-10}-10^{-5} S cm^{-1} can be converted into semi-conductive or conductive states with conductivities of 1-10^4 S cm^{-1} through chemical or electrochemical redox reactions. Conjugated polymers are treated as a quasi one-dimensional (1D) system, wherein the polymer chains are assumed to behave independently. Their physical and chemical properties depend on interactions within the single chains. The π-bonding scheme of conjugated polymers decreases the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states. The band gap of these polymers lies between 1.5 and 3 eV, in the same range as of inorganic semiconductors [3].

Most conducting polymers possess conductivities comparable with those of traditional metal at room temperature. However, the temperature dependence in the conductivity of polymers is mostly non-metallic, especially at lower temperature. In order to achieve high conductivity in conducting polymers the so-called doping is necessary [4, 5]. The study of the conductivity of polyacetylene shows that the conductivity could be increased by more than seven orders of magnitude upon doping of iodine or arsenic pentafluoride (AsF_5) [6]. This draws a great interest of the researchers and similar works lead to the award of Nobel Prize for chemistry in 2000.

When an electron is added to or withdrawn from a conducting polymer, a chain deformation takes place around the charge, which costs the elastic energy and puts the charge in lower electronic energy state. The competition between elastic and electronic energies determines the size of the lattice deformation that sometimes could be the order of 20 units. As a result, the volume of polymer changes and simultaneously, the absorption bands related to the neutral conjugated polymers reduce as well as new absorption bands associated with charge carriers appear at longer wavelengths.

Based on composition-driven redox behavior and accompanying fundamental characteristics such as optical, electrical, electrochemical and mechanical properties the conducting polymers have been generally considered as potential candidates for a range of technological applications. These applications include biomimetics (biosensors, electronic noses, artificial nerves etc.), medical prosthetics (artificial muscles and limbs), battery technology, corrosion inhibition, field-effect transistors, light-emitting diodes and electrochromic display devices [7-11]. Electronic noses and biosensors specifically utilize the change in the recognition pattern of an array of different conducting polymers. Artificial muscles and other prosthetic medical devices harness the ability of conducting polymer to change shape and size during redox switching and film compositional dynamics. For redox

switching devices, the conducting polymer is deposited on metal nanowires and /or can be grown as freestanding films.

The principle of electrochromic display devices is the use of change in color associated with different oxidation states exhibited by conducting polymers upon the application of voltage. Using the light emitting properties that can be tuned by changing chemical structure, the conducting polymers have been commercially used as light emitting diodes (LEDs) and displays. Moreover, the conducting polymers of which electron-hole pairs could be generated upon illumination of light have been employed as materials for photovoltaic devices. The conducting polymers are being investigated as a candidate for organic/molecular electronics due to their unique combination of properties that make them an attractive, alternative or a complement to the Si based microelectronics.

1.1.1. Electronic Conduction Mechanisms in Polymers

1.1.1.1. Highly Anisotropic ('quasi-1D') Metallic Conduction

A key feature of polymer conductivity is its high anisotropicity, being much greater along the polymer chains. This quasi-1D nature leads to a mechanism that avoids the usual limitation on conductivity due to scattering of carriers by thermally excited lattice vibrations. Basic idea can be understood with reference to the idealized situation depicted in Figure 1.2, where a highly anisotropic (quasi-1D) polymeric metal in which Fermi surface consists of sheets perpendicular to the chain direction (k_F is the electronic Fermi wavevector) is presented in which the charge carriers are taken to have wavevectors k_F or $-k_F$ parallel to the direction of polymer chains.

It may be stated that to scatter these carriers and create resistance, phonons would need to have a wave vector $2k_F$ spanning the Fermi surface [12]. The energy of these phonons is large leading to excitation of few at ordinary temperatures and the resistivity is suppressed in conventional isotropic metals.

Such quasi-1D metals could be expected to possess the conductivities much higher than those of conventional metals of which the scattering of electrons by phonons limits the conductivity to about 0.6×10^6 S.cm^{-1} at room temperature even in the best metals like copper and silver.

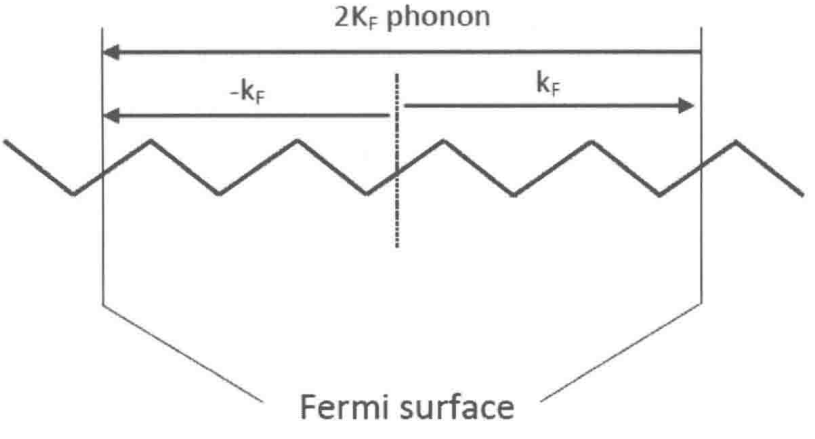

Figure 1.2. A sketch showing backscattering along the polymer chain direction by phonons of wave vector $2k_F$.

1.1.1.2. Hoping in Disordered Semiconductors

For a large variety of disordered materials on the semiconductor side of a metal-semiconductor transition, the conductivity is well-described by Mott's law for variable-range hoping [13]. In disordered semiconductors with localized states in the band gap, conduction occurs by hopping (phonon-assisted tunneling between electronic localized states centered at different positions). As the thermal energy k_BT (k_B is Boltzmann constant and T is temperature in Kelvin) decreases with temperature, there exists fewer nearby states with accessible energies, resulting in increased mean range of hopping. This can be expressed mathematically as the expression for the temperature dependent conductivity σ (T) [14] as follows:

$$\sigma(T) = \sigma_o e^{-(\frac{T_o}{T})\gamma} \tag{3.1}$$

For hopping in 3D, the exponent has the value $\gamma = 1/4$. If the electronic wave functions decay with distance 'r' as $\exp(-r/L_{loc})$, where L_{loc} is the localization length, the constant T_0 is characteristic Mott temperature and given approximately by $k_BT_0 \sim 16/N\ (E_F)L^3_{loc}$, where $N(E_F)$ is the density of localized states at the Fermi level. The prefactor σ_0 is also temperature dependent, with different authors deriving different power laws [14], but this temperature dependence is often neglected compared to the stronger temperature dependence of the exponential term. At sufficiently high temperatures the hopping occurs to the nearest neighbors and the conductivity would instead show a simple activated form given by eqn. (3.1) with $\gamma = 1$. This form also applies for electron transport by thermal excitation into a conduction band of extended states in crystalline semiconductor where the conductivity is approximately proportional to the number of electrons excited across the semiconductor gap. For 2D hopping, $\gamma = 1/3$, and for 1D hopping $\gamma = 1/2$, although according to Efros et al. [15], latter exponent could arise for hopping when electron-electron interactions are considered.

It has been emphasized [16] that quasi-1D hopping could play a key role in conducting polymers where polymer chains traverse disordered regions to connect 'crystalline islands'. Charge carriers would diffuse along such electrically isolated disordered chains as a part of the conduction path, but would readily localize owing to the 1D nature of the chains. In such a case, quasi-1D variable-range hopping along the disordered chains with $\gamma = 1/2$ could dominate the overall resistance of the polymer.

1.1.1.3. Tunneling Between Metallic Regions

According to calculations by Sheng and Klafter [17] and Sheng [18], if conduction is by electronic tunneling through non-conducting material separating mesoscopic metallic 'islands' rather than localized states, the expression for the tunneling conductivity approximately follows eqn. (3.1) with $\gamma = 1/2$ (same form as for 1D variable range hopping). Such a picture should be appropriate for a granular metal in which small metallic grains surrounds by non-conducting shells. These calculations apply when the conductivity is limited by the electrostatic charging energy when an electron is transferred from one island to the next. The inhibition of tunneling when the thermal energy k_BT is less than the charging energy referred to as a 'Coulomb blockade' [19]. However, the metallic regions are large enough that the electrostatic charging energy is much smaller than k_BT for accessible

temperatures. Tunneling can occur between metallic states of the same energy on different sides of the barrier without thermal excitation, provided that the wave functions overlap. Fluctuations in the voltage across the tunneling junction can greatly increase the tunneling current as the temperature increases [20]. The conductivity due to this fluctuation-assisted tunneling for a simple parabolic barrier shape can be written with several assumptions in the simple form:

$$\sigma(T) = \sigma_t e^{-\left(\frac{T_t}{T+T_s}\right)} \tag{3.2}$$

where T_t represents the temperature at which the thermal voltage fluctuations becomes large enough to raise the energy of electronic states to the top of the barrier, and the ratio T_t/T_s determines the tunneling in the absence of fluctuations. The prefactor σ_t is approximated as independent of temperature.

1.1.1.4. Solitons, Polarons and Bipolarons

The elementary excitations for the single polyacetylene chain illustrated in Fig 1.1 are solitons rather than electron-hole pairs as observed in 3D metals. Solitons represent discontinuities in the pattern of alternating single and double bonds that arise when one carbon atom has single bonds to both of its neighboring carbons [21-23]. Additional electronic states are created at the centre of the semiconductor-like band gap in polyacetylene, as shown by optical absorption measurements at low doping levels [21]. Motion of a simple soliton discontinuity along a polymer chain does not lead to charge transport but an inter-chain soliton hopping mechanism could contribute to conduction with conductivity varying as power of temperature [24]. The agreement of a vast amount of conducting polymer data with the hopping laws over a wide range of temperature suggests that once localized states are formed in the gap by any mechanism, conduction takes place predominantly by the usual variable range-hopping processes for lightly or moderately doped samples [25, 26].

In heavily doped samples, the overlap of wave functions means that a metallic picture is likely to be more appropriate at least in the ordered regions. For conducting polymers other than polyacetylene, different solitonic states possess different energies and hence solitonic conduction mechanisms are not expected. On the other hand, states appear in the band gap [21, 27] owing to the formation of polarons having charge and spin and their motion can contribute to charge transport. Polarons of opposite spin often pair up to form bipolarons with zero spin, which can lead to charge transport without spin.

Inspired by the work of Sheng [18] on granular metals, Zuppiroli et al. [28] proposed that conduction in disordered conducting polymers takes place via the correlated hopping between polaronic clusters. In this case, the charging energy for charge-limited tunneling between metallic grains could be defined, and the calculated conductivity has been reported to follow the same temperature dependence as given in eqn. (3.1) with $\gamma = 1/2$.

In the recent years, conducting polymers such as PAni and PPy are studied as gas sensors essentially due to their operation at room temperature and ease of processing for sensor element [29, 30].