THEORETICAL AND SPECTROSCOPIC INVESTIGATION ON THE CONDUCTING POLYMER IN THE CLASS OF CARBAZOLE DERIVATIVES

INTRODUCTION

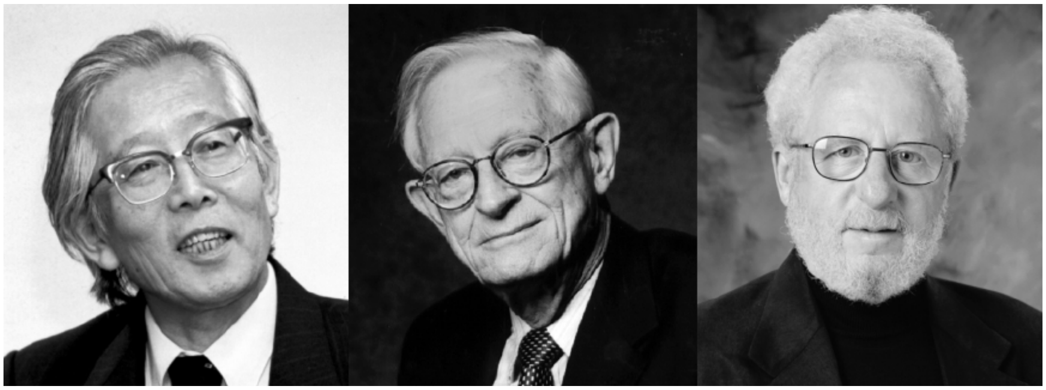
1. <u>Conducting Polymers</u>

1.1 Overview

Twenty years after the discovery by Heeger, MacDiarmid, Shirakawa, and co-workers (Chiang *et al.*, 1977), polyacetylene can be made highly electrically conducting by exposure to oxidizing or reducing agents. A reaction usually called "doped" by loose analogy to what take place in inorganic semiconductivity. A lot of work has focused on conjugated polymers. These studies have led to the achievement of high conductivity in other conjugated polymers, such as poly(1,4-phenylene), polypyrrole, polythiophene or polyaniline. Improved characterization of these compounds has been obtained as a consequence of their solubilization in common organic solvents (Hotta *et al.*, 1987). In this context, conjugated polymers, which are intrinsic semiconductors due to their delocalized π-electrons, have attracted much research effort in the last fifteen years.

Recently, a number of studies have been devoted to the search for polymers that would possess small intrinsic band gap, that are intrinsically good electrical conductors or semiconductors without the need of any chemical or electrochemical doping reaction. The optical properties of small-band-gap polymers also make them interesting. Indeed, most of the conjugated organic polymers are colored as a consequence of their band gaps in the 1.5-4 eV range. However, if the band gap energy is smaller, the lowest electronic transition could lie in the infrared region and the corresponding materials could be transparent in either the neutral or doped state. The possibility of dealing with process, transparent conducting polymers would represent an important breakthrough for applications of conjugated polymeric materials.

Although unified by direct concern with the effects produced by electric fields, the subject of the electrical properties of polymers covers a diverse range of molecular phenomena. Until the latter part of the twentieth century, known polymers generally displayed a much less striking electrical response than inorganic materials. While inorganic solids behave as semiconductors and metals (where the electrical response is overwhelmingly one of electronic conduction), or as insulators, the common polymers were distinctly confined to the latter category. From 1950 onwards this situation changed with the emergence of polymers displaying semi-conducting properties and the discovery in the 1970s of polymers that even had metallic levels of conductivity. Since then there has been an explosion in fundamental and applied research and numerous conductive polymers have been produced and studied. While the macroscopic properties of these materials resemble those of their inorganic counterparts, their microscopic behavior is markedly different and reflects fundamental differences between the rigid crystal lattices of inorganic materials and the deformable, molecular structure of polymers. The significance of this class of polymers was recently highlighted by the awarding of the 2000 Nobel Prize in Chemistry to H. Shirakawa, A. G. MacDiarmid, and A. J. Heeger, the three scientists who pioneered this novel materials field.



(a) (b) (c)

The discovery of conducting polyacetylene was recognised by the award of the Chemistry Nobel Prize in 2000.

Figure 1 (a) Hideki Shirakawa, (b) Alan MacDiarmid and (c) Alan Heeger.

The absence of conduction in insulating polymers allows a whole set of more subtle electrical effects to be readily observed. For instance, polarization resulting from distortion and alignment of molecules under the influence of an applied field becomes apparent. Examination of such polarization not only gives valuable insight into the nature of the electrical response itself, but it also provides a powerful means of probing molecular dynamics. In conducting polymers the presence of charge carriers produces pronounced local deformation of the molecular framework, significantly larger than that found in inorganic semiconductors. The Coulomb interaction of charge carriers is less effectively screened in conducting polymers. Hence electron-phonon and electron-electron interactions have more profound effects in conducting polymers. It should also be noted that single crystal polymers are rare and the complex morphology of partially crystalline polymers has an impact on their electrical properties. For all these reasons electrical studies form a desirable supplement to studies of mechanical and thermal properties aimed at reaching an understanding of the behavior of polymers on a molecular basis. In the remainder of this section we outline the main features of conducting polymers structure and application of conducting polymers.

1.2 Structure of Polymers

Most of the synthetic high polymers are organic compounds consisting of long, chain-like molecules where repeated molecular units are linked by covalent bonds. A single molecular chain can contain a thousand or more repeat units and reach a total length in excess of 1 μm. Such large molecules have complex shapes and form solids that may be either amorphous or crystalline, but are commonly partially crystalline. The atoms, which form the *backbone* of conducting polymers, are predominantly carbon atoms, sometimes in combination with oxygen and/or nitrogen. The nature of the chemical bonding in the polymer directly influences the electrical properties.

1.2.1 Chemical Structure-Saturated Polymers

The carbon atoms in a polymer are primarily bound together by *covalent bonds* formed by the interaction of two electrons, one from each of the atoms linked by the bond. We illustrate this process with the simpler example of bond formation between two hydrogen atoms. As the atoms are brought together their 1*s*-electron orbitals overlap forming two new σ-orbitals around the atoms, which are symmetric and have zero angular momentum with respect to the interatomic axis. One orbital, the bonding orbital, is formed by the linear superposition of the two *s*-orbitals, shown by the solid curves in Figure 2(a). This gives a high electron density between the hydrogen nuclei, the dashed line in Figure 2(a), which reduces their electrostatic repulsion. Thus the nuclei are drawn together and an electron in the bonding orbital has a lower energy than one in the isolated atom orbital. The other, the antibonding orbital, is formed by the superposition of *s*-orbitals with opposite sign, see solid curves in Figure 2(b), giving a lower electron density between the nuclei, shown by the dashed curve in Figure 2(b). The electrostatic repulsion between the nuclei is not screened and the energy of an electron in this orbital is increased, as indicated in Figure 2(c). The Pauli Exclusion Principle allows the two electrons from the hydrogen atoms to *pair* in the bonding orbital, if they are of opposite spin, to give a stable molecule with total energy less than that of the two isolated hydrogen atoms.

A neutral carbon atom has six electrons, which occupy the 1*s*, 2*s* and 2*p* orbitals giving an electronic configuration of $1s^2 2s^2 2p^2$. When a carbon atom forms a bond with another atom, an *s*-electron is promoted to the vacant *p*-orbital to give a sp^3 configuration (s, p_x, p_y, p_z) in the outer valence shell. These electronic orbitals do not bond separately but hybridise, i.e. mix in linear combinations, to produce a set of orbitals oriented towards the corners of a regular tetrahedron. Figure 3 shows the form of the wavefunctions that describe the hybridised orbitals. The sp^3 hybrids allow a much greater degree of overlap in bond formation with another atom, and this, in turn, produces extra bond strength and stability in the molecules. The arrangement of bonds resulting from overlap with sp^3 hybrid orbitals on adjacent atoms gives rise to the tetrahedral structure that is found in the lattice of diamond and in molecules such as ethane, C_2H_6, as depicted in Figure 3.

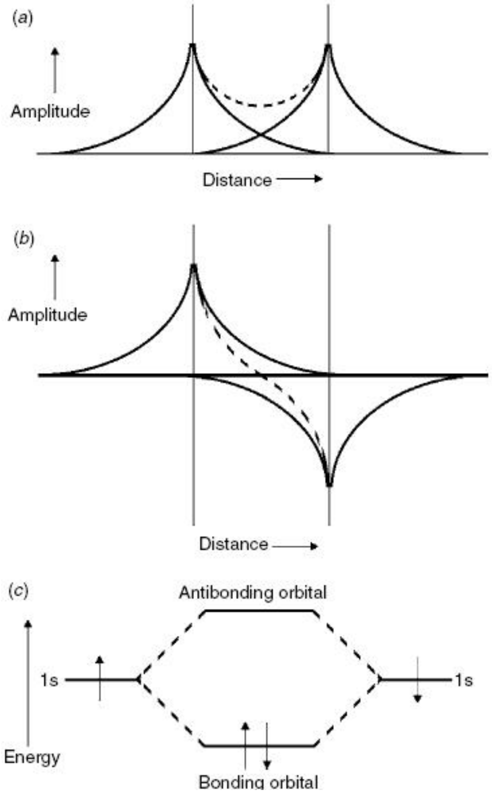


Figure 2 Overlap of hydrogen atom orbitals to form (a) a bonding orbital, and (b) an antibonding orbital, with energies as shown in (c).

In these structures all the available electrons are tied up in strong covalent bonds, σ-bonds. Carbon compounds containing σ-bonds formed from sp^3 hybrid orbitals are termed *saturated* molecules. Polyethylene, $-(CH_2)_n-$, is a typical saturated polymer where the σ-bonds between adjacent carbon atoms form the zigzag of the polymer backbone. The strong σ-bonding gives rise to chemically stable compounds and localize the electrons in the molecular structure rendering saturated compounds electrically insulating.

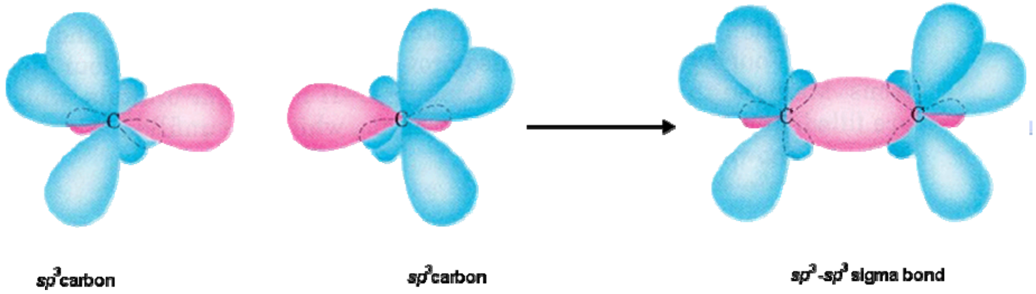


Figure 3 (a) sp^3 hybrid orbitals of carbon atom and the molecular structure of ethane molecule.

1.2.2 Chemical Structure-Unsaturated Polymers

The tetrahedral bonding is common in carbon compounds. It is not the only possibility. A planar σ-bond structure occurs if the hybrid orbitals are formed from one *s*- and two *p*-orbitals. sp^2 hybrid orbitals, which lie in a plane with angles of 120^o between them, are shown by the unshaded lobes in Figure 4, whilst the remaining *p*-orbital (p_z), which lies orthogonal to the plane of the σ-bonds, is shown by the shaded lobes. This p_z electron is then available to form additional π-orbitals, with unit angular momentum about the bond axis, with p_z electrons in adjacent atoms. The resulting *π-bond* will form parallel to the underlying σ-bond, resulting in a multiple (double) bond, as in ethylene, C_2H_4, as shown in Figure 4. Compounds where orbitals are used in this way to form double bonds between carbon atoms, rather than to form single bonds with other atoms, e.g. hydrogen, are said to be *unsaturated*. Where successive carbon atoms in a chain engage in π-bonding, the structure is said to be *conjugated*, and may be represented as a sequence of alternating single and double bonds, as shown in Figure 4, which illustrates the bonding in polyacetylene, –(CH=CH)$_n$–.

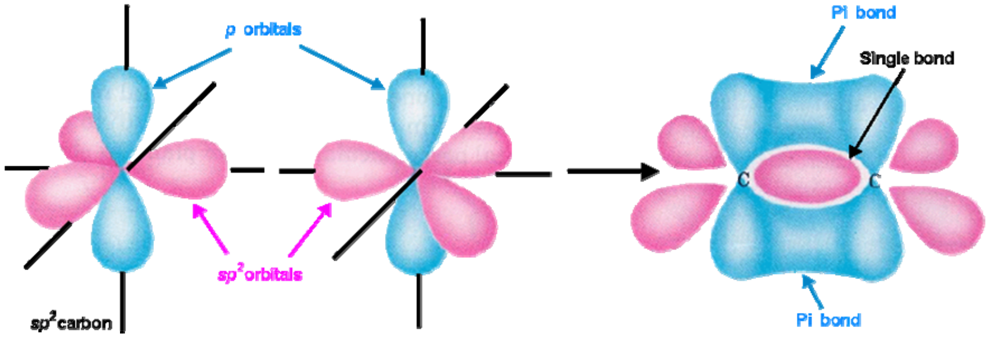
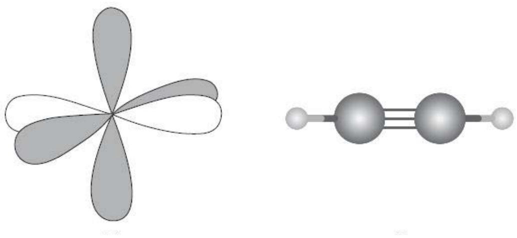


Figure 4 (a) *sp*^{2} hybrid orbitals of carbon atom and the molecular structure of ethylene.

Furthermore, compounds containing triple bonds can be obtained from *sp* hybrid orbitals. *sp* hybridisation produces two orbitals oriented at 180^o to each other, as shown by the filled lobes in Figure 5(a), which can form co-linear σ-bonds. This leaves two *p*-electrons, shown by the shaded lobes in Figure 5(a), which are free to form π-bonds aligned with the σ-bond, as in acetylene, C_2H_2 (shown in Figure 5(b)). The polymer polyyne, –(C≡C)$_n$–, also known as polycarbene, and shown in Figure 5(c), is formed with sp hybrids in this way. Its structure may be either an alternation of single and triple bonds or a sequence of double bonds, depending on the terminal groups (see Figure 5).



(a) (b)

Figure 5 (a) *sp* hybrid orbitals, and the molecular structure of (b) acetylene.

The formation of multiple bonds leads to a reduction in the separation of the carbon atoms involved. Thus a triple bond is shorter than a double bond, which is shorter than a single bond. This gives rise to an alternation of bond length in conjugated polymers such as polyyne and polycarbene, Figures 6. The electrons in the π-bonds are less strongly bound than the electrons in the σ-bonds. Hence the π-electrons can be more easily removed from the bonds than can the σ-electrons. In consequence unsaturated compounds are less chemically stable than saturated compounds. The multiple bonds are subject to chemical attack, being reduced to saturated (single) bonds in the process. The weaker binding of the π-electrons also means that unsaturated compounds have the potential to display either semiconducting or metallic behaviour.

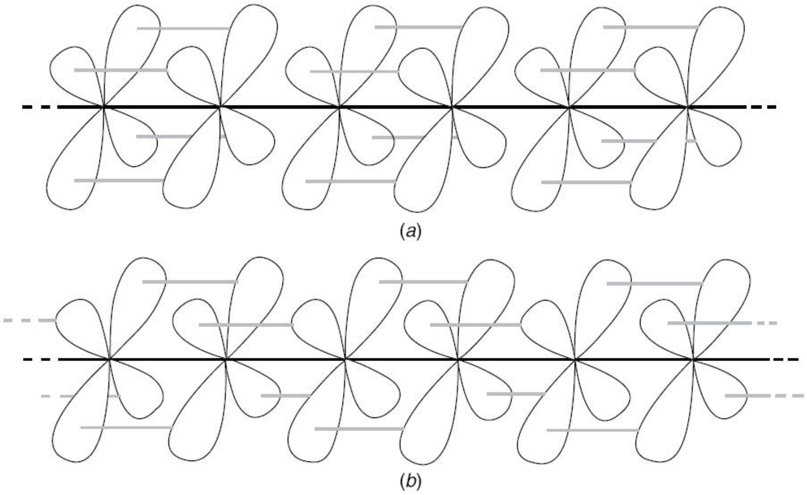
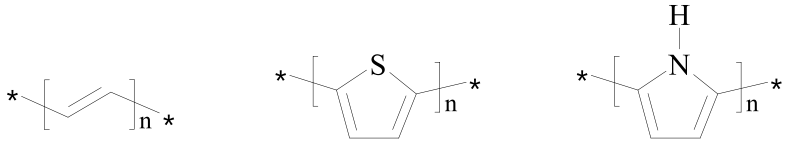


Figure 6 Alternative structures of polymers formed with *sp*-hybridised orbitals, (a) polyyne and (b) polycarbene. Overlap of the π-electron orbitals, shown by the off-axis lines, gives an interatomic π-bond. The σ-bonds are shown by on-axis lines.

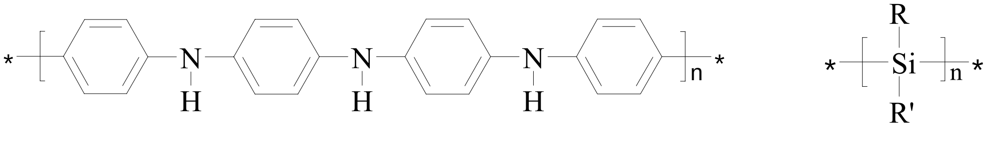
In organic semiconducting polymer, this continuous string of orbitals creates degeneracy in the highest occupied and unoccupied orbitals and leads to the filled and unfilled bands that define a semiconductor. However, conductive polymers generally exhibit very low conductivities. This is because conduction in such relatively disordered materials are due to mobility gaps with phonon-assisted hopping, tunneling between localized states but not band gaps as in crystalline semiconductors.

As mentioned before, organic semiconductor can be doped either by removing an electron from valence band or adding an electron to the conduction band to increase its conductivity. Doping organic semiconductor creates more charge carriers which move in an electric field. This movement of charge is responsible for electrical conductivity in organic semiconductor. Doping a polymer is different from that of inorganic semiconductor in which elements with excess and shortage of electrons are introduced. In polymer, both doping process involves an oxidation and reduction process. The first method involves exposing a polymer to an oxidant such as iodine or bromine or a reductant such as alkali metals (Wu *et al.*, 1997 and Kim *et al.*, 1998). The second is electrochemical doping in which a polymer-coated electrode is suspended in an electrolyte solution. The polymer is insoluble in the solution that contains separate counter and reference electrodes. By applying an electric potential difference between the electrodes, counter ion from the electrolyte diffuses into the polymer in the form of electron addition (n-doping) or removal (p-doping). One of the problem with organic semiconductor is that p-type material is much more prevalent than n-type because electron rich n-type is unstable in the presence of oxygen. Organic semiconductor can only be useful for devices if both p-type and n-type are both incorporated. Most of the conjugated polymers studied (see Figure 7) have a regular alternation of single and double bonds like in the polymer. As a consequence of the bond alternation, the band gap of the neutral polymers lies in the range of 1.5 (near IR) to 4 eV (UV), resulting in semiconductor properties. The field of conjugated oligomers and polymers has enjoyed a tremendous development (Brédas, 1985, 1995; Brédas *et al.*, 1986, 1994, 1995, 1999, 2001). In Figure 7 some examples of the most commonly used conjugated polymers are presented.



Polyacetylene (PA) Polythiophene (PT) Polypyrrole (PPy)

Poly(para-phenylene) (PPP) Poly(para-phenylenevinylene) (PPV)



Polyaniline (PANI) Polysilanes

Figure 7 Chemical structure of some commonly used conjugated polymers.

Organic (both low molecular weight compounds and polymers) conjugated materials have recently received much attention due to their potential applications in light-emitting diodes, field effect transistors, charge storage devices, photodiodes, sensors, etc (Lux *et al.*, 1997; Skotheim *et al.*, 1998). In organic semiconductors, the macroscopic properties of the material can be attributed to both the properties of the individual molecules and the structural order of the molecules in the film. These properties can be controlled by either synthesizing molecules with optimal characteristics or by controlling the fabrication conditions. For example, carrier mobility in rod-like molecules can increase if the organic material has long π-conjugation length along the long axis and close molecular packing of the molecules. Another example of fabrication affecting carrier mobility is growing an amorphous film which is achieved by keeping the substrate temperature low during deposition. This makes an insulating film. However, when the substrate temperature is kept at room temperature during deposition, a very well-ordered film is deposited with a high mobility.

2. Polymer Light-Emitting Diodes

The first organic light-emitting diode (OLED) was fabricated with anthracene crystals in 1965 but failed to attract attention because of poor performance (Helfrich *et al.*, 1965). The interest was revived in 1987 when a light emitting diode (LED) fabricated with 8-hydroxyquinoline aluminum (Alq3) emitted light with a green color upon application of a positive bias potential (Tang and Van Slyke, 1987). It was latter found in 1990 that an LED fabricated with, poly(p-phenylene vinylene) (PPV), also emitted green light on positive bias potential application (Burroughes *et al.*, 1990). The progress in the performance of polymer LEDs (PLED)s has been impressive during the last few years and single-color PLED displays will soon be commercially available (Burn *et al.*, 1992; Friend *et al.*, 1988, 1999; Ziemelis, 1999).

A large number of light emitting polymers have been introduced during the last 10 years (Kraft *et al.*, 1998). Polymers with aromatic or heterocyclic units generally absorb light with wavelengths in the range from 300 to 500nm due to $\pi \rightarrow \pi^*$ transitions. The excited states of in their chromophores (excitons) release energy radiatively as well as nonradiatively on returning to the ground state (Friend *et al.*, 1999). The radiative decay of excitons to the ground state can emit visible light. These excitons are also formed when a bias potential is applied to an emissive polymer sandwiched between an anode and a cathode (Burroughes *et al.*, 1990) due to the recombination of holes and electrons. The color of light, quantum efficiency of light emission, turn-on voltage and stability of the devices must be optimized for LEDs to be applicable as commercial light emitting devices.

There have been many attempts to improve the performance of PLEDs. The light emitting layer of an LED can be laminated with charge transporting and/or charge injection layers, which often enhance the quantum efficiency (QE) and/or reduce the bias potential for light emission (Brown *et al.*, 1992 and Greenham *et al.*, 1993). The energy barrier for injection of electrons has been controlled by employing different metals or metal alloys as the cathode (Braun and Heeger, 1991, 1992). Lamination of the layer materials with specific functions for the fabrication of LEDs should be carried out to match the work functions of the electrodes and either the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the layer materials (Gustafsson *et al.*, 1992, 1993) in order to lower the operation voltage of the devices. The charge mobilities as well as charge blocking capabilities of the layer materials are also considered important for the effective recombination of electrons and holes for a high quantum yield in the LEDs (Greenham *et al.*, 1993). The surface of transparent indium-tin oxide (ITO) used as the anode should be plasma-treated to give a smooth surface and to reduce electrical shorts (Wu *et al.*, 1997 and Kim *et al.*, 1998). A typical single-layer polymer LED is presented in Figure 8a. A thin polymer film is spin-coated from solution on a semitransparent bottom electrode, normally indium-tin-oxide (ITO), which forms the anode. A low work-function metal (calcium or barium) is evaporated on top of the polymer and serves as cathode (Ding *et al.*, 2002).

The main processes that govern the operation of the polymer LED are: charge injection, charge transport and recombination (Figure 8b). Under forward bias, holes and electrons are injected from the anode and cathode, respectively. The charge carriers move through the polymer film and recombine. The energy released upon recombination is emitted as a photon through the semitransparent electrode.

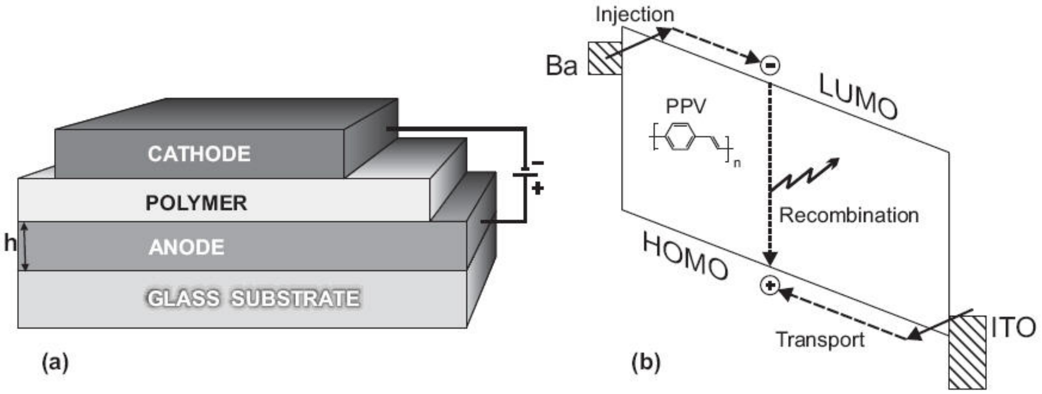


Figure 8 Schematic representation of a polymer LED (a) and energy-band diagram of a PPV-based LED (b).

The emitted light can be tuned from red to blue, depending on the band gap of the polymer. In order to be injected from the electrodes, the charges must surmount or tunnel through a barrier at the polymer/electrode interface, which is determined by the position of the highest occupied molecular orbital (HOMO or π orbital) and the lowest unoccupied molecular orbital (LUMO or π* orbital) and the position of the electrode metal work-functions. In the case of PPV, which has the HOMO level at 5.2 eV and the LUMO level at 2.9 eV, a good choice for the hole injecting electrode is ITO due to its work-function of ≈ 5 eV, resulting in a small injection barrier for holes (Cornil *et al.*, 1994, 1996; Bradley *et al.*, 1988). In order to have a small interface energy barrier for electrons, low work-function metals such as calcium (Ca) or barium (Ba) ($\phi_M \approx 3$ eV) must be used in the case of PPV. A schematic band diagram of a PPV-based LED under forward bias using ITO as a hole injector and Ba as an electron injector is shown in Figure 8b. In this case the injection does not limit the device performance. However, the control of the anode/polymer and polymer/cathode interfaces is important, since it controls the charge injection process. A consequence is that it may influence the electronic structure and luminescence properties of the polymers (Yan *et al.*, 1994). The chemistry involved at these interfaces is always related to the nature of the polymer and the metal in question, the cleanliness of the materials and the evaporation process.

A high purity for all materials is essential for good LED performance since impurities act mostly as quenching sites for excitons. The stability of devices can be improved by stripping off oxygen and moisture vigorously (Berntsen *et al.*, 1998). LEDs must be encapsulated to reduce failure due to moisture or oxygen in the system (Berntsen *et al.*, 1977). It has been reported that a single carbonyl group per 400 phenylenevinylene units in PPV is sufficient to quench half of the luminescence generated (Yan *et al.*, 1994). Since the performance of an LED is determined by so many factors, it is difficult to judge light emitting qualities of a material solely by the performance of a device. The QE of an LED fabricated with a given material reported in literature may not be solely correlated with the inherent emitting qualities of the material but with the qualities of both the material and the device. Recent progress with PLEDs has provided QE values of 10% (Friend *et al.*, 1988) and lifetimes of

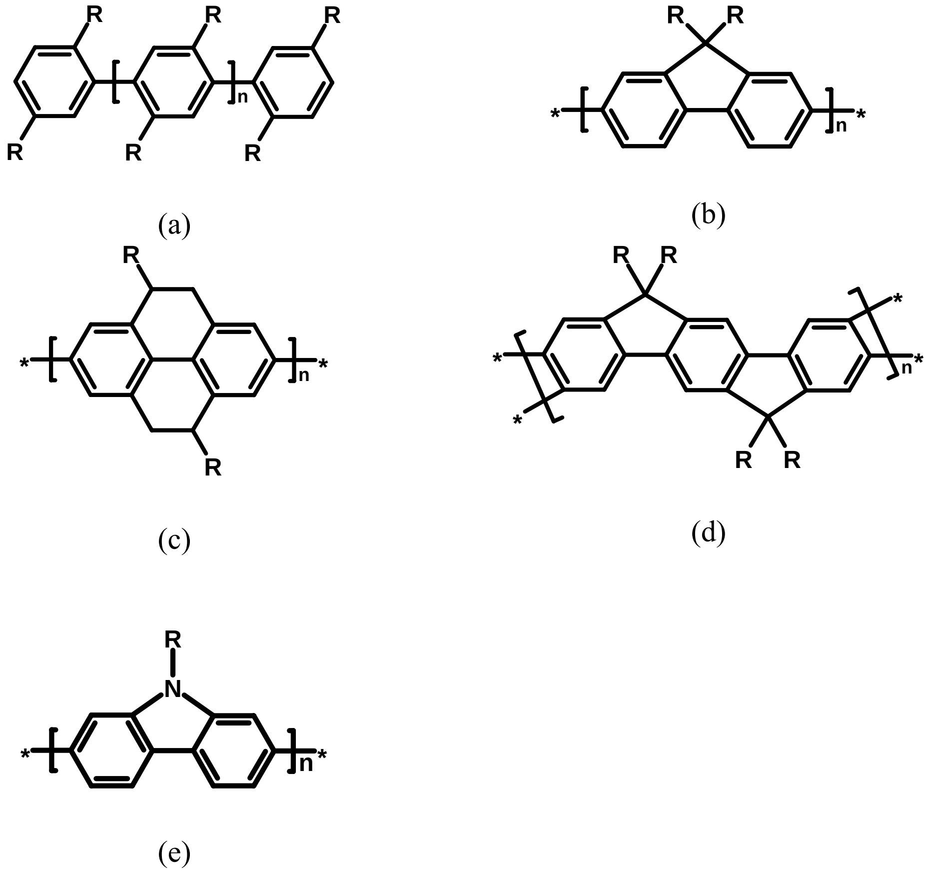
20,000 h (Schenk *et al.*, 1999). The commercialization of PLEDs is imminent in the fields of automobile navigation systems, mobile phones, and backlights for LCDs, (Friend, 1988). The ink-jet process has been introduced for the pixelization of PLEDs (Chang *et al.*, 1999; Kanbe *et al.*, 1999). Since a PLED is light in weight and self-emissive at a low power, and the fabrication of a wide screen is simple, PLEDs have a chance to be used as a main display system in our information society in the near future (Ziemelis, 1999).

Full color LED displays may be constructed in different ways such as filtering white light for a specific color, applying different bias potentials to LEDs, using efficient dyes to convert colors, or patterning pixels for the three principle colors (blue, green, red) independently (Tasch *et al.*, 1997; Kraft *et al.*, 1998; Friend *et al.*, 1999). Color filtering of white light is simple but wastes energy due to the generation of unwanted colors. Some light emitting materials produce different colors depending on the operation potential (Berggren *et al.*, 1994; Wang *et al.*, 1999). However, it may not be easy to control the light intensity and the emission color at the same time. There are very efficient dyes for converting the energy of incident light of a short wavelength to that of a longer one. Blue light can be converted to green or red with proper dyes, which means a blue PLED alone may generate all colors while green or red cannot be converted to blue by the same method (Rothberg and Lovinger, 1996; Janietz *et al.*, 1998; Grice *et al.*, 1998; Virgili *et al.*, 2000). Although all three principle colors have been demonstrated in PLEDs, only green and orange PLEDs currently have the abilities to meet requirements for commercial uses. Blue light-emitting polymers for commercial use are still undeveloped, and the red light-emitting polymers must be further improved.

The fluorophores for blue color emission consist of chemical structures like phenyl, or fluorene, or heterocycles such as thiophene, pyridine and furan as shown in Figure 9. These fluorophores are either in the polymer backbone or in the side chain. Multiple substitutions of alkyl, alkoxy or aromatic groups on the fluorophores are practiced to enhance interactions in order to change fluorophore planarity for a color-shift of the emission spectrum, to disturb excimer formation and/or to enhance the solubility of the polymers.

Poly-*p*-phenylene (PPP) (Figure 9(a)) (Grem *et al.*, 1992) and its derivatives have been studied as blue-light-emitting materials for some time and have been incorporated into LED devices. Although unsubstituted PPP is an insoluble and intractable material, the introduction of sterically demanding solubilizing side chains leads to a considerable torsion about the phenylene-phenylene bonds, which seriously inhibits the conjugative interaction along the polymer chain. It is the remarkable feature of ladder-poly-*p*-phenylene (LPPP) (Figure 9(d)) (Gruner *et al.*, 1994; Stampfl *et al.*, 1995) that the bridging of neighboring phenylene groups causes a perfect flattening of the polymer π-system, at the same time allowing the attachment of solubilizing substituents without hampering the π-conjugation. The only disadvantage of the perfectly planarized LPPP is the tendency to aggregate, which leads to excimer formation and undesired blue-green emission in LEDs. The "stepladder" polymers, poly(2,7-fluorene) (PF) (Figure 9(b)) (Ohmori *et al.*, 1991; Pei and Yang, 1996; Ranger *et al.*, 1997) and poly(2,7-carbazole) (PCz) (Figure 9(e)) (Kido *et al.*, 1993), can be regarded as synthetically less demanding analogues of LPPP.

Along these lines, poly(2,7-fluorene) derivatives (homopolymers and copolymers) are very interesting because of their excellent solubility, good film-forming property, high luminescence quantum yield, and color tunability. However, blue-light-emitting poly(2,7-fluorene)s show poor optical stability in the solid state due to π-π stacking, which results in the formation of excimers or aggregates that shift emission spectra at longer wavelengths and decrease fluorescence quantum yields. Both excimer and aggregate formations in such fluorene-based conjugated polymers can be avoided by the use of spiro-bifluorene unit, rod-coil block copolymers, random copolymers, asymmetric fluorene units, and sterically hindered side groups or by introducing flexible spacers between the chromophores. However, these different approaches are long and complicated from a synthetic point of view. Moreover, poly(2,7-fluorene)s are subject to oxidative electro and photodegradation that form carbonyl-containing species, namely fluorenone, when nonsubstituted or monosubstituted fluorene units are present in the polymer main chain. A very low concentration, as few as 0.1 mol %, of fluorenone can induce significant optical changes.



(a) (b) (c) (d) (e)

Figure 9 (a) Poly-*p*-phenylene, (b) poly(2,7-fluorene), (c) polytetrahydropyrene, (d) ladder-poly-*p*-phenylene and (e) poly(2,7-carbazole).

As an alternative, Morin and Leclerc (Marin and Leclerc, 2001, 2002; Zotti *et al.*, 2002) recently briefly reported the first syntheses of electroactive and photoactive poly(2,7-carbazole) derivatives. Interestingly, this class of materials is not subject to the formation of ketone defects. The synthetic strategy was based on a prefunctionalization at the 2,7-positions, followed by ring closure and polymerization (Yamamoto, Suzuki, Stille) reactions. Poly(2,7-carbazole) derivatives are a particularly suitable class of materials for applications in light-emitting devices because they contain a rigid biphenyl unit (which leads to a large band gap with efficient blue emission), and the facile substitution at the remote N-position provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone. Considering that poly(2,7-carbazole) and carbazole-containing copolymers emerge as promising materials for light-emitting displays since the color of the emitted light can span the entire visible range as a function of the nature of the comonomer unit. Luminescent materials spanning the entire visible range have been prepared from these polymers, and can be used in Organic Light Electronic Devices (OLED). This has stimulated recent experimental and theoretical studies aimed at better understanding the electronic and optical properties of these systems and assessing their performance in electro-optic devices.

3. Scope and Outline of this Thesis

In this present study, the conformational analysis, structural geometry and excitation energy of oligomers of poly(2,7-carbazole) and derivatives were investigated by quantum-chemical calculations with the aims of:

Chapter I: To investigate the potential energy surface for the bicarbazole and bifluorene, using distinct theoretical approaches and basis sets, aiming to assess the role played by both correlation effects and the size of the basis set for the determination of the equilibrium and transition state structures located on the torsional potential energy. In addition to, this procedure, methods have been tested methods for study the potential energy surface of biphenyl molecule and we showed that this process can use for validate methods.

Chapter II: To study a series of oligomer of polycyclic aromatic hydrocarbon polymers polymers, include oligomer of fluorene $(FL)_N$ (R= >CH), carbazole $(Cz)_N$ (R= >NH), dibenzofuran $(DBZF)_N$ (R= >O) and dibenzothiophene $(DBZTh)_N$ (R= >S) and investigate their equilibrium geometry and electronic properties by quantum-chemical calculations. An understanding of these factors will lead to more systematic tailoring of band gaps and improved electronic devices.

Chapter III: To investigate the torsional energy curves for the carbazole-based molecules using various theoretical approaches and basis sets. The effect of the size of the basis sets in determining the equilibrium and transition state structures with respect to the torsional energy was assessed. They were used here to describe the nature of the conformational analysis of five carbazole-based molecules: Cz-dimer, Cz-co-Phenyl (Cz-co-P), Cz-co-Fluorene (Cz-co-Fl), Cz-co-Thiophene (Cz-co-Th) and Cz-co-Furan (Cz-co-F). Also, the electronic properties of these molecules as calculated by TD-DFT, in combination with a variety of exchange-correlation functions and basis sets, were compared to the electronic structures and the excitation energies of the compounds.

Chapter IV: To investigate the structural properties of the ground (S_0) and excited (S_1) states for carbazole-based polymers, Cz-dimer, Cz-co-Fluorene (Cz-co-Fl) and Cz-co-Thiophene (Cz-co-Th). Due to, there is no study of carbazole-based polymers by quantum-chemical calculations at high level of theory. Calculating the vertical ($S_0 \rightarrow S_1$: absorption) and adiabatic ($S_1 \rightarrow S_0$: fluorescence) excitation energy of oligomers of carbazole-based polymers using time-dependent density functional theory and other methods.