

CONDUCTIVE POLYMERS: FROM SYNTHESIS TO PROPERTIES AND APPLICATIONS

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*The paper is a homage
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Conductive polymers are a distinct domain of the macromolecular science established as a cross-disciplinary research developed by the contribution of organic and macromolecular chemists, physicists, electronics, biomaterials specialists, etc. This minireview gives a brief introduction of conductive polymers and highlights the developments and main applications of this polymer class. The principal conjugated polymer structures are shortly presented with emphasis on substituted polyacetylenes. Some applications, such as electroluminescent materials, photovoltaic cells and sensors are also discussed.

Keywords: conductive polymers; synthesis; properties, applications

1. INTRODUCTION

Electrical conduction in polymers is a paradox, because most of the known organic polymers have the ability to inhibit conductivity, being excellent insulators. As a consequence, study of the electronic properties of organic polymers received only sporadic attention. However, in the middle of the 1970's, polymers with electrical conductivity – such as inorganic semiconductors – have begun to be synthesized and studied. Now, intrinsically conducting polymers are known as synthetic materials having a better electrical conductivity than the common polymers used as insulating materials [1,2]. In some cases, their conductivity is comparable to that of inorganic semi-conductors and conductors, being therefore named "synthetic metals" or "organic metals". These polymers have the ability to combine specific properties of the macromolecular state, such as solubility, processability and flexibility, with the electrical and optical properties of metals and semiconductors. Initially, the target of the researches on this topic was to obtain inexpensive, lightweight materials of controllable mechanical properties, chemical

inertness and durability and high electrical conductivity, able to replace inorganic partners (*i.e.*, copper) as electrical wires for electrical engineering applications. Now, due to the newly discovered opto-electronic properties (electroluminescence, light-induced charge generation, stimuli-responsive, biocompatibility, etc.), the interest in conducting polymers has moved to other applications, such as organic light emitting diodes (OLEDs), all organic photovoltaic cells, sensors and biosensors, etc.

2. BRIEF HISTORY

A first classification of conductive polymers (CPs) can be made into: (i) inorganic polymers, for example polysulfur nitride, (ii) organometallic polymers, such as polyphthalocyanins, polyferrocenes, and (iii) organic polymers, to which the present paper refers. The essential condition for the existence of electronic conduction in organic polymers is the presence of the conjugated double bond chains. For example, polyethylene, a well-known polymer used as an insulator in electrical engineering, seems at first glance hardly different from polyacetylene, the simplest conjugated polymer, their structural unit differing only by the presence or absence of two hydrogen atoms (Fig. 1). However, its properties are drastically different from those of polyacetylene, a strongly colored, insoluble polymer which can be shifted into a highly conductive state by treating it with iodine, unlike polyethylene – known as a very good insulating, transparent and soluble material.

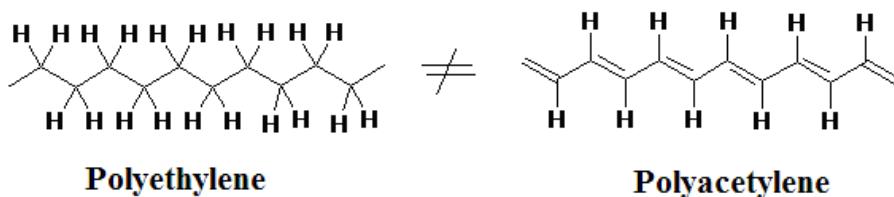
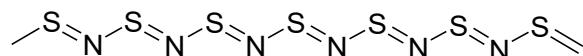


Fig 1. Chemical structure of polyethylene and polyacetylene chains

A first step in the development of polymers with conductive properties was made in 1973, when it was discovered that a completely inorganic polymer, polysulfur nitride, $(\text{SN})_x$ (Fig. 2), behaves like a metal with electrical conductivity at room temperature ($10^3 \text{ S} \cdot \text{cm}^{-1}$) comparable to that of copper ($\sim 6.10^5 \text{ S} \cdot \text{cm}^{-1}$), as opposed to the electrical conductivity of polyethylene – which is about $10^{-14} \text{ S} \cdot \text{cm}^{-1}$ [3].



Polisulfur nitride

Fig. 2. Chemical structure of polysulfur nitride, $(SN)_x$

Moreover, below 0.3 K, $(SN)_x$ becomes a superconductor [4]. These results were of major importance at that time, as they have evidenced the possible existence of a conducting and superconducting state in polymers, which greatly stimulated research in this field, with the primary objective of obtaining other macromolecular systems to conduct electricity.

From this perspective, mention should be made of the fact that, even before 1970, at the "P. Poni" Institute of Macromolecular Chemistry of Iasi, on the initiative and under the leadership of Professor C. I. Simionescu, a new department, entitled The Semiconducting Polymers Laboratory was established, having as research topic "Semiconducting and Photoconducting Polymers". Initially, the research activity was directed (as mentioned in *The short presentation of Institute* of 1978) to the synthesis, characterization and some applications of semi- and photoconducting polymers obtained by polymerization of arylacetylene and vinyl aromatic monomers and complexing with electrono-acceptor compounds. Approaching such a topic in the early 1970's shows an extraordinary vision on the future of research in the field of macromolecular chemistry and physics. Today, it is unanimously accepted that the chemistry of conjugated polymers is a new and fascinating domain of macromolecular chemistry.

It should be noted that the metallic state in polysulfur nitride is an intrinsic property of the polymer, induced by the presence of an unpaired electron for each structural unit $-SN-$, the highest occupied electronic levels (valence band) being only half full. Therefore, there is no forbidden gap between the valence band and the conduction band, so that the electrons can move freely when applying an electric field. In 1977 it was observed that, by exposure to bromine vapors or other oxidizing agents, the electrical conductivity of $(SN)_x$ shows a tenfold increase [5].

Another milestone in the history of conductive polymers can be considered the synthesis of polyacetylene as a film, in 1974, by polymerization of acetylene using $Al(C_2H_5)_3/Ti(OC_4H_9)_4$ as catalytic system [6], and then its doping with iodine, in 1977 [7].

Polyacetylene has been synthesized since 1866 [8], yet drew the interest for researchers only after 1930, due to the work of Champetier [9]. Several reviews presenting both the pioneering polymerization of acetylene [10] and the modern era achievements have been published in our country. [11]

Polyacetylene was initially obtained as a black powder, insoluble and infusible, unstable in air, with an almost unknown structure, so that it could not be studied in terms of structure and properties. However, in 1974, Shirakawa (who, together A.G. MacDiarmid and A.J. Heeger, received the Nobel Prize in Chemistry for his research in this field in 2000) managed to obtain a polyacetylene film (due to an experimental error, using a 1,000 times more concentrated catalyst solution than the usually used one), very flexible and which could be oriented by mechanical stretching, manipulated in an inert atmosphere and studied in terms of electrophysical properties [6]. The color of the film was copper- or silver-like, depending on the steric structure and reminiscent of a metal film. Polyacetylene has a high degree of crystallinity (~ 85%), being an example of a polymer obtained by simultaneous synthesis and crystallization. [12] The intrinsic electrical conductivity of polyacetylene is $10^{-5} S \cdot cm^{-1}$,

in 1977 being observed that, by exposing a polyacetylene film to iodine vapors, electrical conductivity increases by 8 orders of magnitude, up to 10^3 S.cm^{-1} [7]. These results have unequivocally led to the emergence of a new field in the chemistry and physics of macromolecular compounds, that of polyconjugate systems, which is a currently an interdisciplinary field of major interest to chemists, physicists, electronists, biochemists, etc., and which already has applications in top areas. The following years contributed decisively to the expansion of conjugated polymeric structures that can be doped into a conductive state under the action of organic or inorganic compounds, acting as oxidants or reducing agents.

3. TYPES OF CONDUCTIVE POLYMERS

SUBSTITUTED POLYACETYLENES

Study of polyarylacetylenes started in the 70's at the "P. Poni" Institute of Macromolecular Chemistry of Iasi (with acad. C. I. Simionescu' group, titled Semiconducting Polymers Laboratory), when conjugated polymers were still considered by researchers' community as a scientific "curiosity". As polymerization of acetylene with different catalysts led to an insoluble and infusible polymer, unstable in air, its structure was difficult to study. Under these conditions, it was decided to use substituted acetylene monomers which, by polymerization, lead to soluble and stable polymers, so that study of their structure and properties correlation became much easier.

The following arylacetylenes (Fig. 3) have been synthesized and polymerized with various catalytic systems and experimental conditions and the structure of polymers was studied. Polymerization with Ziegler-Natta catalysts has led in all cases to a solvent-insoluble polymer fraction and a benzene-soluble but methanol-insoluble fraction.

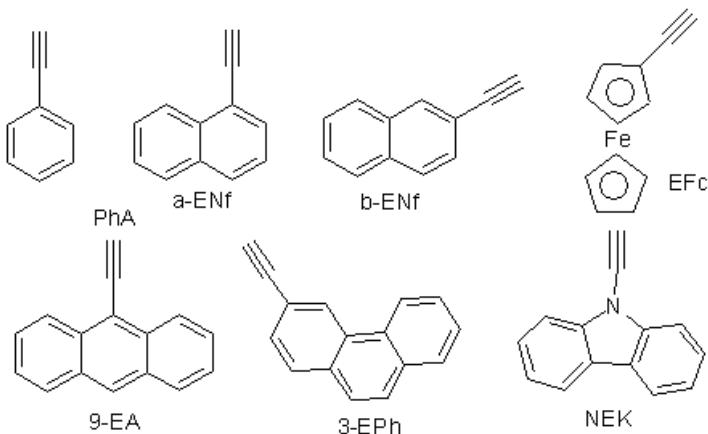


Fig. 3. Chemical structure of arylacetylene monomers

Theoretically, a monosubstituted polyacetylene can exist in four configurations: trans-transoidal, trans-cisoidal, cis-transoidal and cis-cisoidal (Fig. 4).

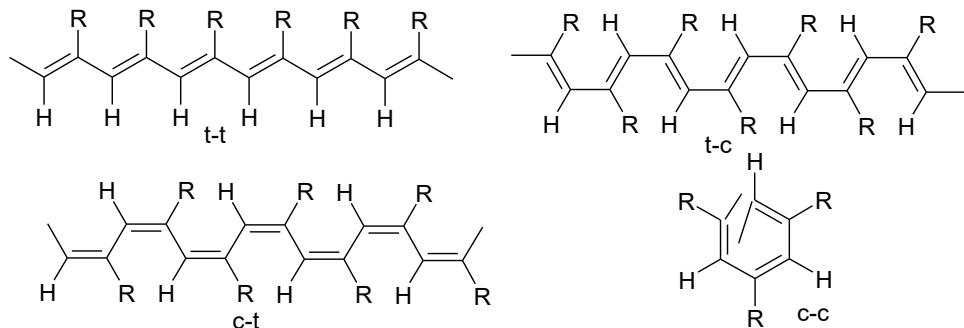


Fig. 4. Sterical structures of polyarylacetylenes

The sterical structures of the two fractions are presented in Table 1.

Table 1
Sterical structures of polyarylacetylenes

Polymer	Structure		References	
	A	B		
	I	II		
Poly(phenylacetylene)	c-c	c-t	t-c	13,14
Poly(α -ethynylnaphthalene)	c-c	c-c	t-c	13,15
Poly(β -ethynylnaphthalene)	c-c	t-c	t-c	16
Poly(9-ethynylanthracene)	c-c	c-t	t-c	13,17-19
Poly(3-ethynylphenanthrene)	c-c	c-t	t-c	20
Poly(N-ethynylcarbazole)	c-c/c-t	c-c/c-t	t-c	21
Poly(3-ethynylferrocene)	c-c	c-t	t-c	22,23

A= Ziegler-Natta polymerization, I= insoluble fraction; II= soluble fraction; B= ionic, radical or phosphine complexes polymerization; c-c= *cis*-cisoidal; c-t= *cis*-transoidal; t-c= *trans*-cisoidal; c-c/c-t= *cis*-cisoidal and *cis*-transoidal stereoblocks.

Ziegler-Natta polymerization at low temperatures ($<20^{\circ}\text{C}$) with heterogeneous ($\text{TiCl}_4/\text{AlEt}_3$) or homogeneous ($(\text{Al(C}_2\text{H}_5)_3/\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Fe}(\text{dimethylglioxime}/\text{AlEt}_3)$) catalysts led to polymers with *cis* structure. Our studies have shown that polymerization takes place by *cis* opening of the triple bond and head-tail addition to form *cis* structures. Some *trans* sequences appear by *cis-trans* isomerization during the propagation step or during the separation of polymer. Even if the triple bond is opened in *cis* position, polymerization at high temperatures ($>20^{\circ}\text{C}$) is accompanied by *cis-trans* isomerization and formation of *trans* sequences. By ionic, radical or phosphine complex catalysts polymerizations, polymers with *trans*-cisoidal structure and cyclohexadiene and phenylene sequences have been obtained

by cyclization, aromatization and chain scission [24]. Thermal isomerization is accompanied by color change from red to brown-yellow and by polymer transformation from crystalline into amorphous. Enthalpic changes associated with *cis-trans* thermal isomerization increase with increasing substituent size. The highest effects are observed for polyarylacetylenes with anthryl and carbazolyl substituents [25]. Analysis of UV-emission spectra of *c-t* polyphenylacetylene shows that the length of uninterrupted conjugated blocks corresponds to 4–7 structural units, whereas *trans* polymer shows conjugation over 3–5 structural units [26]. Therefore, the length of uninterrupted conjugation is not identical with chain length because the sterical hindrances between bulky substituents introduce torsion and bending. As a conclusion, thermal, paramagnetic and electrical properties depend on polymer configuration that determines effective conjugation length, polymer crystallinity and other opto-electronic properties.

Cis-trans isomerization was also performed by chemical methods. Halogenation of *cis* polyarylacetylenes led to cyclic halonium ions of the corresponding polymers (Fig. 5). Halogen addition to the conjugated double bonds chain was reversible. When treated with acetone, the recovery of parent was performed, but it had a *trans* structure. *Cis-trans* isomerization by intermediate of halonium ions led to pure *trans* structures (by thermal way, the *trans* polymer also contains aromatic and cyclohexadiene units in the chain) [27].

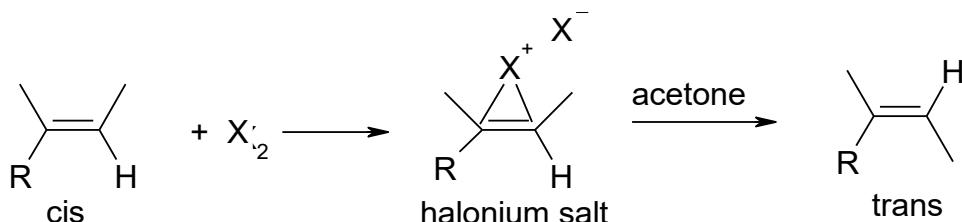


Fig. 5. Chemical *cis-trans* isomerization

Simionescu *et colab.* [22,23] were the first to study polymerization of ethynyl ferrocene, an organometallic monomer. Thermal, radical and phosphine catalysts polymerization occurs only at high temperatures, and the polymer has a low molecular weight and *trans*-structure. Polymerization with Ziegler-Natta or MoCl₅ catalysts led to an insoluble (*cis-cisoidal*) and soluble (*cis-transoidal* fraction). Thermal *cis-trans* isomerization generates an insoluble polymer due to the crosslinking reactions involving the cyclopentadiene ring.

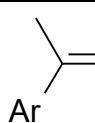
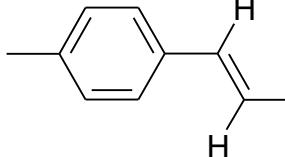
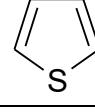
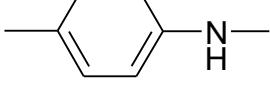
The Simionescu group reserches have firstly evidenced the dependence of the sterical structure and properties of polyenes on the synthesis conditions and studied the *cis-trans* isomerization process. Isomerization is accompanied by cyclization, aromatization and chain scission with modification of color, crystallinity

degree and paramagnetism. Therefore, details on polyarylacetylenes microstructure have been obtained due to the solubility of some polymer configurations, and these results have facilitated the study of polyacetylene microstructure and also favoured the realization of other conjugated polymers [28].

OTHER CONDUCTING POLYMERS

The most important types of conjugated polymers are polyacetylenes, polyphenylenes, polyphenylenevinylenes, polypyrole, polythiophene, and polyaniline [1]. Table 2 shows the main polyconjugate structures that can be changed into the conductive state by doping.

Table 2
Main typical structures of conjugated polymers

Polymer	Structural unit	Conductivity ^{a)} , S · cm ⁻¹
Polyarylacetylenes		Ar=H, 10 ⁵
Polyphenylenes		5. 10 ²
Polyarylenevinylenes		10 ³
Polypyroles		2.10 ²
Polythiophenes		10 ²
Polyanilines		10 ⁰

a) in doped state

A large pool of synthesis methods has been used for the preparation of conductive polymers, either chemically or electrochemically, each one with its advantages and disadvantages. Acetylene and substituted acetylene polymers are synthesized by chain-growth polymerization of the respective monomers. The other polymers, *i.e.*, polyphenylenes and polyphenylenevinylenes are obtained by step-growth polymerization of functional monomers and different catalytic systems. The last three polymers can be mainly synthesized by chemical and electrochemical oxidative polymerization of monomers; pyrrole, thiophene or aniline. The electrochemical method is based mainly on anodic oxidation of monomers, being carried out in a three-electrode cell using a monomer solution and an electrolyte. Polymerization starts with the oxidation of monomer on the electrode surface and formation of cation-radicals, followed by coupling with other monomer molecules or cation-radicals, forming doped thin film of insoluble polymer directly on the electrode surface. Thickness and film morphology can be controlled *via* the electrochemical parameters (applied potential, intensity of current, rate of potential sweeping, time, temperature, electrolyte, etc). The general drawback of the electrochemical method is that the polymer is obtained in small amounts, it tends to be insoluble so that characterization of polymers by standard analytical methods is difficult, if not impossible.

Structurally, polythiophene (PT) and polypyrrole (PPy) remember of *trans*-*cis*oidal (t-c) polyacetylene, where two hydrogens from adjacent monomer units are replaced with heteroatom bridges (-S-, -NH-), PPy being the first conjugated polymer obtained by electrochemical polymerization by Diaz *et al.*, through electrooxidation of pyrrole using a wide variety of solvents [29].

Among conducting polymers, polyaniline (PANI) is one of the most studied one during the last years, due to a combined sum of factors: it is a cheap and easy to prepare monomer (aniline), it can be synthesized in both aqueous and organic solutions, it is environmentally stable and has a lot of commercial applications [30]. The first reference about electrochemical synthesis of polyaniline as an insoluble material was recorded almost 150 years ago. In 1862, Lethaby [31] reported the anodic oxidation of aniline in a solution of diluted sulphuric acid, and also that the blue-black shiny powder was insoluble in water; polyaniline was rediscovered as a semiconducting polymer after 1980, due to work of MacDiarmid *et al.* [32].

It has to be pointed out that PANI is unique among other conjugated polymers. Its metallic state can be obtained besides the using of common *p* or *n* dopants and also (and more importantly) by “acid-doping” using protonic inorganic or organic acids (HX). The doping process takes place by protonation of the polymer chain at the imine atoms of emeraldine base form, which subsequently induces an internal redox reaction in which an electron is transferred from each p-phenylenediamine to p-quinodiiminium unit, with formation of bipolarons (dicitations) and polarons (cation-radicals) after geometrical relaxation and redistribution of the charge on the chain (Fig. 6). In the emeraldine salt (the conducting form of PANI), there is one

unpaired electron per two aniline units, and all aniline units are in the same intermediate oxidation state with all equivalent nitrogen atoms.

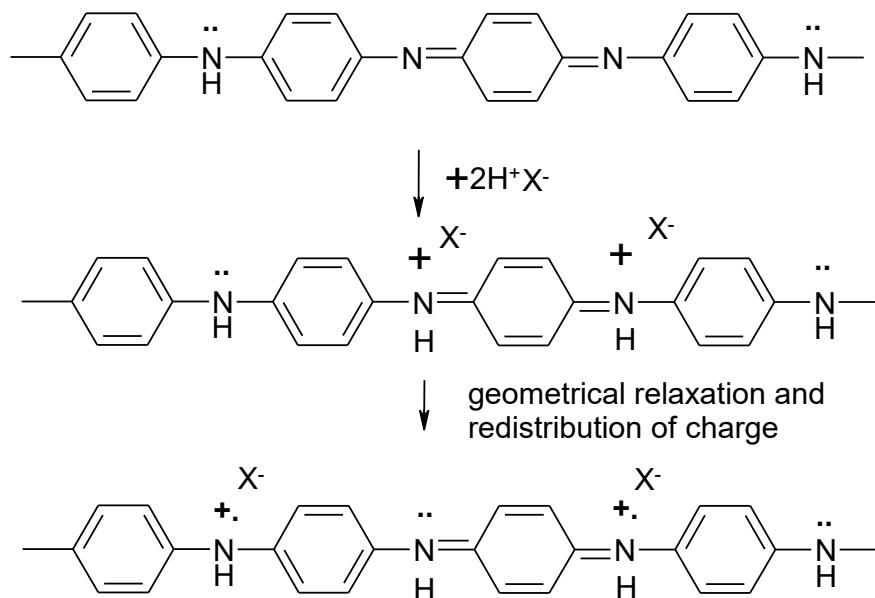


Fig. 6. Doping of polyaniline with protonic acids.

Unfortunately, all doped and unsubstituted polymers are insoluble and infusible materials and can be rendered soluble by the introduction of long and flexible pendant substituents, which diminishes electrical conductivity. The term “doping” is taken over from the physics of inorganic semiconductors, however the meaning is not the same. Doping is the process of oxidizing (p-doping) or reducing (n-doping) a neutral polymer and of providing a counter anion or cation (*i.e.*, dopant), respectively. This process introduces charge carriers, in the form of charged polarons (*i.e.*, radical ions) or bipolarons (*i.e.*, dications or dianions) into the polymer.

In recent years, a new generation of CPs has been developed, namely conjugated covalent organic frameworks (COFs) [33]. These materials have conjugated two- or three-dimensional structures with strong covalent bonding, being synthesized by polycondensation or polymerization reactions using selected organic building blocks. They have a crystalline and porous structure with intrinsic porosity and functionality that can be tuned by carefully choosing the type of monomers. COFs can be used as heterogeneous catalysts, proton-conductive materials, gas storage and separation, energy storage, enantioseparation, and other applications specific to linear conductive polymers.

Besides the synthesis of new polymer structures, another strategy is to realize conjugated polymers at nanometer scale [34]. Many efforts are directed to obtaining of polymer nanostructures (structures with dimensions smaller than 100 nm), such as: nanoparticles, nanofibriles, nanowires, nanotubules, etc., where a high surface is very important for sensing and biosensing applications. Also, polymer light emitting devices have been prepared from nanoparticles, as an alternative to processing from solution in organic solvents. Also, the proof of the concept of preparation of photovoltaic devices from aqueous conjugated polymer nanoparticle dispersions has been provided. In this case, utilization of nanoparticles offers the possibility of generating blends with controlled domain sizes.

Hybrid nanocomposites with inorganic oxids, metal nanoparticles or mesoporous or layered materials are other investigated topics, due to their interesting properties and applications.

4. SOME APPLICATIONS

The range of conductive polymers has diversified from year to year, so that their practical applications have not been long in coming. [1,2,30] The structure of polymers at molecular level determines the appearance of very interesting properties: photo-, thermo-, piezo- or electrochromism, liquid crystal properties or optical activity, nonlinear optical properties, that led to their investigation for very diverse and promising applications. An (incomplete) enumeration of these applications would be: organic light emitting diodes, all-organic solar cells, large extra-flat screens, dissipation of electrostatic charge of surfaces, electromagnetic shielding, microwave absorption (anti-radar coatings for military equipment), very effective protective paints for metal surfaces working in highly aggressive environments, windows that change their transparency depending on the time of day and season, electrodes for electric accumulators and electrochemical batteries in solid state (without liquid electrolyte), gas separating membranes, membranes with electrocontrolled permeability, sensors and biosensors, etc. Moreover, if we imagine that all these materials can be obtained at molecular level, then we can explain why the field has become so attractive for large companies and universities and large funds are invested in such researches.

ELECTROLUMINESCENCE

Electroluminescence (EL) in conjugated polymers was first reported in poly(*para*-phenylene vinylene) (PPV) in 1990 [35]. Since then, considerable effort has been devoted to developing conjugated materials as active units in light-emitting devices (LEDs) for use in display applications.

The advantages of using conjugated polymers, as well as of all macromolecular materials, are their good processability, flexibility and

environmental stability compared to the inorganic counterparts; also, they can be deposited on a substrate from solution or melt, by different conventional techniques (spin casting or dip coating). Organic light-emitting diodes (OLEDs) using luminescent-conjugated polymers as emissive medium are currently under active development for display applications. Electroluminescent (EL) polymeric materials offer a number of advantages, such as low operating voltages, completely visible colors, fast response times, high-quality displays, and ease device processability with semiconductor technologies, compared with inorganic EL materials. The basic structure of an OLED consists, in the simplest device, of a thin electroactive polymer layer sandwiched between two electrodes, one of them being a transparent and hole-injecting electrode (indium/tin oxide as anode) and the other one as the electron-injecting top contact (a low work function metal, usually calcium, magnesium or aluminum as cathode). Electroluminescence is generated from the radiative decay of singlet excitons produced by recombination of the opposite charged carriers in the luminescent polymer layer, separately injected from the two electrodes under a bias voltage. The luminescent efficiency of the LED is dependent on the number of injected carriers from the electrodes, on the capture of the carriers in traps and probability of singlet exciton formation. Further improvements of this model have to be done by changing the nature of the electrode materials or by using two or three layers of different active polymers. Multicolor display applications need at least three basic colors: red, green and blue, which can be obtained using different polymer structures and/or the same polymer type, but having different conjugation lengths. Now, current efforts in conjugated polymers are focused on the optimization of their photophysical properties; high quantum efficiencies of both photo- and electro-luminescence, and tuning of emission wavelength.

PHOTOVOLTAICS

Photovoltaic devices are considered some of the most important scientific and technological challenges for conversion of the most important source of inexpensive and renewable energy (solar energy) into electricity. However, traditional photovoltaic silicon solar cells are still deemed too expensive to be a serious concurrent to fossil fuels or other renewable energy sources (wind, waterpower, biomass, etc). *All-organic* solar cells are considered now as a very promising alternative for conversion of solar energy into electricity, as they can be fabricated based on low-cost advanced materials and using the bulk heterojunction technology. However, the power efficiency of organic photovoltaic devices is still low, compared with the traditional inorganic devices, due to a sum of factors, and huge research efforts have to be done to find the optimal polymer donor/ acceptor combination for building commercial organic solar cells. The inefficiency of the organic photovoltaic cells with a **single layer** or **bi-layer** active component configuration is due to the limited exciton lifetime that only allows the diffusion at short distance. Donor

excitons created far away from the heterojunction interface decay to the ground state without the chance to reach the acceptor and dissociate to electron/ hole pair, leading to very low power conversion efficiency. It is only the excitons generated near the interface that can be dissociated in free carriers. In order to separate the excitons into free charges, a donor/ acceptor (D-A) system must be employed. When the exciton reaches the donor/ acceptor interface, it will dissociate and the electron will transfer to the material with larger electron affinity, while the hole will be accepted by the material with the lower ionization potential. Since the exciton diffusion length of organic materials is short (typically 1–10 nm), only the excitons generated within the exciton diffusion length of organic material from interface can diffuse into it and then dissociate into free charge carriers. Other excitons generated deeply within the active layer may recombine or be trapped before they reach the interface. Thus, this problem can be overcome by molecular blending of the donor and acceptor together, to form a nanocomposite, followed by casting from solution as a thin photoactive layer between two electrodes, which is called **bulk heterojunction device** (BHJ) [36]. The BHJ configuration requires a single active layer to create an internal D-A heterojunction, in which donor and acceptor materials form an interpenetrating network with a large D-A surface area. In a typical polymeric BHJ photovoltaic cell (Fig. 7), the active layer is sandwiched between a transparent indium tin oxide (ITO) anode and a metal (Al, Ca, Mg) cathode. The photoactive layer is a homogeneous mixture composed of a low band gap conjugated polymer **donor** and a soluble nanosized electron-**accepting** material. Formation of an interpenetrating network with an acceptor requires the donor polymer to have a certain interaction with the acceptor, preventing severe phase separation. In this case, the excitons are dissociated into electrons and holes at the donor/ acceptor interface, are transported through the two respective phases and collected at the electrodes with the aid of the internal electric field generating the photocurrent and photovoltage. Formation of a bicontinuous network creates two channels to transport holes in the donor domain and electrons in the acceptor domain. The major interests in increasing the efficiency of the photovoltaic cells are to improve the photoinduced electron transfer in donor/ acceptor heterojunction. Conjugated polymers combine the optical and electronic properties of semiconductors with processing advantages and serve as p-type materials in assembling organic solar cells with low weight, integrated flexibility, and low cost. The basic requirements for an ideal donor polymer include: good solubility and film-forming properties; strong and broad bandwidth absorption; high hole mobility; suitable HOMO/ LUMO energy levels; high purity and molecular weight. It is commonly accepted that the open circuit voltage (V_{oc}) of the bulk heterojunction device is proportional to the difference between the highest occupied molecular orbital (HOMO) energy level of the donor and the lowest unoccupied molecular (LUMO) energy level of the acceptor. The HOMO energy level of the p material has to be at least 0.3 eV higher than that of the acceptor

derivative in order to favor the electron transport and to overcome the binding energy of intrachain exciton. Conjugated poly (*p*phenylenevinylene)s have attracted a great deal of attention, due to their conducting and photoluminescent properties. Its derivatives remain the most popular conjugated polymers for this application and continue to generate considerable interest and much research for photovoltaic applications. Unfortunately, the unsubstituted PPV is insoluble and infusible and therefore difficult to process in solid state. By incorporating arylamine derivatives (*i.e.*, carbazole, indolocarbazole) as donor sequences in the PPV structure, the polymer band gap can be reduced and solubility improved by introduction of substituents at amine nitrogen. In BHJ organic solar cells, conversion of incident solar energy to photocurrent (the photovoltaic mechanism) takes place by a cascade of four steps: (1) absorption of sunlight by conjugated donor polymer and generation of excitons (electrically neutral bound electron-hole pairs), (2) diffusion of excitons to the heterojunction, (3) dissociation of the excitons into free charge carriers, and (4) transport of these carriers to the contacts, as illustrated in Figure 7.

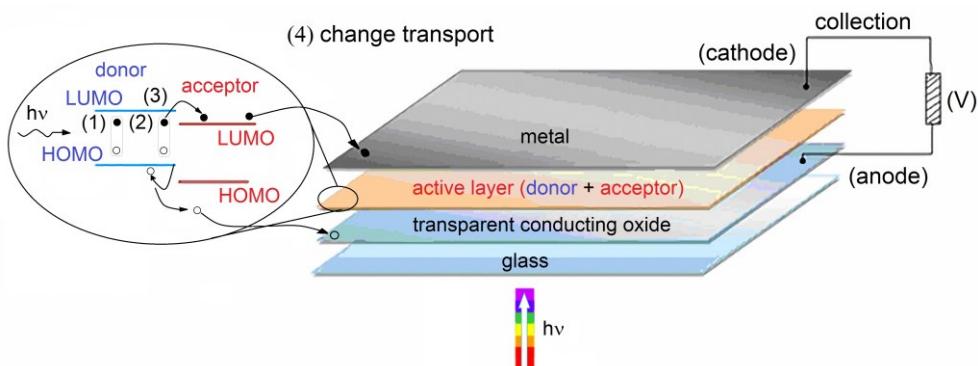


Fig. 7. Energy diagram of an organic solar cell based on the BHJ concept

Every step has to be optimized so that to have an overall high efficiency of the photovoltaic process. Power conversion efficiencies of up to 15–17% have been recently reported using blends of conjugated polymers with fullerene or other small acceptor molecules. However, commercial application is limited, due to their low reproducibility and stability in time. Many researchers have observed that small structural deviations on the backbone of conjugated polymers or slight modification of processing influence their photovoltaic properties. Therefore, the challenge here is to provide and study new conjugated polymer/ acceptor combinations with well-defined structure, and to improve every step in photovoltaic process. Optimization of organic solar cells is a fine balancing activity. It requires finding the optimal compromise among a combination of materials characteristics that can work in opposite directions.

OTHER APPLICATIONS

Organic transistors: Another application of conductive polymers is as active thin layers in transistors that act as on/ off switch in the next generation of cheap and flexible integrated circuits. Discovered in the 1980's [37], they consist of an organic semiconducting thin layer, a gate insulator layer and three electrodes, (drain, source and gate electrodes). A large number of organic micro- and macromolecular compounds has been studied and the results obtained are encouraging [38].

Sensors and biosensors: Modification of the electrical conductivity of conductive polymers in the presence of volatile compounds and gases was used for building of chemical sensors [39,40]. They can also detect biological molecules and have the advantage of being compatible with many biomolecules used in diagnosis, imaging and therapy. They have the ability to entrap and controllably release biomedical molecules, drugs, etc., making these materials very useful for biomedical applications (biosensors, drug delivery, artificial muscle, etc.). To make them water-soluble and able to interact with biomolecules, the hydrophobic backbone is modified by introducing charged side chains, such as anionic or cationic groups. The first biosensing device was created by integrating an enzyme into an electrode [41] and, since that time, much progress has been made in monitoring and diagnosing metabolites (*e.g.*, glucose, hormones, neurotransmitters, antibodies, antigens) for clinical purposes. A biosensor is composed of a sensing element (*i.e.*, biomolecule) and a transducer [42]. The sensing element interacts with the analyte of interest, producing a chemical signal that is transmitted to the transducer, which ultimately transforms the input into an electrical signal. Conductive polymers are extensively used as transducers that integrate the signals produced by biological sensing.

5. CONCLUSIONS

Many efforts have been devoted over the last years towards the development of organic conducting polymers, and future success requires achieving a much better understanding of the nature of electronic structure and charge transport properties that will come from a close cooperation among synthetic chemists, physicists, and theoreticians. The superconductivity state in the mentioned polymers is not completely eliminated and the future can bring clarifications.

Although not all hopes or expectations have yet been realized, the commercial use of conjugated polymers as electronic materials is already an established fact, and it is probably more extended than we believe. One example is the use of polymers in the electrophotography industry to replace selenium as a photoactive layer. Exploitation of piezoelectricity and the pyroelectricity properties observed in polymers, such as polyvinylidene fluoride, has found applications as thermal or sonic transducers. Other conjugated polymers, poly(3,4-ethylenedioxy)

thiophene is now commercially available from Bayer in multiton quantities. The complex between this polymer and the polystyrene sulfonic acid is used as an intermediary hole-injection layer in OLED, photovoltaic cells transistors, antistatic coatings, etc.

In the preface to the 1986 book entitled *Polyacetylene* [1], Professor Simionescu said referring to conjugated polymers: “*Without proving an exaggerated enthusiasm and overestimating the potential of this field, I still dare to say that its exploration with tenacity will bring a considerable contribution in state-of-the-art technology. It is enough to mention the contingency with the energy and raw materials crisis...*”. The future has totally confirmed all these predictions. The use of conducting polymers as active materials in light emission diodes and flat displays and photovoltaic cells with power efficiency over 15% is today reported.

The use of conducting polymers in different applications will depend on the degree of understanding of their structure at molecular level, academic and industrial efforts being ceaselessly necessary to further develop this field in which new interesting results and new applications are expected.

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