

Electrosynthesis and spectroelectrochemical characterization of conducting polymers

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Abstract:

Conductive polymers are special type of organic compounds that have conjugated system enable them to conducting electrical current. They have distinctive properties render them attractive to be used in different application such as capacitors, sensors, anodes for fuel cells, or for protection against corrosion, the photo-degradation of semiconductor electrodes in galvanic cells and for other applications. Synthesis and investigation of new conjugated polymers are essential to improving the electronic and optoelectronic properties of these materials and in turn improvement of the performance of the devices. For instance, this review aims to define important sides of electrochemical synthesis and electrochemical characterization of conducting polymers and some of their applications, with special prominence to carbazoles and some of its derivatives.

Keywords: conducting polymers, carbazoles, Electropolymerization, Electrochromism

مستخلص:

البوليمرات الموصلة هي نوع خاص من المركبات العضوية يتميز بمقدرته على توصيل التيار الكهربائي نتيجة لاحتوائها على نظام مترافق. خصائصها المميزة جعلتها جاذبة لتستخدم في تطبيقات مختلفة مثل المكثفات، المجسات، أقطاب خلايا الوقود أو وقاية الأقطاب شبه الموصلة من التآكل أو التحلل الضوئي في الخلايا الجلفانية. تخليق البوليمرات المترافقة ودراساتها لإبد منه لتحسين خصائصها الالكترونية و الالكتروبصرية وبالتالي تحسين أداء الاجهزة التي تستخدم فيها. هذه المقالة العلمية تهدف الى التعريف بجوانب هامة عن البوليمرات الموصلة مثل طرق تخليقها، خصائصها الالكترونية و مجالاتها التطبيقية و ذلك اعتمادا على نتائج البحوث المنشورة في المجالات و الدوريات الرصينة. تم التركيز علي مركب الكاربازول و بعض مشتقاته. كلمات مفتاحية: البوليمرات الموصلة، الكاربوزولات، البلمرة بالكهرباء.

1. Introduction

In 1977 polyacetylene was proved to gain metallic properties i.e. electrical conductivity. This early discovery encouraged scientists to test polyacetylene as rechargeable active battery electrode. Their promising results motivated global efforts to create polymer battery. The simple conjugated polymer, can be transformed to conductive material through process known as doping reaction, which consists of partial oxidation (p-type doping) or partial reduction (n-type doping)⁽¹⁾

Conducting polymers are developing steadily and their application in technology, is expanding. Therefore, the conducting polymers with conjugated double bonds, such as, polypyrrole, polythiophene and polyaniline have drawn the attention of researchers as new advanced materials. Conducting polymers are often synthesized by electrochemical polymerization. The monomer, the supporting electrolyte, and the solvent are taken into the electrolytic cell and the electrolysis is carried out by applying a voltage between the working electrode (Pt, Au, C, etc.) and the counter electrode. Usually, the film of the conducting polymer is formed during anodic polarization⁽²⁾.

Recently, carbazole is receiving considerable attention as conducting polymer because; it has a good electrical and photoelectrical properties; also carbazole is charge transporting material (hole transporting) and different substituents can be introduced into carbazole backbone to prepare polycarbazole derivatives with various properties and promising applications⁽³⁾.

2. Conducting polymers

Conducting polymers are materials that are capable to conduct electricity. They are not plastics and hence, are not thermoflexible. They belong to organic family due to their insulating nature. Like metals and alloys, inorganic semiconductors, molecular and electrolyte solutions, and inorganic electroactive solids, they include a group of compounds and materials with very distinctive properties. Conducting polymers have resemblances from an elec-

trochemical perspective to all of the other compounds and materials stated above, making them a highly attractive research area. Furthermore, such research has led to several new uses, extending from corrosion prevention to analysis. In addition, the descriptions of conducting polymers, such as reversibility, obtainability in film shape and worthy environmentally friendly, improve their budding use in practical applications. Therefore, conducting polymers have invaded many arenas. Of the many noteworthy conducting polymers that have been developed over the last eras, those based on polyaniline, polypyrrole, polythiophene, polyphenylene and poly(p-phenylenevinylene)s have attracted much attention (**Figure 1**). Regarding conductivity of such polymers, the motion of delocalized electrons happens through conjugated systems; however, the electron hopping mechanism is likely to be effective, especially between chains (interchain conduction) and defects. Electrochemical transformation usually leads to a reformation of the bonds of the polymers prepared by oxidative or less frequently reductive polymerization of benzoid or nonbenzoid (mostly amines) and heterocyclic compounds. The instability of polyacetylene, which is recognized as a conducting polymer, in air retards its practical use. However, substituted polyacetylenes (**figure.2**) into which substituents are introduced are convenient for feasible applications, because they have high oxidative stability and grant the formation of films from their solutions.

Generally, organic compound have very faint electronic conductivity with values of specific conductivity σ that are as much as 10^{12} time less than those of metals.

Conductivity $\sigma = J \setminus E$

Which J is charge motion or current density, E is electric field.

The degree of conductivity of organic conducting polymers varies between two states of relative oxidation and reduction. In case of polymer it self loses electrons (partial oxidation) polymer produced two positive charge polarons, in case further oxidation resulting more polarons (doped) ⁽⁴⁾.

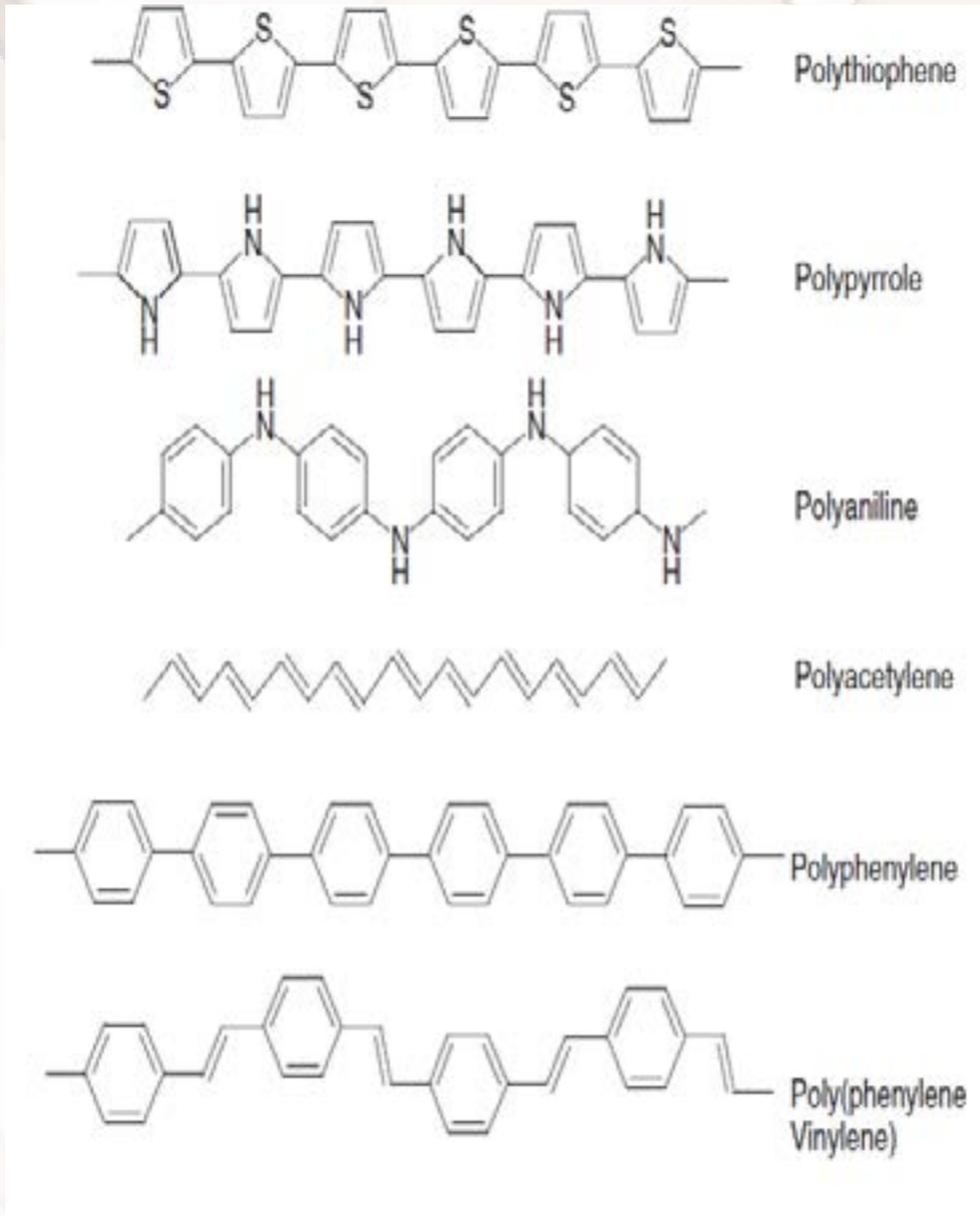


Figure1. The structure of most known conducting polymers in their neutral insulating form

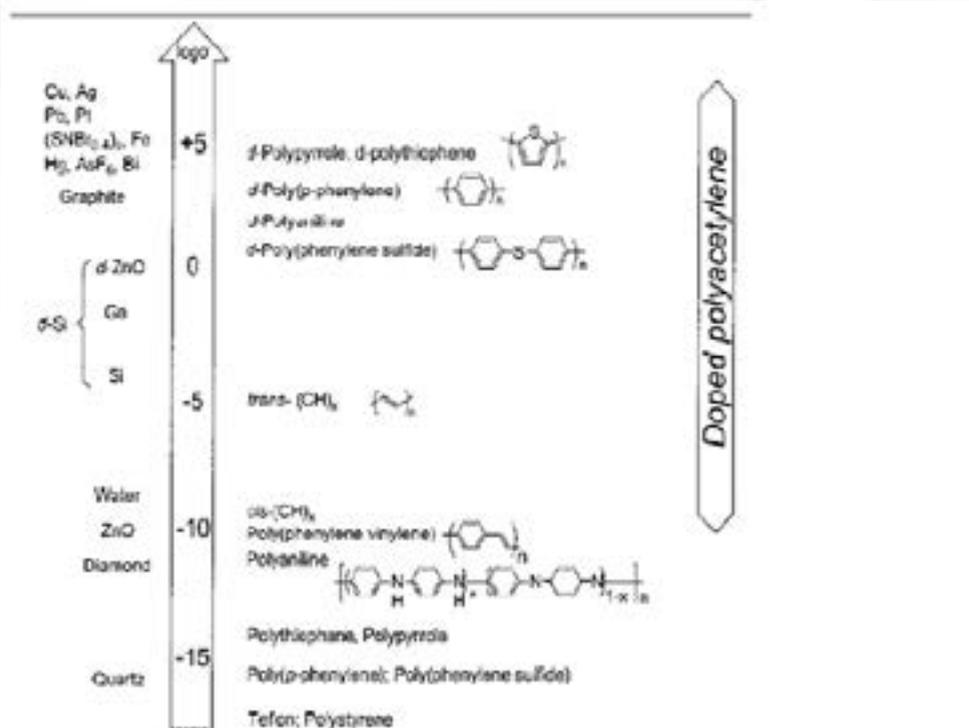


Figure 2. Electron conducting polymers (5).

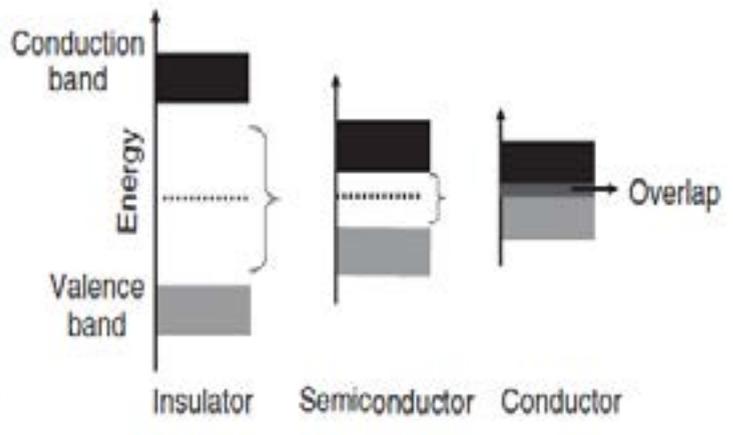


Figure 3. The band gap in solid (5).

2.1. Synthesis of conducting polymers

Conducting polymers could be synthesized by either chemical or electrochemical polymerization methods. Electropolymerization is more advantageous since the reactions can be performed

at room temperature, the thickness of the films can be controlled, polymer films can be directly formed at the electrode surface, and it is possible to obtain homogeneous films ⁽⁶⁾.

Oxidation of monomers can be achieved within two mentioned methods where the polymerization reaction is stoichiometric in electrons. One challenge is usually the low solubility of the polymer. However, in some cases, the molecular weight need not be high to achieve the desired properties. The electrical properties can be fine-tuned using the methods of organic synthesis.

Several other methods for the synthesis of conducting polymers have been developed, such as electrochemical, photochemical or biocatalytic oxidative polymerization using naturally occurring enzymes. Most conducting polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation.



Synthesis and investigation of new conjugated polymers are crucial to refining the electronic and optoelectronic properties of these materials and in sequence enhancement of the performance of the devices. One general encounter in the field is realization of high electron affinity (n-type) conjugated polymers, for improving electron injection/transport and low ionization potential (p-type) conjugated polymers for better hole injection/transport in polymer electronic devices. Of particular attention are polymers that merge high fluorescence quantum yields with low ionization potential or high electron affinity ⁽⁷⁾.

In recent times, little attention has been paid to chemical polymerization of the above conducting polymers. Chemical polymerization is of particular significance since this synthesis is the most practicable route for the outsized scale production. Besides, it was shown that chemical synthesis produces a polymer having a higher molecular weight. In general, chemical oxidation delivers conducting polymers as powders, whereas the electrochemical synthesis lead to films deposited on working electrode.

More recently, increasing attention has been directed towards their functionalised derivatives primarily polypyrrole, polythiophene and polyaniline because functional groups enable fine-tuning of monomer and polymer properties and may also provide attaching points for polymer postmodification. The conducting polymers can be polymerized by two methods via chemical and electrochemical techniques, electrochemical method compromises a better control over properties as they can be achieved by changing experimental conditions such as electrolyte, oxidation potential, solvent, etc. Conjugated polymers are organic semiconductors, the semiconducting behaviour being associated with the π molecular orbitals delocalized along the polymer chain. Their main advantage over non-polymeric organic semiconductors is the possibility of processing the polymer to form useful and robust structures. The response of the system to electronic excitation is nonlinear, the injection of an electron and a hole on the conjugated chain can lead to a self-localized excited state which can then decay radiatively, suggesting the possibility of using these materials in electroluminescent devices ⁽⁸⁾.

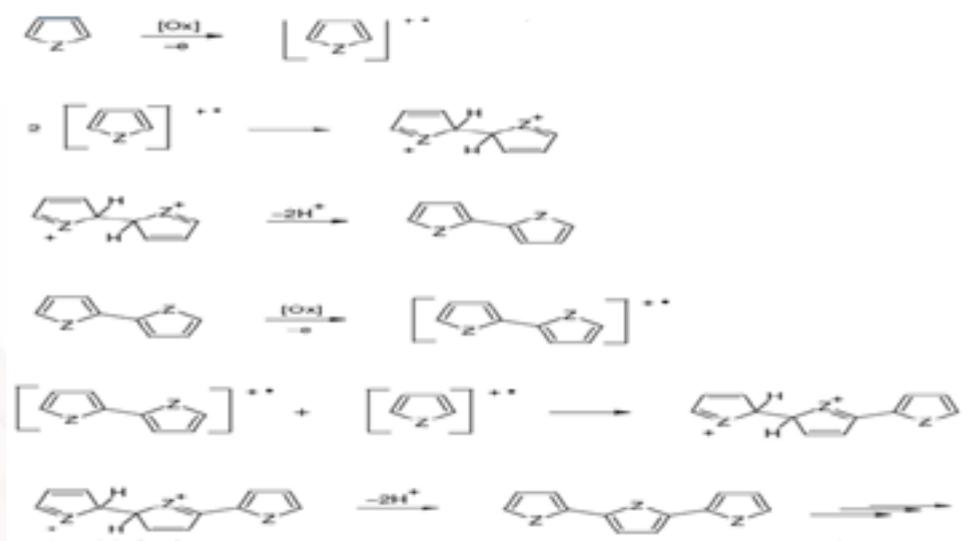


Figure 4. Mechanism of the first step of the electrooxidation of monomer

2.2 Application of Conducting polymers

A range of applications towards technology of these materials has been projected and established. Conducting polymers (CPs) have been, carefully, studied during the last eras regarding their potential application for example as capacitors, sensors, anodes for fuel cells, or for protection against corrosion, the photodegradation of semiconductor electrodes in galvanic cells and for other applications. Generally, conducting polymers are infusible and insoluble in common solvents. The preparation of conducting polymer nanocomposites is a promising route to provide the hybrid material with some kind of processability (colloidal stability or mechanical strength), extending the applications of these materials. Moreover, chemical origin and the special properties of the incorporated materials add new characteristics to the resulting nanocompos. Conducting polymers have attracted great fundamental and applicative interest due to their special properties, such as tailoring of electronic properties by the molecular structure, controllable electrical conductivity and nanostructured shapes (films, nanowires, nanoparticles), and low cost high yield synthesis.

The electrochemical preparation of a variety of conducting polymers has been extensively explored due to their electrical redox and photochemical properties and ability for a number of practical applications, i.e. as batteries, and light emitting diodes. Carbazole-containing polymers have been expansively studied for the various applications due to their good hole transport, luminescent and electroactive properties. Most of these polymers contain carbazolyl groups as pendants. Much less presentations are reported on the polymers containing carbazole moieties in the main chain⁽⁹⁾.

Polymers have long been thought of and applied as insulators. Indeed, not so long ago, any electrical conduction in polymers mostly due to loosely bound ions was generally regarded as an undesirable phenomenon. The unique properties of inherently conductive polymer backbones from the possibility of fine-tuning

the conductivity by adjusting the amount of dopant incorporated within the polymer, doping/undoping reversibility, and the optical absorption characteristics in the UV, visible and near infrared as well as, electromagnetic, absorption, characteristics. Conductivity of polymer related to low band gap which is both p- and n-dopable, as both the anode and the cathode has been reported. The uses of conducting polymer in many practical applications depends on their environmental, electrochemical and thermal stabilities. The time and temperature dependences of conductivity have been made to understand the aging process and mechanics of conduction.

Molecular electronics ME materials differ from conventional polymers by having a delocalized electronic structure that can accommodate charge carriers such as electrons and holes. CPs such as polypyrroles, polythiophenes and polyanilines have been projected for applications for a wide range of Molecular electronics ME devices. One of the main reasons for such a wide-spread interest is due to the reported observation that these interesting electronic materials exhibit full range of properties from insulator to superconductor depending upon chemical modification. CPs have been found to have applications as optical, electronic, drug-delivery, memory and biosensing devices. The major challenge confronting the materials scientists including chemists and physicists is how do the properties of these electronic materials differ from those of conventional semiconductors. Another advantage lies in the fact that these materials possess specific advantages such as high packing density, possibility of controlling shape and electronic properties by chemical modification ⁽¹⁰⁾

2.3. Polycarbazoles and its derivatives

Carbazole unit (figure. 5) can be substituted at the 3- and 6-position as well as 2- and 7- position to provide poly carbazole derivatives with different properties and potential application, carbazole exhibit high thermal and photochemical stability and available. In addition to is cheap material and can be produced from

coal-tar distillation and has biological activity and as attractive building blocks for construction of functional materials. Figure 5. Mechanism of polymerization of carbazole.

Carbazole is rich electron donor, (reversible redox behavior), and high charge carrier mobilities. Due to the ease of formation of relatively stable radical cations (polarons), carbazole readily polymerize at electrochemical polymerization process. The first report of electropolymerization of carbazole was carried out by Ambrose and Nelson in 1968. They have exhibited that carbazole could polymerize from 3, 6 and 9, positions and also noted that coupling could proceed through the 1 and 8 positions; however, these positions are sterically hindered due to rigid structure of carbazole. Carbazole containing polymers are of interest due to their applications in electrochromic devices, hole transport layers, microcavity photoconduction, and as photovoltaic components that provide a very efficient matrix as a current carrier transport ⁽⁹⁾.

Carbazole compounds are also efficient electron-transfer photosensitizers for a wide variety of onium salt photoinitiated cationic polymerizations, and polymers containing carbazole compounds are generally very good photosensitizers. Crivello et al., found that the inclusion of even a small amount of a carbazole photosensitizer, such as PVCz, was effective in markedly accelerating the photopolymerizations of epoxide and vinyl ether monomers. The broadening of the spectral response through the use of these carbazole-based photosensitizers accounted for the rate enhancement of the polymerization reactions. Copolymers of N vinylcarbazole with two vinyl monomers and a dimeric photosensitizer were synthesized and also shown to be efficient photosensitizers (11).

2.3.1 Electrochemical polymerization of carbazoles

The polymerization is reaction to convert monomers to a polymer. The methods of synthesis polymers was divided into two methods; chemical methods and electrochemical methods. Chemical synthesis has the advantage of being a simple process capable of producing bulk quantities of polymers. However, electrochem-

ical methods has a good processability. A new class of polycarbazole-CPs has been industrialized lately. The polycarbazole-CPs found, a rather limited applications, except poly-vinylcarbazole presenting unique optical and electrochemical properties. It is known that, during poly-N-carbazole growth, N-alkylated monomers electropolymerized at the 3-3' and 6-6' heterocyclic positions, affording mainly tetramers soluble in the electrochemical medium. Because of this solubility issue forbidding film production, interest in this CPs class for sensing applications was rather limited calling for newly designed electropolymerizable carbazole monomers overcoming this limitation.

During the past two decades, conjugated polymers with different chemical structures emitting different colors in the whole visible range have been widely investigated, and devices based on these materials have been fabricated. These organic electroactive and photoactive materials are usually based on carbazole moieties. Among them, increasing interest has been paid to polycarbazoles (PCzs) because they are one of the most promising candidates for hole-transporting and photoluminescence efficiency units. Moreover, PCzs have the possibility of substitution at N position. This facile process provides the opportunity to improve both the solubility and functionality of the resulting polymer. On the other hand, flexible side chains can cause steric hindrance and thereby provide a means to control the effective conjugation length and thus tuning the color of the emitting light in devices.

The principal properties of polycarbazole (PCz) might be improved by the introduction of a proper moiety in the backbone of the polymer, which can be easily achieved by electrochemical copolymerization process. Polycarbazole (PCz) thin film synthesized on SnO₂ coated glass substrates. The electrolyte type used was a hydric LiClO₄. It is shown that, after optimization of potential scanning domain PCz are systematically obtained. The film obtained with LiClO₄ as electrolyte is homogenous, their coverage efficiency on SnO₂ is very high. Also we can obtain PCz

by carbazole oxidation in solution with acetonitrile in the volume ratio 1/2, containing 0.1M tetraethyl ammonium perchlorate. It is shown the film is also homogenous and the coverage efficiency can be obtained only when a thin film of carbazole was deposited by evaporation under vacuum before electro polymerization (12).

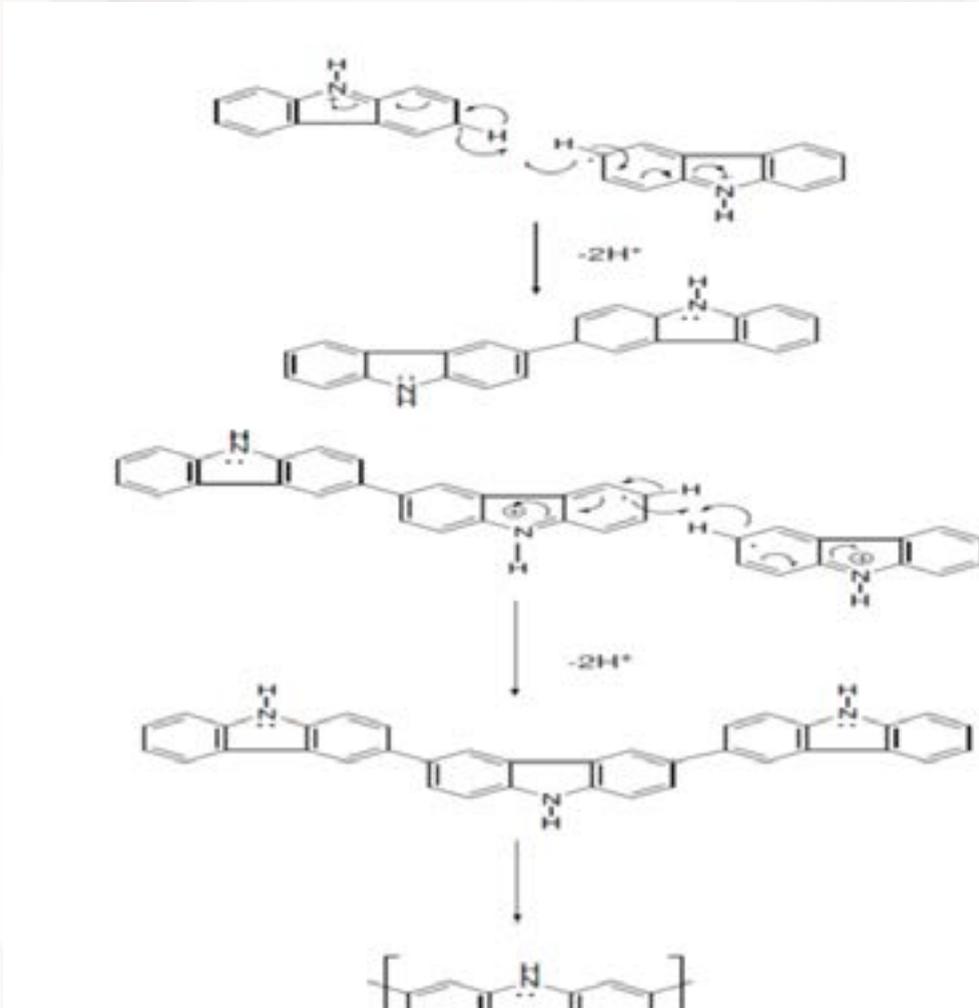


Figure 5. Mechanism of polymerization of carbazole

Soluble conducting polycarbazole using 4-methyl carbazole-3-carboxylic acid monomer were synthesised by electrochemical oxidation in acetonitrile. . The synthesized electrochromic

poly(4-methyl carbazole-3-carboxylic acid) was characterized by electrochemical and spectroscopic techniques. Introduction of side chain (alkyl, withdrawing, donating group) increase the processability and electronic properties of the polymer

High quality polymer films can be easily electrodeposited by low-potential anodic oxidation of carbazole and its alkyl derivatives Noctylcarbazole, N-(6 bromohexyl) carbazole, 1,6-bis(-carbazolyl) hexane in boron trifluoride diethyl etherate (BFEE) or mixed electrolytes BFEE + CHCl_3 . A set of alkyl substituted carbazole-based conducting polymers have been synthesized by direct anodic oxidation of carbazole and its derivatives N-OCz, N-BHCz and 2Cz-H in BFEE and BFEE + CHCl_3 solutions. They all showed much lower oxidation potentials in BFEE than those in ACN (13).

2.3.2. The polymerization of N- substituted carbazoles

Poly (N-vinylcarbazole) (PVCz) materials have been extensively studied. They exhibit interesting electrical and optical properties as light emitting diode materials, solar cells, and applications in various electrochromic devices. Specifically, PVCz shows good hole-transport properties which have important applications for improving the performance of organic electroluminescent devices. Others have reported applications in amperometric chemical sensors. PVCz exhibits these interesting properties primarily due to the carbazole group (14).

Electropolymerization by cyclic voltammetry and chronoamperometry of N-ethylcarbazole (ETCZ) and 3,4-ethylenedioxythiophene (EDOT) was carried out in water /methanol (v/v: 1/3) 0.01 M sodium dodecylsulfate (SDS) and 1.25 M perchloric acid on platinum button electrodes. Methanol improves the ethylcarbazole solubility and allows a well-defined polymer growth on the working electrode. The SDS makes easier the ETCZ and EDOT electropolymerization. Indeed, the presence of micelles decreases the monomer oxidation potential and induces an acceleration of the polymerization. ETCZ and EDOT have similar monomer ox-

idation potentials in this medium. Moreover their polymers show a better stability than the polymers obtained without surfactants. Therefore, electropolymerization mixtures of these monomers was carried out with different ratios (v/v, 70/30, 50/50 and 30/70) in order to prepare copolymers and the resulting products were characterized by electrochemistry, IR and UV-/visible spectroscopy and SEM. (15).

From the literature we found that N-(Hydroxymethyl) carbazole was synthesized electrochemically coating thin film on carbon fiber micro electrodes. Surface characterization of electrocoated poly (N-(hydroxymethyl)carbazole) of carbon fiber microelectrode (CFME) was performed by reflectance FTIR spectroscopy, scanning electron microscopy, and cyclic voltammetry (15).

In previous study, the scientists synthesized and polymerized some tertiary arenes based on N-ethylcarbazole and thiophene. N-ethylcarbazole was chosen as an internal conjugated moiety so as to provide a planar, synthetically flexible core, which could easily be derivatized with no loss in extent of conjugation. Since discovery of photoconductivity of PVCz by Hoegl, carbazole containing polymers have great importance in photo-electronic technology. Due to ease of formation of relatively stable radical cations (holes), high charge carrier mobilities, high thermal and photochemical stabilities, these polymers have been used in electrochromic devices, hole transport layers, electro-xerography, microcavity photoconduction, and as photovoltaic components that provide a very efficient matrix as a current carrier transport. Carbazole could also be easily functionalized at (3,6) (2,7) or N-positions, and then covalently linked into polymeric systems, both in the main chain as building blocks and in a side chain as pendent groups (16)

Poly (3,6-N-vinylcarbazole) films were prepared by electrochemical oxidation of N-vinylcarbazole on a Pt electrode using acetonitrile as solvent and tetraethylammonium tetrafluoroborate as electrolyte. The electrosynthesis was carried out by electrical potential cycling in the presence of two different bases: tetraeth-

ylammonium benzoate (Bz₋) and tetraethylammonium phthalate (Ph₋). These salts were expected to modify the acidity level of the electrolyte since they can act as scavengers for the protons released during the polymerization, when the reaction takes place in the carbazole unit. Products were characterized by cyclic voltammetry, scanning electron microscopy, FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, absorption spectroscopy and four-probe electrical conductivity measurements. Both bases influenced significantly the chemical structure and morphology of the deposited materials. The presence of Ph₋ in the electrolyte decreases the cross-linking of the electrodeposited polymer, leading to a poly(3,6-N-vinylcarbazole) bearing a more uniform morphology, higher thermal stability and electrical conductivity compared to those of the polymers obtained in the presence of Bz₋ and without acidity control (16).

Carbazole could also be easily functionalized at its 3,6- or N positions and then covalently linked into polymeric systems, both in the main chain as building blocks and in a side chain as pendent groups. Due to the ease of formation of relatively stable radical cations (polarons), carbazole readily polymerize at electrochemical polymerization process. The first report of electropolymerization of carbazole was carried out by Ambrose and Nelson They have exhibited that carbazole could polymerize from 3, 6 and 9, positions and also noted that coupling could proceed through the 1 and 8 positions; however, these positions are sterically hindered due to rigid structure of carbazole(9)

Since polyacetylene doped by oxidizing or reduced agents showed good electrical conductivity. Many studies have been devoted to the electrical properties of the conjugate polymers. Among these conducting polymers, polyaniline(PANI) has received greater attention owing to its good stability in the presence of oxygen and water and has electrochemical properties for development of batteries and electrochromic display devices. Carbazole derivatives also have been of greater interest because of their useful applica-

tion especially in electrophotograph and electroluminescence device (8).

2.3.3 The conductivity of polycarbazole

The solid state conductivity of polycarbazole with respect to initial carbazole concentration was linearly proportional to conductivity. i.e., an increasing monomer concentration leads to an increase in the amount of radical cations. This increases the conjugation length of the polymer and also increases the conductivity of the polymer. The conductivity of polycarbazole was found as $7.0 \times 10^{-3} - 1.27 \times 10^{-3} \text{ S}$ (17).

Polycarbazole (PCz) can be electrochemically deposited to yield conducting thin films on desired electrodes and are known to be electrochemically stable and show better redox behaviour in protic acid medium. It has been revealed that reduced Polycarbazole (PCz) show yellow colour and low conductivity ($> 10^{-9} \text{ Scm}^{-1}$) where oxidized Polycarbazole (PCz) are green and have enhanced conductivity ($> 10^{-3} \text{ Scm}^{-1}$). The electrical conductivity of PCz at room temperature is quite low (about $2.5 \times 10^{-12} \text{ Scm}^{-1}$) (17).

3. Electrochromism

Electrochromism refers to the reversible color change of electroactive materials upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current after the application of an appropriate electrode potential. Electrochromic polymers have received increasing attention due to their potential for structurally controllable HOMO–LUMO band gap, fast switching speeds, high contrast ability, and easily processing. With these properties they become more advantageous than the ones which are in inorganic nature. The optical change in these electrochromic polymers is influenced by a low electric current at low potentials in the order of a fraction of a volt to a few volts. The color is determined by the band gap, defined as the onset of the $\pi - \pi^*$ transition. Then, band gap control becomes an important issue in the construction of dual-polymer based electrochromic devices where

a low band gap (cathodic coloring) polymer is matched with a high band gap (anodic coloring) polymer to obtain a high degree of contrast during the switching process. A material which has more than two redox states may exhibit electrochemically several colors and it can be termed as poly-electrochromic. Theoretical considerations suggest that the absorption and emission spectra of certain dyes may be shifted by hundreds of angstroms upon application of a strong electric field. This effect is called “electrochromism”, in analogy to “thermochromism” and “photochromism” which describe changes of color produced by heat and light. Electrochromism refers to the reversible color change of electroactive materials, during the electrochemical redox reaction. When switching the redox states generates new or different visible region bonds, color changes are commonly between transparent (bleached) state where the chromophore only absorbs in UV region and coloured state or between two coloured states electrochromic material may exhibit several colours so called (polychromics). Electrochromism can be defined as a reversible color change in a material caused by an applied voltage. The first studies about electrochromic materials started with inorganic semiconductors such as tungsten trioxide (WO_3) and iridium dioxide (IrO_2), and then organic small molecules such as viologens, metallophthalocyanines and finally conducting polymers, received much attention for electrochromic applications. In the most of the researches onto electrochromic materials, donor and acceptor moieties are conjugated to the main chain of the polymers (18)..

Electrochromic materials are generally first studied at a single working electrode, under potentiostatic or galvanostatic control, using three electrode circuitry. Electrochemical techniques such as cyclic voltammetry, coulometry, and chronoamperometry, all with, as appropriate, in situ spectroscopic measurements are employed for characterization. An electrochromic device is essentially a rechargeable battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a

charge balancing counter electrode, and the color changes occur by charging and discharging the electrochemical cell with applied potential of a few volts. After the resulting pulse of current has decayed and the color change has been effected, the new redox state persists, with little or no input of power, in the so called "memory effect". Carbazole containing polymers are of interest due to their applications in electrochromic devices, hole transport layers, electro-xerography, microcavity photoconduction, and as photovoltaic components that provide a very efficient matrix as a current carrier transport, also can use the electrochromic devices in controllable light reflective or light transmissive device for optical information and storage, sunglasses, protective eyewear for military, example of electrochromic materials is viologens (19).

4. Electrochemiluminescence (ECL)

Electrochemiluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer films. Electro generated chemiluminescence (ECL) has widely been applied as a sensitive and selective detecting technique for many analytical applications; it is also an excellent model for investigating the mechanism of electron transfer. ECL is a process that involves photon generation by homogeneous electron transfer (ET) between electrochemically generated radical cations and radical anions that form in close proximity to the electrode surface in an ECL cell. Mechanism of ECL the electro active species is excited to excited state and with redox can be emitting with emission of light with appropriate (20)

Carbazole is rich electron donor, (reversible redox behavior), chemiluminescence (ECL) is a process involve photon generation by

homogenous electron transfer(ET) between radical of cations and anions in close to surface of electrodes in the cell.Mechanism of ECL the electro active species is excited to excited state and with redox can be emitting with emission of light with appropriate wave length depending on (ΔH enthalpy),carbazole or molecules incorporating carbazole moieties have been investigated as light emitting materials and as hole- transporting materials in (OLED) because they have high reversibility upon electrochemical oxidation .As an electron transfer function, carbazole has been proven to be a good hole-transport material in organic light emitting diodes (21)

5. Light emission diode (LED)

Consist of a chip of semiconducting material impregnated, or doped, with impurities to create a p-n junction.As the other diode current flows easily from the p-side,or cathode,to the n-side,or anode but not in reverse direction.Charge- carriers electrons and electron holes flow into the junction from electrodes with different voltages,when an electrons meets the hole,it falls into lower energy level and releases energy in form of photon.the wavelength of light emitted depends on band gap energy of materials forming the p-n junction.LEDs are usually built on an n-type substrate,with electrode attached to the p-type layer deposited on its surface. If the emitting layer materials of an LED is an organic compound, it known as an organic light emitting diode(OLED), to function as semiconductor, the organic emitting material must have conjugated pi bonds,the emitting material can be small organic molecule in acryalline phase,or apolymer. Polymer can be flexible;such LEDs are known as PLEDs orFLEDs. Compared with regular LED,- PLED are lighter,and polymer LEDs can have the added benefit of being flexible.Some possible future applications of OLEDs could be:

- Inexpensive,flexible displays
- Light sources
- Wall decoration.

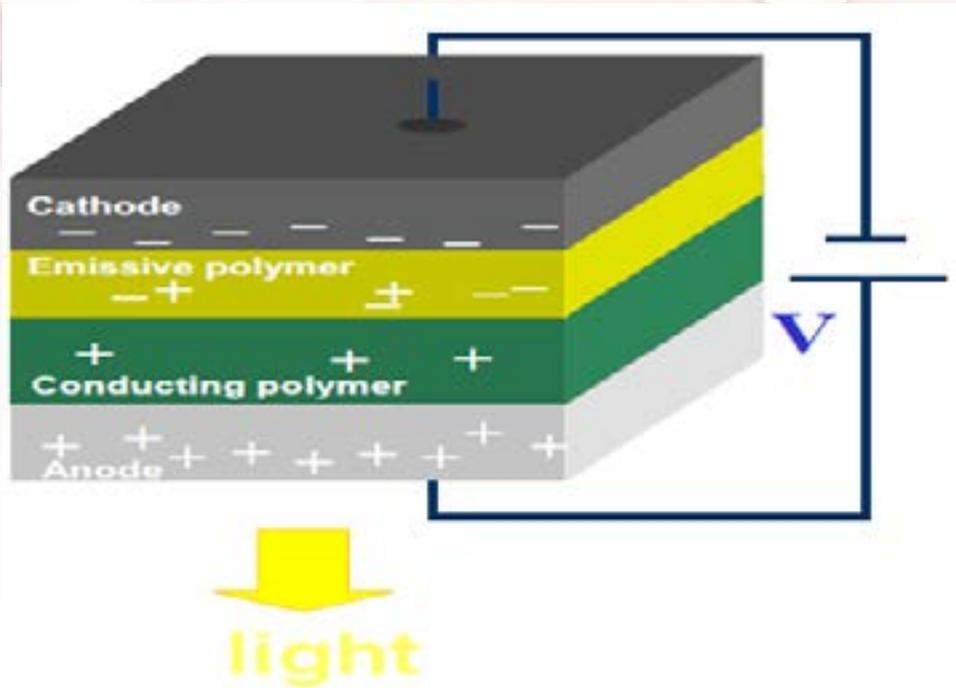
There is substantial interest in the development of new light sources based upon formation of emissive states in thin films of organic dyes, through direct injection of electrical charge into single layer or multilayer thin films (organic light-emitting diodes, OLEDs, or organic electroemissive devices, OLEDs). The interest in this type of electrically pumped luminescence can be traced back several decades to observations of light emission in thin films of single-crystal molecular materials such as anthracene and to studies of several electrochemically driven light emission processes at molecular crystal electrodes². Two different classes of materials have emerged recently based upon ultrathin films of (a) extended conjugation polymers exhibiting strong luminescence (e.g., derivatives of, poly(paraphenylenevinylene) PPV, and related luminescent polymers) and (b) vacuum-deposited small molecule systems including tris(8-quinolinolato-N1O8) aluminum and several other vacuum-compatible luminescent dyes.

5.1 Polycarbazolein OLED

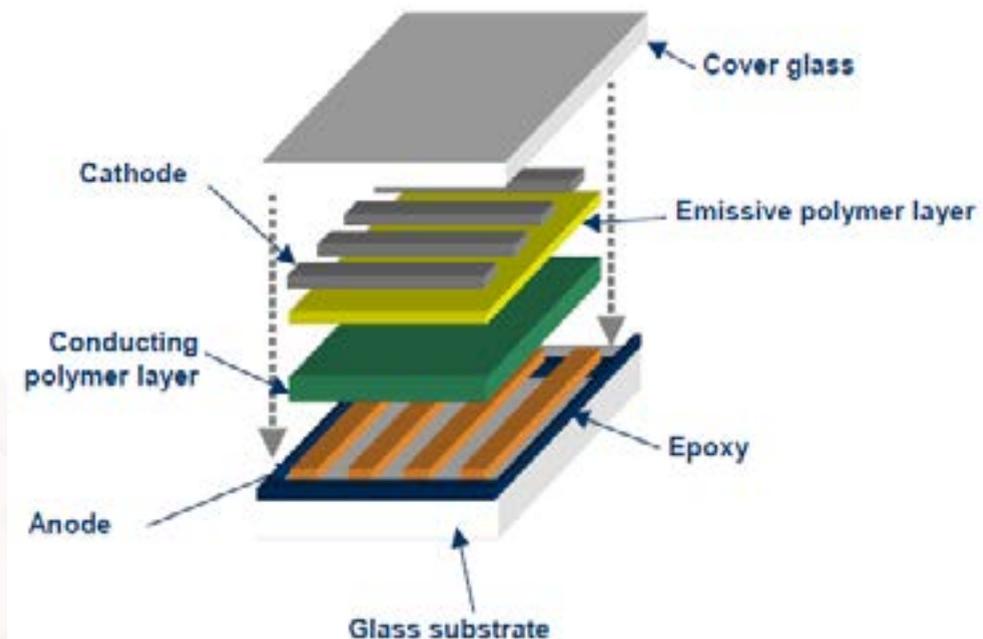
The carbazole family forms a subset of the organic materials under study for blue EL applications. Polyvinylcarbazole, polycarbazole, and many others derivatives have been used to achieve blue OLED. Siove et al. recently showed that the dimer of N-ethyl-carbazole exhibits a remarkable blue photoluminescence. These good electro-photoactive properties make carbazole containing polymers as suitable materials for LED and other optoelectronic devices. Carbazole units can be linked in two different ways leading to either poly(3,6-carbazole) or poly(2,7-carbazole) derivatives. While the former class seems to be very interesting for electrochemical and phosphorescence applications, the latter shows very promising optical properties in the visible range for organic light emitting diodes (OLED)(22).

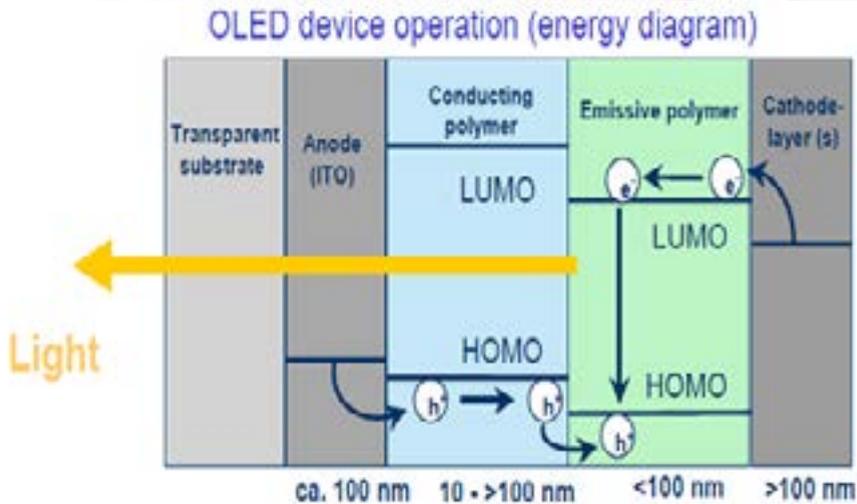
Owing to their promising electrical and photophysical properties¹⁵⁷ polycarbazoles are interesting candidates for applications in optoelectronic devices such as OPVs, OFETs and OLEDs. Polycarbazoles are strong blue emitters with high fluorescence quantum yields and they are excellent hole transport materials with high thermal stability and glass forming properties. Moreover, depending on the substitution and connection pattern (3,6- vs. 2,7-linkage,) they can closely match the hole injection energy of ITO electrodes. The 2,7-linked polycarbazoles are often favoured to 3,6-linked polycarbazoles because of their higher fluorescence quantum yields in solution and their extended conjugation over several monomer units. OLEDs have been fabricated from both 2,-7 and 3,6-linked, polycarbazoles. However, compared to the devices made from D-A conjugated polymers mentioned above these were rather low performing OLED devices. As an acceptor moiety in D-A compounds triarylboranes have been successfully used in small molecule OLEDs in the past decade. They have been shown to be applicable as electron transport layer, hole blocking layer and light emitting layer with colours ranging from blue, over green, yellow to orange depending on the donor and the bridge. Even white light-emitting devices have been fabricated from triarylborane containing molecules.⁽²²⁾

An OLED is an electronic device made by placing a series of organic thin films between two conductors. When electrical current is applied, a bright light is emitted. A device that is 100 to 500 nanometers thick or about 200 times smaller than a human hair. Organic light-emitting devices (OLEDs) have shown potential to be low-cost, full color flat panel displays due to their merits of high brightness, easy fabrication, and the availability of a wide range of



emission colors (Figure 7).





The battery or power supply of the device containing the OLED applies a voltage across the OLED.

An electrical current flows from the cathode to the anode through the organic layers (an electrical current is a flow of electrons).

At the boundary between the emissive and the conductive layers, electrons find electron holes.

The OLED emits light.

Generally, OLEDs are composed of functionally divided organic multi-layers, a hole-transporting, an emitting, and an electron transporting layers sandwiched between two electrodes. Charge carriers (holes and electrons) are injected and transported from the anode and cathode, and are recombined in the emitting layer to emit light. The primary role of the hole-transporting layer is to assist the hole injection from the anode into the light-emitting layer and block electrons within this layer, transporting the holes to the emitting layer, thus maximizing the recombination probability of the injected carriers. The materials used as hole-transporting materials should be good hole conductors and possess good mechanical, thermal and electrochemical properties (23).

The rapid development of our information-intensive society has increased the technological demands of flat panel displays. In par-

ticular, organic light emitting diode (OLED) devices are attractive for their application in next generation flat panel displays due to their low-cost fabrication, high pixel density, bright electroluminescence with high contrast, high efficiency, wide visual range, and low direct current (DC) voltage requirements. Recently, OLED devices have been commercially applied for cellular phones and small-sized televisions by Samsung and Sony, respectively. Although research on OLED devices has been continued for a long time, they have been inadequate for larger size of displays, where-in the most challenging technical problem has been involved with the selection of an organic material that is both efficient and stable. (24).

Currently, many carbazole compounds have been used as host materials for OLEDs. It is very important to balance between the hole, electron injection, and transportation. The multi-functional electroluminescent small molecules and polymers have already been discussed whereby light emission and electron- and hole-transporting properties are combined in one material to achieve high efficiency (25)

The vacuum-deposited small molecule OLEDs are also often doped with low concentrations of other dyes such as quinacridones with longer wavelength emissions, which allow for enhancement of the electroluminescent response and color tuning. (25)

Organic light emitting devices (OLEDs) have shown potential to be low-cost, full color flat panel displays due to their merits of high brightness, easy fabrication, and the availability of a wide range of emission colors. The past decade has seen great progress in both device fabrication techniques and materials development (25)

Initial studies on poly (2,7-carbazole) derivatives indicated great potential as blue-light-emitting materials. For instance, homopolymers exhibit blue fluorescence with a maximum of emission near 415-440 nm with relatively high quantum yields.^{9,27} Taking advantage of the chemical versatility of the carbazole unit, many poly(2,7-carbazole) derivatives were specifically developed to

maximize their electroluminescence properties.

The carbazole family forms a subset of the organic materials under study for blue EL applications. Polyvinylcarbazole Polycarbazole and many others derivatives have been used to achieve blue OLED. Siove et al. recently showed that the dimer of N-ethyl-carbazole exhibits a remarkable blue photoluminescence These good electro-photoactive properties make carbazole containing polymers as suitable materials for LED and other optoelectronic devices. The most important topics of the rapidly developing field of conducting polymers especially on carbazole containing ones are reported recent literatures (22).

Carbazole containing polymers are of interest due to their applications in electrochromic devices, hole transport layers, electro-xerography, microcavity photoconduction, and as photovoltaic components that provide a very efficient matrix as a current carrier transport. These polymers also constitute an important part of the photoconductive polymers and organic photoreceptors These polymers obtained have also various advantageous properties; such as, high charge carrier mobilities, high thermal and photochemical stabilities. Carbazole could also be easily functionalized at its 3,6- 2,7- position or in N-positions and then covalently linked into polymeric systems, both in the main chain as building blocks and in a side chain aspendent groups (9).

Molecules incorporating carbazole moieties have been investigated extensively as light-emitting materials and as the hole-transporting materials in organic light-emitting devices (OLED) because of their high reversibility upon electrochemical oxidation..Previously, we established a feasible synthesis, using Suzuki coupling reaction, of molecules containing pyrimidine moieties. These pyrimidine-containing materials undergo reversible reduction processes, which suggests that they hold promise for use in light-emitting and electron transport materials. We anticipated that the preparation of a molecule that combines the individual characteristics of carbazole (i.e., electron richness) and pyrimidine (i.e., high electroneg-

ativity) moieties would afford a new kind of material. In this letter we report the synthesis and properties, including ECL behavior, of such a novel molecule(20).

6. Application of polycarbazole

Polycarbazole (PCz) is one of many relatively new conducting polymer groups with good electrochemical characteristics, and its conductive form can easily be obtained by the electrochemical method. Investigations related to chemical modification or copolymerization of carbazole with other monomers have led to the use of PCz and its derivatives as redox catalysts, photoactive devices, sensors, electrochromic display, electroluminescent devices and biosensors (8).

A new class of polycarbazole-CPs has been developed recently. The polycarbazole-CPs found rather limited applications, except poly-vinylcarbazole presenting unique optical and electrochemical properties. It is known that, during poly-N-carbazole growth, N-alkylated monomers electropolymerized at the 3-3' and 6-6' heterocyclic positions, affording mainly tetramers soluble in the electrochemical medium. Because of this solubility issue forbidding film production, interest in this CPs class for sensing applications was rather limited calling for newly designed electropolymerizable carbazole monomers overcoming this limitation. Moreover, if successfully grown, such polycarbazole-CPs films should include an appropriate grafting surface chemistry to link covalently capture probes of interest (post-polymerization functionalization) resulting in innovative polycarbazole-CPs based transducing surfaces. (26)

Polycarbazole in electronics industry are overtaking their long established passive roles as insulating and encapsulating materials to more active new application. Polymers and oligomers can be used as materials for diodes, thin film transistors and light emitting diodes (LEDs). Acceptor-substituted carbazole derivatives also were designed as novel photoconductive materials and non-linear optical materials with large photorefractive effect. Several elec-

tro luminescence (EL) materials containing carbazole group had been used in light emitting diodes (LEDs) devices (27)

carbazole and its N-substituted derivatives were extensively studied by Ambrose et al. They investigated the reactivity of cation radicals formed from benzene ring substituted carbazole using electrochemical and spectroscopic techniques. It was reported that the 3, and 9 positions on carbazole were extremely reactive and anodic oxidation of carbazole produced very unstable cations, such as 9,9'- and 3,3'-bicarbazyls. Though conducting polymers can be polymerized by two methods viz chemical and electrochemical techniques, electrochemical method offers a better control over properties as they can be tailored by changing experimental conditions such as electrolyte, oxidation potential, solvent, etc. To date, polycarbazole is extensively synthesized using electrochemical techniques and this polymer is mainly studied for its optical and electrochemical properties (27)

An electrical battery is one or more electrochemical cells that convert stored chemical energy into electrical energy. Batteries have become a common power source for many household and industrial applications. One of the major reasons which has promoted the speedy development of conducting polymer is their anticipated use as electrodes in light weight and rechargeable batteries. Compared to lead-acid batteries, polyacetylene (CH)_x battery is not only lighter in weight but also has higher energy and power densities respectively. However, the major disadvantage still confronting the large scale commercial exploitation of (CH)_x/Li cell is that only 7-8% of the injected charge is used. Polypyrrole and polythiophene now appear and are used efficiently in batteries because they have some properties, light weight, long-lasting and higher conductivity. The use of conducting polymers as electrodes in lithium secondary batteries and supercapacitors (pseudocapacitors) was discussed above. From the standpoint of electrochemistry in non-aqueous solutions, the use as electrochromic materials is also interesting. Conducting polymers usually have different colors between the

doped- and undoped-states. The color change of the transmitted light by the undoped doped conversion is red_blue for the polythiophene film, yellow_blue for the polypyrrole film, and light yellow-green for polyaniline(2).

carbazole derivatives are promising as advanced amorphous materials for photorefractive systems. (27)

7. Conclusions

- Conducting polymers can be obtained from organic compounds
- Carbazole monomers are electrochemically, polymerized to give polymers that consist of carbazole backbone
- The polymers show electrical characterizations.
- The electrochromic systems formed exhibit strong green colour on oxidation and transparent on reduction
- Spectroscopic data give strong evidence of the formation of polymer material.

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