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Conductive polymers; review

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الخلاصة

تضمن المقال الحديث عن البوليمرات الموصلة للكهرباء والبوليمرات الكهروضوئية وذلك لاهميتها وللخصائص التي تتمتع بها هذه البوليمرات من ناحية نشاطها الكهربائي والضوئي بالاضافه الى سهولة تصنيعها وتشكيلها وكذلك خفة وزنها وخمولها الكيمياوي وخاصة بعد ان اخذت مدى واسع في تصنيع الرقائق واشباه الموصلات وفي البطاريات العالية الطاقة والخفيفة الوزن. كما تطرق المقال عن انواع البوليمرات الموصلة والعازلة واشباه الموصلات ونظرية الحزمة كما تتطرق الى بعض انواع البوليمرات الموصلة مثل البولي استلين والبولي انيلين والبولي فنيلين كما تضمن المقال الحديث عن قدرة البوليمرات السيطرة على التعتيم واخيرا تحدث المقال عن الخلايا الفولتائية الضوئية وقدرتها على توليد التيار الكهربائي
.

Abstract

The article included a discussion of electrically conductive polymers and photoelectric polymers due to their importance and the properties that these polymers have in terms of their electrical and optical activity, in addition to their ease of manufacture and formation, as well as their lightweight and chemical inertness, especially after it has taken a wide range in manufacturing chips and semiconductors and high-energy and lightweight batteries. The article also dealt with the types of conductive and insulating polymers, semiconductors, band theory, and some types of conductive polymers such as polyacetylene, polyaniline, and polyphenylene. The article also included a recent article on the ability of polymers to control opacity, and finally, it talked about photovoltaic cells and their ability to generate electric current.

Keywords:- Conductive polymers, Photo optical polymers, Noninsulating polymers, and Electroactive polymers

Introduction

Studies and research have focused on the subject of electrically active and photoactive polymers. It is expected that these studies will increase in the near future, due to the properties that these materials have.

Most of the ideal organic polymers are electrical insulators. While many metals are good conductors of electricity, and their importance lies not only in their electrical conductivity but also in their strength and ductility, most of them are heavy and not rustproof; as for metallic semiconductors, they are brittle and difficult to purify and manufacture to the greatest extent. While the importance of polymers appear to be easy to manufacture and form, as well as they are characterized by their flexibility and strength in addition to their lightweight and chemical inertness, these features nominated polymers (conductive to electricity) to take a wide range in various fields of use **[1]**. Such features as the ease of manufacturing chips (including semiconductor chips) made them favorable and the circuit assembly for electrodes and in the lightweight battery components. Three different types of polymers conduct electricity **[2]**:-

- Ion-polymer solid electrolyte systems.
- Composites of electronic conducting materials in non-conducting polymers.
- And polymers that conduct electricity by electronic transport.

Electronic-optical polymers are materials that are characterized by a change in some of their optical (optical) properties when an electric current passes through them, such as refractive index or color, or they may emit light and may sometimes generate electricity when we shine light on them (irradiated) **[1-3]**.

If we go back to the history of polymers, it is known to specialists in the field of polymers that the first polymer to be classified as a chain of sulfur and nitrogen atoms was x (SN) in 1973 by Wataka, and it was shown that this polymer has electrical conductivity at room temperature from During experiments conducted on it by (Temple) University,

It has been shown that this polymer can become superconducting with a temperature slightly higher than absolute zero by studies conducted by IBM at their research laboratories Based on that, the search for other polymers that are easy to prepare and stable with the presence of air and for this, many organic polymers have been manufactured, such as polyacetylene, Natta first manufactured that, have been manufactured. Some important applications of these polymers are in manufacturing multi-rechargeable and discharging batteries hundreds and in alternative uses **[2-4]**.

Electrical or thermal conductivity in solid polymers:

Some salts, such as Nac1, dissolve in liquids (such as water) and become conductive of electricity through the migration of Na^{+} and $C1^{-}$ ions to the opposite poles of their charge under the pressure of the applied electric voltage. This behavior depends on the ability of water molecules to dissolve the ions and ease their separation from each other, and the greater the concentration of the salt significantly In general, the conductivity of the solution has increased due to the increase in the charges present and transported in the system.

Some polymer molecules act as solid solvents of salts, as these large molecules contain coordinate sites that enable them to make weak bonds with the cat ion of the element.

The ions responsible for the charge transfer must be well separated. Otherwise, they will remain as an ionic pair strongly bound together (due to their electrical nature). They will not contribute to the charge transfer (by moving quickly toward the electrodes), and thus, the electrical conductivity may be weak.

It is noticeable that the non-glass polymers (Amorphous polymers) are considered one of the best systems for conduction, and as we note that the conductivity increases with increasing temperature (as this is done by the mechanics of the cat ion transfer towards the cathode from one polymer molecule to another), and of course taking into account the degree of transfer of the polymer into consideration Low glass transition temperature and low crystallinity as well **[5-6]**.

Host polymers for solid electrolytes

There are several polymers that possess this property, some of which have been studied in detail. Of these polymers

$$\text{n} - \text{polyethylene oxide} \qquad (CH_2 - CH_2 - O)_n$$

$$[(CH_2 - CH_2 - O)_x(CH_2 - CH(CH_3) - O)_y]_n$$

A co-polymer of both oxyethylene and oxypropylene, polyoxide is one of the first polymers to be studied in detail (1970), and the structural oxygen atoms in it are the coordinate sites that are covalently linked with the alkali metal cat ions. The ion transfer occurs in the amorphous region only, systems based on this polymer must be heated to $70C^O$ or to $100C^O$ (before crystal fusion occurs, and it is possible to obtain the highest level of conductivity). It is possible to overcome such problems using an amorphous copolymer containing both oxy-ethylene and oxy-propylene chains.

Camb polymers

In this type of polymer, the side groups are what equip us with weak coordination sites that will bind with cat ions (for positively charged ions), while in highly elastic polymers, they will aid in the morphological transfers that allow the movement of ions, an example of these polymers is:-

Poly [bis (methoxy ethoxy ethoxy) phosphazene] or what is known as [MEEP]. Which is prepared and manufactured to obtain the highest specifications required for a solid electrolyte system. It has a low glass transition, is amorphous, and dissolves in organic solvents such as tetra hydrofuran, a solvent for terephthalate salts. The conductivity of the MEEP-lithium tri-flat system at room temperature is 1,000 times higher than the value for a similar system based on oxyethylene polymer. The stability of this system (collapse resistance) can be increased by increasing chemical or radiological entanglement orders without any significant decrease in conductivity.

And the salts used should have a low crystalline cross linking energy. On the other hand, crystal and ion duplication forces will help dissolve the polymer and separate the ion pair. The salt concentration in the polymer greatly influences the conductivity behavior.
The conductivity will become low at low salt concentrations, and we find that the ionic double units will be well separated. Still, their number will be small, and when the salt concentration increases, the conductivity will increase to the maximum; adding a small amount of Coordinative organic solvents such as propylene carbonate will increase the conductivity.

Uses of solid polymeric electrolytes

There are many uses, but the most important use, as mentioned above, lies in its lightweight; this is why it is used in high-energy (condensed) batteries, and there are other applications such as in solid photochemical cells, sensors and transistors .... etc.

Conductors (Proton Conductors):

The second class of ionic conductors is the proton-carrying conductors, as the membranes (the most important part of fuel cells) responsible for converting chemicals such as hydrogen, methane, or methanol into electrical energy are manufactured from this type of polymers. The anode is composed of a mixture of platinum-lithium minerals, and the cathode contains platinum powder. At the same time, hydrogen contributes as fuel at the anode and is converted into electrons and protons.
The electrons move through the circuit to the cathode while the protons migrate through the polymer membrane to the cathode, at which the hydrogen is oxidized to water. A methanol fuel cell works on the same principle, except that it converts methanol into Co_2 and water and gives a series of benefits over hydrogen, such as its use in cars, laptops, and cellular phones.
The type of polymers used in this field are large molecules with acid side groups that allow a proton to move from an acid site to an acid site through the membrane, usually with the help of the water present. the classical proton conductive membrane is a material known as Nafion-117 which is a carbon fluoride polymer carrier of active sulfuric acid groups (So_3H-).

Pyrolysate polymers composite polymers with conducting Domains:

Electrically insulating polymers are transformed into conductive materials by thermal decomposition into graphite or by introducing graphite powder or mineral particles to contribute to their internal structure. This transformation (into conductive materials) has made them at the forefront of polymer technology for several years. The presence of conductive graphite in polyacrylonitrile or polyester polymers gave it a semiconductor characteristic. Preparing a useful conductive material requires a balance between the high conductivity required against deterioration of strength and other mechanical properties. These polymers have many uses and are included
in the various tools used in the electrical engineering industry

Electronically conducting polymers:

The third class of electrical conduction polymers includes large molecules (macromolecules) responsible for electronic conduction. The process depends on the presence of conjugated double bonds, as is the case in polyacetylene, and often, this type of polymer requires electron injection or removing electrons and leaving a positive hole.

The widespread availability of electrical conduction polymers lies in the possibility of using them as lightweight and easy-to-form materials, for this case, used to replace semiconductor chips and integrated circuits. The importance of lightweight appears in electrode materials for fuel cells, batteries, and components for many other purposes.

Band theory:

Electronic conduction in polymers occurs by the easy migration of electrons through a molecular and solid-state structure. This process occurs because large molecules containing delocalized unsaturated molecules generate the electronic structure (many double or triple contacts with each other) this generates properties that are not present in small molecules. The electrical properties differ because the electronic structure are different; the energy levels of these electrons differ before and after the formation of the bond. Where the formed bond contains two new energy levels (the bonding level occupied with two electrons and the level of the empty anti-bonding level), and when the electron present in the interaction plane acquires sufficient energy (from heat or light) it will move to the higher energy level of anti-bonding. The formation of the bonds in complex molecules follows the same principle; for example, it will be automatically large in a high-polymer molecule or a solid-state system. In the space of the interstitial orbital particles, they become crowded with each other on the energy scale to form energy levels (closely spaced), known as symbiosis or in physics (solid state terminology).
The same thing happens with the anti-bonding orbital, described as conductive beams. The two beams are always separated by what is known as a (gap) beam, and the degree of saturation of the valence beams with electrons is estimated whether the material is considered conductive (for example, a metal), (semi-conductive), (semi-metal) or (non-conductive).

insulators:

The electrical conduction is usually due to a free (single) electron moving in the direction of the power supply applied. When the valence beams are full, it becomes difficult (impossible) for the electrons to flow in one direction, and there is only one way for the individual electrons to jump the gap from the highest level to the lowest level (after being stimulated by thermal energy or Light).

So insulators are materials that have wide gaps, so the electron needs a lot of energy to jump over it. Most of the polymers are located in this region. It is noticeable that there are no exact boundaries between dielectrics and semiconductors, where the difference is approximately one degree more for each type.

Semi-conductors:

They are materials with narrow gaps, and single electrons or some methods generally achieve conduction.

First, The gap is very small, and it supplies (heat or light) enough energy to jump the electron from high energy levels in the valence beam to the low levels of the conduction beam. The transported electron is free to move in the conduction beams and will carry current when it migrates along the chain toward the anode.

Meanwhile, it leaves a gap in the valence beams and is charged with a positive charge, which will also migrate along the polymeric chain, but in the opposite direction, the electric current will pass. Some polymers are called semiconductors; their conductivity increases when the temperature or light intensity increases.

Second, The electrical conductivity of semiconductor polymers can be improved by injecting and removing electrons from the source, as it is possible to inject electrons by adding a chemical donor to the electron or by reducing the polymer to an electrochemical cell.

It is possible to remove electrons by treating the polymer with electron receptors or by electrochemical oxidation, and this is known as (doping), as it is not only intended to increase the number of existing charges carried but may also include reducing the gap by injecting electrons that will be a new energy state. (new energy level) in the gap range.

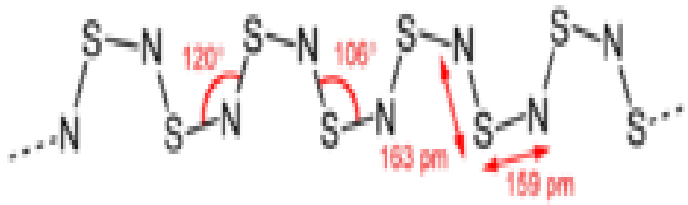
Metals:

Substances for which the conductive beams are not full and the valence beams partially full: Since most atoms of materials contain electron pairs that do not bind to form covalent beams, instead the electrons will fall into the lowest energy level of the valence beam, and are ready to move to higher energy levels that are not full for the same beam. That is, the electron here does not need to overcome the energy of the gap to move because it will remain in the same beam, as is the case with the sodium metal.

It is noticeable that the increase in temperatures will lead to a decrease in the conductivity, as the heat will increase the thermal vibrations, leading to an increase in the dispersion in the movement of electrons. therefore, as with metals, the blank levels are easy to reach, so conduction occurs **[5-6]**.

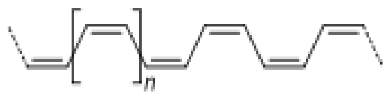
[Poly (Sulfur nitride (SN)x)

A polymer in which the valence beam is half full and the electrons in this beam are prepared to act as charge carriers by moving inside the beam. It behaves at room temperature as a metalloid. Its benefits as a model for conduction polymers are more than what is useful in practical applications, and it is a polymer sensitive to oxidation, and this explains its attempt to pop when heated in air or exposed to high pressure. Its bromine derivatives consist of exposing it to bromine vapor, where a black polymer is formed and its electrical conductivity increases **[6-7].**

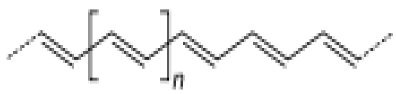


Poly acetylene

Polymer has more attention than other electronic conductive polymers.



Trans- polyacetylene



Cis- polyacetylene

Where it is available and cheap, its manufacturing process is relatively easy, and its conductivity can be changed within a wide range (by adding dopants), when controlling the degree of (doping), it is possible to convert the material from semiconductor to metal or stabilize it in any intermediate state. The Shirakawa technique is one of the most widely used methods in its manufacture, and the polymerization involves using Zecler-Nata agents.

It is a metallic polymer despite its porous composition. It is mentioned that if the polymerization process occurs at (-78 ℃), a golden-colored polymer will be produced, and its composition is of the cis-trans type. If the reaction temperature is (150), then the resulting polymer will have a silver color in the form of trans-trans (the latter is preferred thermodynamically) **[7-8]**.

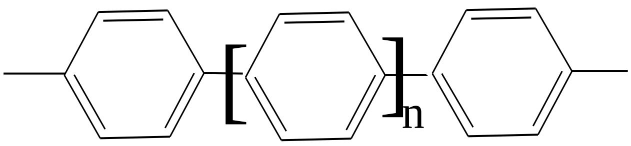
Conduction in it may occur after thermal or optical excitation of the electrons to give them sufficient energy to cross a gap to the low level of the conduction beam. Or by the effect (dopants) in which the chemical reduction is made by injecting single electrons (not double) into the low energy level of the conduction beams, which are responsible for carrying the current. And vice versa with oxidation, where electrons are removed from the top of the valence beams to give positive holes. Electrons are alone (remaining) the carriers of the resulting current. It is suggested that oxidation and reduction generate the radical anion or cat ion (with energy levels inside a gap) occupied by an electron double from a single, double bond with an electron added in the reduction process. This state is known as polaron.

When adding a second electron (on the same site), i.e., an additional reduction or oxidation procedure, we have a (bipolaron), i.e. (di-anion) which does not contain individual electrons (double electrons). Still, the energy levels in a (gap) beam allow easy transfer of electrons into a beam Conduction. Polyacetylene is unique among unsaturated polymers due to differences in the presence of two states of equal energy resonance.

Polyethylene is used as wires for its lightweight to replace copper and other metals in electrical circuits and as electrodes in batteries and fuel cells for its lightness and high porosity structure. It is considered the best candidate for electronic or photoelectric applications (electro-optical). His study is considered a starting point for later work on conduction polymers. For this reason, scientists (Shirakawa Heegert Mac Diarmid) were awarded the Nobel Prize in Chemistry in (2000 AD) for their leadership in the investigation and research on this polymer **[9].**

Phenylene Polymers:

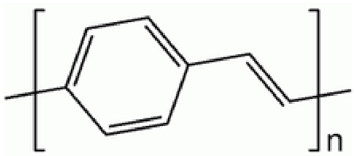
One of the polymers contains a long chain of double bonds linked in the structure, and the aryl rings in the polymer chain play an important role in the structure of the polymer **[10]**.



Poly Phenylene

Poly (para phenylene): -

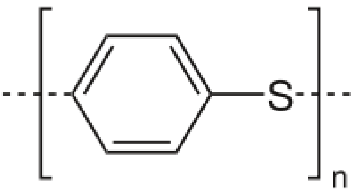
The polymer is electrically conductive due to the lack of concentration of electrons π in its composition to the maximum extent. Its short chains do not dissolve in most solvents, and it has a high melting point. Also, we have a state (polar on) due to oxidation and reduction, and when additional oxidation and reduction are performed, a (bi-polar on) state is formed.



Poly phenylene vinylene

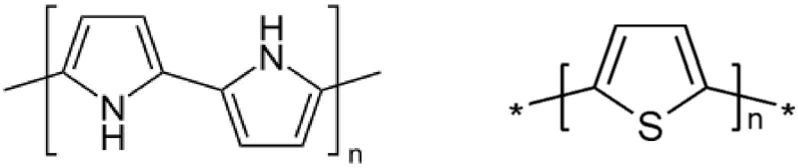
For this polymer, as shown by its composition, aliphatic side groups are linked with aryl rings to improve solubility in polar solvents, and without them, dissolving the side groups will be difficult. The polymer is more stable than polyacetylene in air, which is one reason for its wide circulation and spread. It is also used commercially in light-emitting electrical appliances-**[10-11]**.

Poly phenyl sulfide:



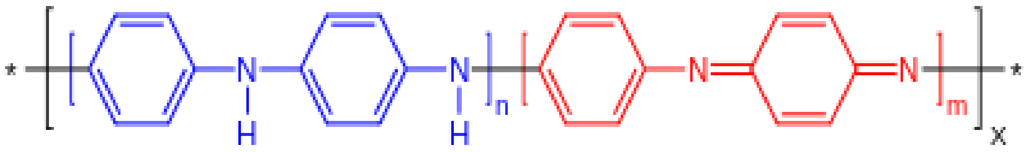
Commercially available, it has excellent chemical properties and thermal stability, and can be easily converted into films or fibers.

Poly pyrrole and poly thio phene



Polyaniline"

Known about a hundred years ago, it was called black aniline or emeraldine, and it is formed by oxidation of aniline, and it is made newly to prepare electrically active substances for use in electrochemistry and the chemical oxidation of aniline **[12]**.



Deferent optical properties:

In general, lenses, waveguides, nonlinear optical devices, and LEDs are traditionally made of inorganic materials. Still, the lightweight and ease of manufacture of polymers have made them a candidate to replace traditional metals in applications. It is possible to observe the optical uses of polymers in the manufacture of three types of properties: -

First: Clarity and transparency (colorlessness), where it changed as glass polymers for the manufacture of lenses, prisms, light guides or windows ... etc., in such materials, the color or refractive index does not change with differences in the intensity of light or the presence of the electric field.

Second, these polymers' color and optical density change when the electric field is applied.

Third: The refractive index of glass polymers varies with changes in the intensity of the light and the change in the applied field, so it is called (NLO) any nonlinear optical minerals.

Finally, some polymers send light when an electric current is shed. They are known as electrophoresis minerals or photo-emission diode polymers and can change**[13]**.

Linear optical metals

One of the types of inorganic glassware, such as silicate, is used in windows, lenses, prisms ... etc. It has the advantage of not absorbing the mud in the visible area and its refractive index depends only on the composition and temperature. Heavy and brittle metals must be manufactured within high thermal limits, and their production processes are easy, cheap, fast, and bulletproof windows ... etc. However, one of its disadvantages compared with inorganic glasses is that it does not give an average refractive index when different types of it are mixed, but rather the mixture tries to give heterogeneous phases. Therefore, we try to control the relative refractive index by performing random co-polymerization of two or more different monomers or microbial partial compensation. It is relatively easy to prepare a colored glassy polymer for a light filter (optical filter) by dissolving an organic dye or linking the dye to the polymer by co-polymerization or by macromolecular-substitution**[14]**.

Polymers with controllable opacity

The well-known photochromic sunglasses use materials that suppress the color of the lens, which increases as the intensity of the incident light increases, as the light transmittance through the lens becomes less as the intensity of the light increases. This feature was used not only in lenses but in other industries, such as manufacturing some types of windows. When strong light (especially ultraviolet light) is radiated, this type of all-polymer atmospheric photochromic organic molecule dissolves into the polymer and pairs with a chain like (Spiropyrans) to (merocyanines).

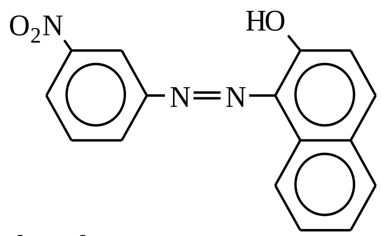
The polyaromatic compounds will suffer π-$^{*}\pi$ -transitions into the colored state when exposed to intense light rays. This has been investigated and researched in the field of eye protection applications.

The second method of controlling color suppression depends on the behavior of the liquid crystal molecules in the electric field. The most prominent application, as we mentioned, is in sunglasses, where when the intensity of light increases, the transmittance will decrease through it, meaning it changes to the colored state after it is not colored**[15-16]**.

Nonlinear Optical Polymers

Transparent glass polymers are not desirable, which is why this type of nonlinear photopolymer is designed to withstand changes in the refractive index due to exposure to an electric field or when the intensity of light changes. Two types of nonlinear optical polymers (NLO) are known as they are designed as second and third-class materials.

Polymers (x^2) have side groups and organic units that can be polarized, such as azo aromatic groups.



3-Nitrophenyl-azo-p- naphthol

In general, they carry the electron of the polar group at each end and are connected with the main chain through flexible space groups. The importance of (x^2) effectiveness lies in the fact that all side groups must point in the same direction and subject the polymer to an electric field with a strong voltage (poling) then it is cooled, the polymer reaches a temperature less than its glass transition point with the continuation of the applied electric field, below the glass transition point the orientation of the NLO groups must remain due to the hardening of the polymeric system however, if the (Tg) is not higher than the room temperature, it will be thermal movement of matter is random and slow and takes days or weeks, and then loses its effect (NLO) **[17]**.

The crosslinked of the polymer during the so-called (poling) will improve the chances for the residues of the arrangement to continue to occur. For this, the light of the lamp used in the device may change inside the waveguide either (A or B) depending on whether the electric field applied to the electrodes is (on) or (off).), Where the refractive index will change depending on these two conditions. This may be useful in some devices (which give an electronic signal to convert it into a light signal to be emitted to one of the optical waveguides), as in the telephone exchange or any devices that give the same features**[18,19].**

The second class of (NLO) polymers is (x3) materials that contain highly eccentric electrons in the main chain, such as polystyrene, polypropylene, vinyl, etc. The effect of (x^3) is weak compared to (x^2), but the particles do not have to be cushioned by (poling) so that (x^3) has a longer time before losing the effect of (NLO).

One of the problems with NLO polymers is that they are likely to be unstable before using all laser light in communications **[20]**.

Photo voltaic cells:

It is a device that generates an electric current directly from light. The current technology uses crystalline semiconductor materials – silicon type, which is expensive, or non-crystalline silicon semiconductor, which requires special devices to produce it. Here lies the benefit of using (photovoltaic) cells in this application, as it relies on a thin polymer strip of organic solvents, giving an important alternative In this technology, theoretical photovoltaic cells show that the absorption of a photon causes the excitation of an electron at (p-n junction) from the valence beam to

Conductive beam. If the polymer is a donor (doped), then the electron moving will be from or to the energy level inside the beam, and its loyalty will leave a gap. The electron and the gap will move in opposite directions, and an electric current will be generated that flows as long as the region is exposed to light **[16,21]**.

Electro Lumines Polymers:

Poly (p-phenylene vinylene) is a commercial polymer for use in the flat glass plate of optical emission devices, as these devices work on the principle that electrons and holes are injected at opposite sides of the polymeric semiconductor when the two meet, they will dissipate each other and the energy is released in the form of photons that is, the light is emitted when the electric current passes through the polymeric semiconductor, the color of the emitted light depends on the composition of the polymer and the (gap) beam. For example, a polymer containing a high gap will emit blue light, the other containing a slightly smaller gap will emit green light, and a smaller gap will emit red light. Mixing the red, blue, and green spectrums emitted will allow the generation of any visible spectrum color.

In the beginning, devices were made of polyphenylene vinylene and played a large role and were used in cell phones, as they were combined with electronic printer technologies. As it turns out, conduction polymers may one day be used on color TV or laptop screens**[20,22]**.

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