MODULE II

Polymers used in electrical and electronics applications

Conducting polymers.

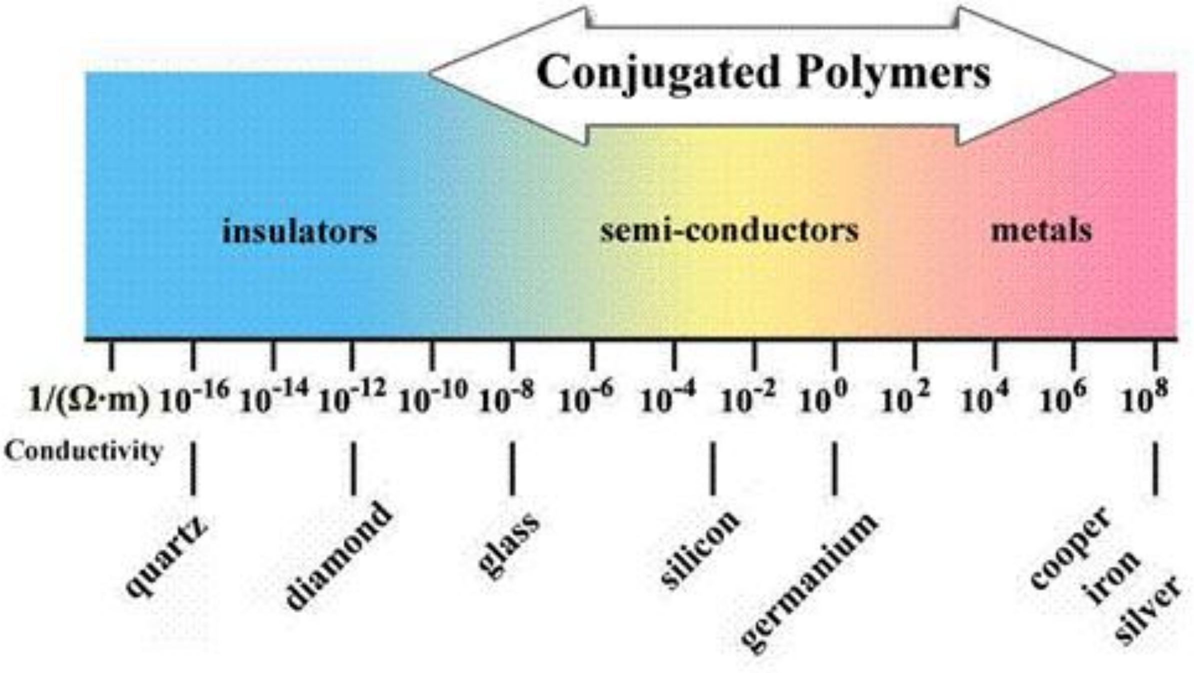
Polymers having conductivity either in pure stage or in doped stage is called conducting polymers. Conjugated structured polymers and organometallic polymers are generally having conductive properties.

Or in other words

Conductive polymers or, intrinsically **conducting polymers** (ICPs) are organic **polymers** that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of **conductive polymers** is their processability, mainly by dispersion.

Polymers are very good insulators! Most plastic materials are not conducting and used to insulate good conductors such as metals.

Unit of conductivity is the reciprocal of electrical resistivity (ohms). Therefore **conductivity** is used to measure the concentration of dissolved solids which have been ionized in a polar solution such as water. The **unit** of measurement commonly used is one millionth of a Siemen per centimeter (micro-Siemens per centimeter or µS/cm).



There are four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers.

The conductively filled conducting polymers were first made in 1930 for the prevention of corona discharge. The potential uses for conductively filled polymers have since been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. Therefore, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

Describe the electrical and electronic properties of polymers

Polymers which can directly use in electrical and in electronics applications based on properties such as conductivity, magnetic , optical, light emissions, photo conductivity, photo resistivity etc are Electrical and electronic properties of polymers. Conductive polymers have the potential advantages of lower manufacturing cost and that they can be processed into thin films.

Today, a number of electrically conducting and electroluminescent polymers exist that find applications as chemical sensors, electro-magnetic shielding, antistatic coatings, corrosion inhibitors, electrically conducting fibers, and in “smart” windows that can regulate the amount of light passing through it. One of the most exciting potential uses of these novel materials are compact electronic devices such as polymer-based transistors, light-emitting diodes and lasers. Some of these electronic devices might find novel applications in the electronic industry, for example in flat flexible television screens, and as acceptors in polymeric solar cells (PSCs). We can see many other new electroluminescent plastics.

Electroluminescence (EL) is an opto-electrical phenomenon in which a material emits light in response to an electrical current flowing through the material or to a strong electrical field. Electroluminescence is caused by recombination of electrons and holes in a (semi-) conducting material. The excited electrons emit their energy as photons (light) during recombination with holes. The electrons and holes may be separated either by doping the material to form p-n junctions (semiconductor electroluminescent) or by excitation when high-energy electrons, accelerated by a strong electric field, pass through the material.

S*olvatochromism* is the shift of the absorption / emission band of a compound in a solution when the polarity of the solvent is changed. Thus, the compound (dye) will have different colors in different solvents of different polarity.

Thermochromism is the reversible change of a materials color due to a shift of the absorption / emission band when the temperature changes. Thus, these materials change its color when the temperature is raised or lowered.

Conducting Mechanism

Electrons in the outermost orbit is in valance band materials like metals shows conductivity.

Most of the polymers shows conductivity by its conjugate structure by adding dopents conductivity is enhanced.

While the addition of a donor or an acceptor molecule to the polymer is called "doping ", the reaction that takes place is actually a redox reaction.

•The first step is the formation of a cation (or anion) radical, which is called a solitonor a polaron.

$Pn \Leftrightarrow [Pn^{+}A^{-}]$

(reduction oxidation)

This step may then be followed by a second electron transfer with the formation of a dication(or dianion) known as a bipolaron.

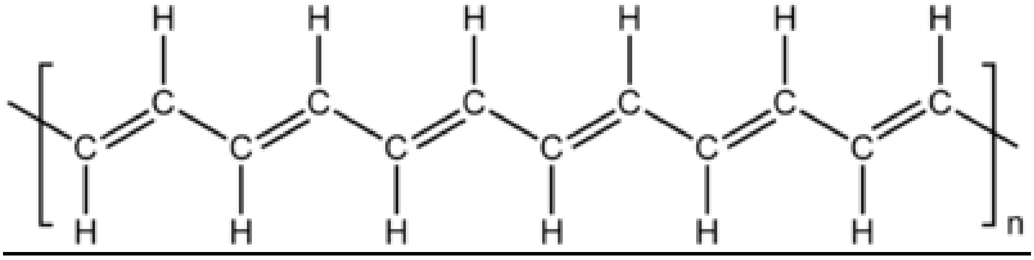
$[Pn^{+}A^{-}] \Leftrightarrow [Pn^{2+}2A^{-}]$

(reduction oxidation)

•Alternatively after the first redox reaction, charge transfer complexes may form between charged and neutral segments of the polymer when possible.

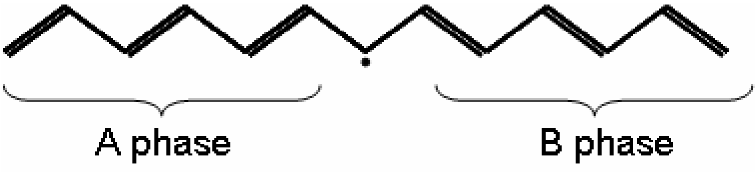
$[Pn^{\bullet +}A^{-}] + Pm \rightarrow [(PnPm)^{\bullet +}A^{-}]$

Poly acetylene



Shows a small conductivity already at room temperature. Polyacetylene is a conjugated polymer (alternating single and double bonds). The trans-structure of polyacetylene has a 2-times degenerated ground state with an A und B structure: Single- and double bonds can exchange with no change in energy. A free radical forms at the position at which the two ground states A and B meet. → This defect is called a soliton.→ Charge storage on the polymer chain leads to a structural relaxation (and vice verse), which in turns localize the charge.

For simplicity, the chemical structure of the soliton is drawn as an abrupt change From phase A to B; but as shown by experiments and calculations, **the structural relaxation** in the vicinity of the domain boundary **extends over approx. 14 carbon atoms.**



Production

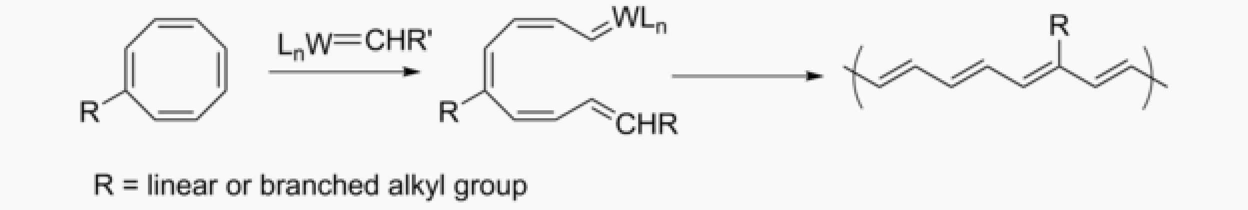
A variety of methods have been developed to synthesize polyacetylene, from pure acetylene as well as other monomers. One of the most common methods uses titanium and aluminum catalysts, known as Ziegler-Natta catalysts, with gaseous acetylene. This method allows control over the structure and properties of the final polymer by varying temperature and catalyst loading.

Scientists obtained films by coating the walls of a reaction flask under inert conditions with a solution of the Ziegler-Natta catalyst and adding gaseous acetylene, resulting in immediate formation of a film. It also further improved polyacetylene synthesis by changing the catalyst to a $CoNO_3/NaBH_4$ system, which was stable to both oxygen and water.

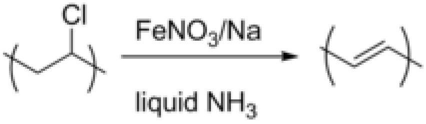
Polyacetylene can also **be** produced by radiation polymerization of acetylene. Glow discharge radiation, γ-radiation, and ultravioletirradiation have been used. These methods avoid the use of catalysts and solvent, but they require low temperatures to produce regular polymers. Gas-phase polymerization typically produces irregular cuprene, whereas liquid-phase polymerization, conducted at −78 °C produces linear *cis*-polyacetylene and solid phase polymerization, conducted at still lower temperature produces *trans*-polyacetylene.

Ring-opening metathesis polymerization.

Poly acetylene can be synthesized by ring-opening metathesis polymerization (ROMP) from cyclooctatetraene, a material easier to handle than the acetylene monomer. This synthetic route also provides a facile method for adding solubilizing groups to the polymer while maintaining the conjugation. Robert Grubbs and coworkers synthesized a variety of polyacetylene derivatives with linear and branched alkyl chains. Polymers with linear groups such as *n*-octyl had high conductivity but low solubility, while highly branched *tert*-butyl groups increased solubility but decreased conjugation due to polymer twisting to avoidsteric crowding. They obtained soluble and conductive polymers with *sec*-butyl and neopentyl groups, because the methylene (CH_2) unit directly connected to the polymer reduces steric crowding and prevents twisting



From precursor polymers.



Polyacetylene synthesis from poly(vinyl chloride)

Dehydrohalogenation route to polyacetylene

Polyacetylene can also be synthesized from precursor polymers. This method enables processing of the polymer before conversion to insoluble polyacetylene. Short, irregular segments of polyacetylene can be obtained by dehydrohalogenation ofpoly(vinyl chloride). Thermal conversion of precursor polymers is a more effective method for synthesizing long polyacetylene chains.

Doping

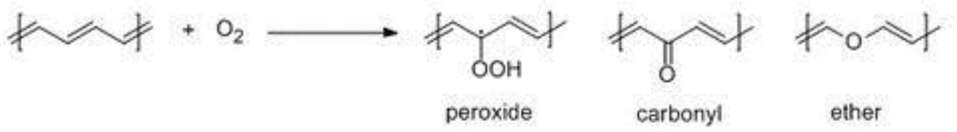
When poly acetylene films are exposed to vapors of electron-accepting compounds (p-type dopants), the electrical conductivity of the material increases by orders of magnitude over the undoped material. p-type dopants include Br_2, I_2, Cl_2, and AsF_5. These dopants act by abstracting an electron from the polymer chain.
The conductivity of these polymers is believed to be a result of the creation of charge-transfer complexes between the polymer and halogen. Charge-transfer occurs from the polymer to the acceptor compound; the polyacetylene chain acts as a cation and the acceptor as an anion. The “hole” on the polymer backbone is weakly associated with the anionic acceptor by Coulomb potential. Polyacetylene doped with (p-type) dopants retain their high conductivity even after exposure to air for several days. Electron-donating (n-type) dopants can also be used to create conductive polyacetylene. n-Type dopants for polyacetylene include lithium, sodium, and potassium. As with p-type dopants, charge-transfer complexes are created, where the polymer backbone is anionic and the donor is cationic. The increase in conductivity upon treatment with an n-typedopant is not as significant as those achieved upon treatment with a p-type dopant. Poly acetylene chains doped with n-type dopants are extremely sensitive to air and moisture.

The conductivity of polyacetylene depends on structure and doping. Undoped *trans*-polyacetylene films have a conductivity of 4.4×10^{-5} $\Omega^{-1}cm^{-1}$, while *cis*-polyacetylene has a lower conductivity of 1.7×10^{-9} $\Omega^{-1}cm^{-1}$ Doping with bromine causes an increase in conductivity to 0.5 $\Omega^{-1}cm^{-1}$, while a higher conductivity of 38 $\Omega^{-1}cm^{-1}$ is obtained through doping with iodine. Doping of either *cis*- or *trans*-polyacetylene leads to an increase in their conductivities. Doped *cis*-polyacetylene films usually have conductivities two or three times greater than doped *trans*-polyacetylene even though the parent film has lower conductivity.

Properties

The structure of polyacetylene films have been examined by both infrared[.] and Raman spectroscopy, and found that structure depends on synthetic conditions. When the synthesis is performed below −78 °C, the *cis* form predominates, while above 150 °C the *trans* form is favored. At room temperature, the polymerization yields a ratio of 60:40*cis*:*trans*. Films containing the *cis* form appear coppery, while the *trans* form is silvery.[16] Films of *cis*-polyacetylene are very flexible and can be readily stretched, while *trans*-polyacetylene is much more brittle.

The synthesis and processing of polyacetylene films affects the properties. Increasing the catalyst ratio creates thicker films with a greater draw ratio, allowing them to be stretched further. Lower catalyst loadings leads to the formation of dark red gels, which can be converted to films by cutting and pressing between glass plates. A foam-like material can be obtained from the gel by displacing the solvent with benzene, then freezing and subliming the benzene. Polyacetylene has a bulk density of 0.4 g/cm^3, while density of the foam is significantly lower, at 0.02–0.04 g/cm^3. The morphology consists of fibrils, with an average width of 200 Å. These fibrils form an irregular, web-like network, with somecross-linking between chains. The insolubility of polyacetylene makes it difficult to characterize this material and to determine the extent of cross-linking in the material.



Products of oxidation of poly acetylene

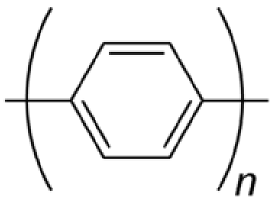
For applications, poly acetylenes suffer from many drawbacks. They are insoluble in solvents, making it essentially impossible to process the material. While both *cis* and *trans*-poly acetylene show high thermal stability, exposure to air causes a large decrease in the flexibility and conductivity. When poly acetylene is exposed to air, oxidation of the backbone by O_2 occurs. Infrared spectroscopy shows formation of carbonyl groups, epoxides, and peroxides. Coating with polyethylene or wax can slow the oxidation temporarily, while coating with glass increases stability indefinitely

Applications

Poly acetylene has no commercial applications, although the discovery of poly acetylene as a conductive organic polymer led to many developments in materials science. Conducting polymers are of interest for solution-processing for film-forming conductive polymers.

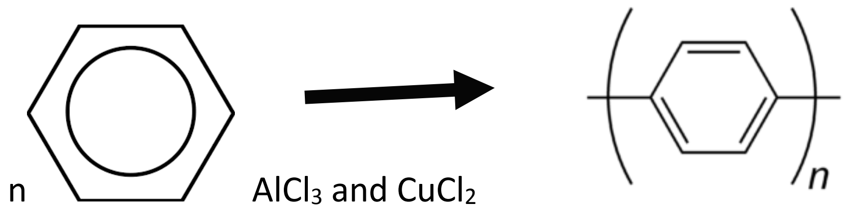
Poly paraphynelene

Structure of PPP



Production

It is produced by Friedal crafts polymerisation of benzene using Aluminium chloride and copper Chloride ($AlCl_3$ and $CuCl_2$)



A 35^0 C

Another method is by soluble precursor method , intermediates are prepared

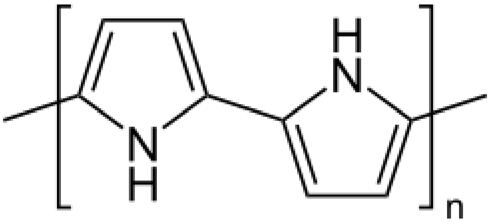
Properties and Applications

Poly phenylenes are an important class of conductive polymers. The phenylene units in these polymers are connected to one another through carbon-carbon single bonds resulting in linear polymers with a backbone that is comprised of aromatic rings only. By far the largest attention received poly (para-phenylene) (PPP). Due to non acetylene structure this polymer is very stable up to temperatures of about 500 to 600°C with minimal and only slow oxidation. It is quite insoluble in most solvents and has a very high melting point. It exhibits unusual electronic and optical properties and can be processed into a crystalline thin film, for example by vacuum deposition, that is electrically conducting when doped. PPP is photoconducting and has the potential for electroluminescence (EL) applications such as light-emitting diodes.

Polypyrrole

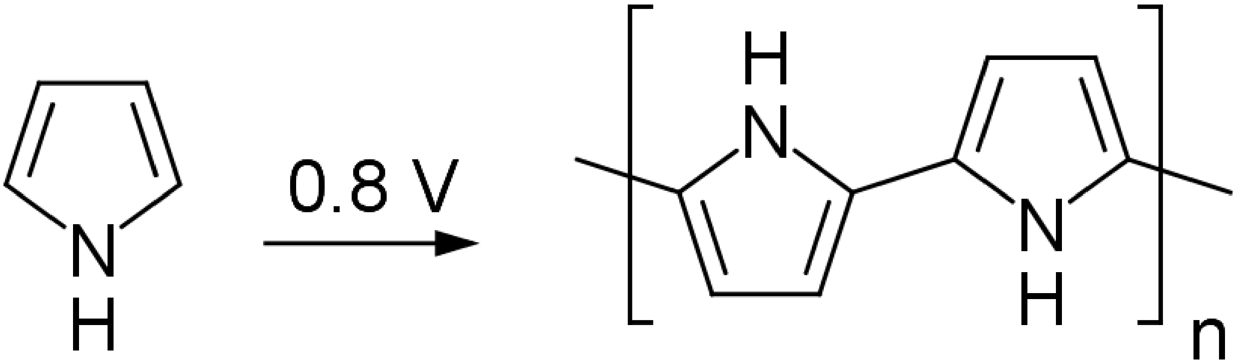
Polypyrrole (PPy) is formed by the polymerization of pyrrole. Polypyrroles are conducting polymers, related members being polythiophene, polyaniline, and polyacetylene.

Structure



Synthesis and Production

Pyrrole can be polymerized electrochemically.



PPy is generally synthesized by chemical or electrochemical means. Chemical synthesis is used when large quantities of material are required and involves mixing a strong oxidizing agent (typically FeCl3) with a monomer solution . Electrochemical synthesis is preferred for research purposes due to the simplicity of the technique, control over material thickness, geometry and location, the facility for doping during synthesis, the wide choice of available dopant ions and the generation of good quality films. It leads to the development of adherent surface conformal deposits i.e. thin solid films, from the bulk solution phase of monomer units. The electrodeposition on the positively polarized working electrode proceeds via a condensation reaction between the monomer units of the five-membered heterocycle pyrrole (figure 2). Concomitantly, negatively charged counterions must be present in solution to maintain charge balance within the polymer since positive charges are developed along the PPy backbone. This latter process is referred to as doping and the choice of counterion, including biomolecules, affects formed polymer properties.

Properties

Films of PPy are yellow but darken in air due to some oxidation. Doped films are blue or black depending on the degree of polymerization and film thickness. They are amorphous, showing only weak diffraction. PPy is described as "quasi-unidimensional" vs one-dimensional since there is some crosslinking and chain hopping. Undoped and doped films are insoluble in solvents but swellable. Doping makes the materials brittle. They are stable in air up to 150 °C at which temperature the dopant starts to evolve (e.g., as HCl)

PPy is an insulator, but its oxidized derivatives are good electrical conductors. The conductivity of the material depends on the conditions and reagents used in the oxidation. Conductivities range from 2 to 100 S/cm. Higher conductivities are associated with larger anions, such as tosylate. Doping the polymer requires that the material swell to accommodate the charge-compensating anions. The physical changes associated with this charging and discharging has been discussed as a form of artificial muscle. The surface of polypyrrole films represent fractal properties and ionic diffusion through them show anomalous diffusion pattern.

Applications

PPy and related conductive polymers have two main application in electronic devices and for chemical sensors.

Py is a potential vehicle for drug delivery. The polymer matrix serves as a container for proteins.

Polypyrrole has been investigated as a catalyst support for fuel cells[11] and to sensitize cathode electrocatalysts.

Together with other conjugated polymers such as polyaniline, poly(ethylenedioxythiophene) etc., polypyrrole has been studied as a material for "artificial muscles", a technology that offers advantages relative to traditional motor actuating elements.

Polypyrrole was used to coat silica and reverse phase silica to yield a material capable of anion exchange and exhibiting hydrophobic interactions.

Polypyrrole was used in the microwave fabrication of multiwalled carbon nanotubes, a rapid method to grow CNT's.

A water-resistant polyurethane sponge coated with a thin layer of polypyrrole absorbs 20 times its weight in oil and is reusable.

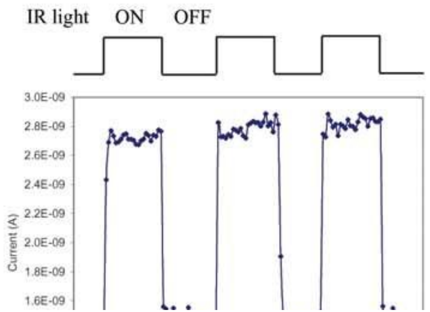
Organometallic polymers

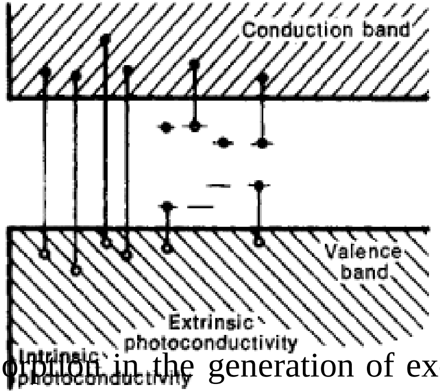
Organometallic polymers are polymers having metallic ions in the structure of polymers. It helps to improve conductivity and related properties

Photoconducting polymers

Photoconductivity is defined as an increase of conductivity caused by irradiation. Thus, photoconductive polymers are insulating or poorly conductive in the darkness and more conductive when illuminated.

This process generates an electron hole pair, increasing the concentration of intrinsic carriers. The photon energy must exceed the band gap and consequently there is a threshold wavelength-energy associated with the process.



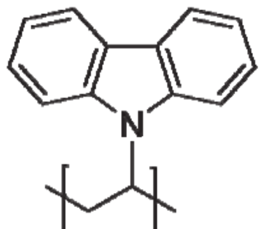


Carriers may also be generated from photon absorption in the generation of excitons. The excitons are themselves unable to transport charge but can produce an electron hole pair if an interface is reached or two excitons collide.

On many common polymers it is very difficult to observe photoconduction even when the samples are irradiated by photons with energies well in excess of theirband gaps. This is largely because the carriers have very short lifetime (<1 ns) due to rapid recombination and deep hole trapping.

Photoconductive polymers can be *p*-type (hole-transporting), *n*-type (electron-transporting), or bipolar (capable of transporting both holes and electrons). Most practical photoconductive charge-transporting polymers are *p*-type.

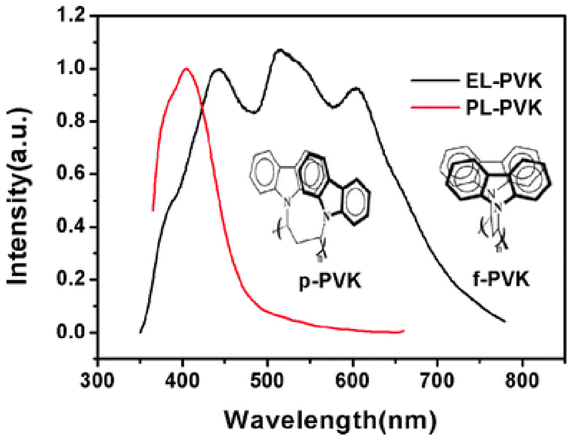
Example: poly(*N*-vinylcarbazole) (PVK)



PVK has charge in side-group.

The the polymer backbone does not contribute to the conductivity.

PVK absorbs ultraviolet light in the 360-nm region and forms an exciton that ionizes in an electric field. PVK takes up a helical conformation with successive aromatic side chains having parallel to each other in a stack along which electron transfer is relatively easy.



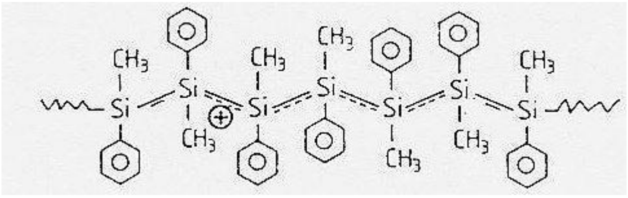
Ye et al. *Phys. Chem. Chem. Phys.*, 2010, **12**, 15410-15413

Photoluminescence (PL) and electroluminescence (EL) spectra of a PVK film at room temperature. The two possible PVK conformations, p-PVK and f-PVK conformation, are shown in the inset.

The hole state is a radical cation and moveable with very small effective mobility of $\mu = 10^{-6}$ $\mathrm{cm^2/Vs}$.

Example: polysilane

Polysilanes can be quasi-conjugated polymers, but their backbones are composed of silicon atoms. The effective mobility can be high: $\mu = 1$ $\mathrm{cm^2/Vs}$



Schematic drawing of p-type (hole) stateApplications:

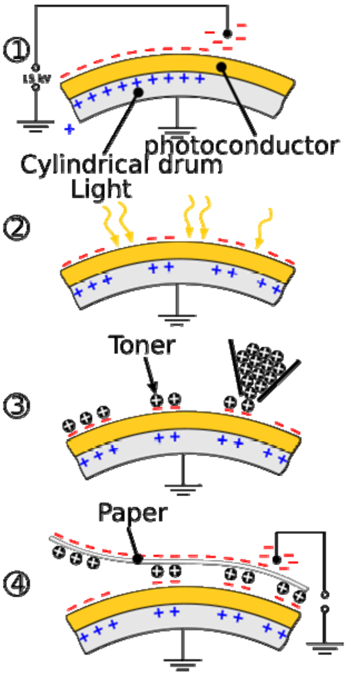
- anti-static coating for photo-films, mobile-phones
- radiation protection of electron-beam based monitor technology
- (auto)darkening windows to reduce passing light

Typical: band gap in UV-regime

However, traps are that shallow that IR-light is sufficient to reactivate the electrons. Color centers are not only source of free electrons but act as very efficient traps as well.

Applications:

Photocopier working with xerography (standard for office copying)
Old: chalkogenide-glasses (Se), toxic – today: photoconducting polymers



1. **Charging**: cylindrical drum is electrostatically charged by a high voltage wire called a corona wire or a charge roller. The drum has a coating of a photoconductive material.

2. **Exposure**: A bright lamp illuminates the original document, and the white areas of the original document reflect the light onto the surface of the photoconductive drum. The areas of the drum that are exposed to light become conductive and therefore discharge to ground. The area of the drum not exposed to light (those areas that correspond to black portions of the original document) remain negatively charged. The result is a latent electrical image on the surface of the drum.

3. **Developing**: The toner is positively charged. When it is applied to the drum to develop the image, it is attracted and sticks to the areas that are negatively Charged (black areas), just as paper sticks to a toy balloon with a static charge.

4. **Transfer**: The resulting toner image on the surface of the drum is transferred from the drum onto a piece of paper with a higher negative charge than the drum.

5. **Fusing**: The toner is melted and bonded to the paper by heat and pressure rollers.

Laser printers work on the same principle. In the optics a laser is used for sampling.

Mechanism of photoconductivity:

Piezoelectricity

Piezoelectricity is the electric charge that accumulates in certain solid materials (such as crystals, certain ceramics, and biological matter such as bone, DNA vand various proteins and now in polyeres) in response to applied mechanical stress.

The word *piezoelectricity* means electricity resulting from pressure and latent heat. It means to squeeze or press, Piezoelectricity was discovered in 1880 by French physicists Jacques and Pierre Curie.

Crystals shows charges when pressure is applied or compressed in a particular direction and disappeared when pressure is removed .

Lot of polymers shows piezo electric properties Poly vinyldene fluoride $(CH_2CF_2)_n$, PVDF shows good **Piezoelectric** response . This is a semi crystalline polymer and shows this property.

The piezoelectric properties of PVDF are exploited in the manufacture of tactile sensor arrays, inexpensive strain gauges, and lightweight audio transducers. Piezoelectric panels made of PVDF are used on the Venetia Burney Student Dust Counter, a scientific instrument of the new horizons space probe that measures dust density in the

Poly vinyldene fluoride $(CH_2CF_2)_n$ - Trifluro ethylene $(CHCF_3)_n$ co polyeres also shows this property and have wide range of applications .

Pyroelectricity

Pyro electricity is the property of certain crystals which are naturally electrically polarized and as a result contain large electric fields.

The most important example is the gallium nitride semiconductor.

The large electric fields in this material are unwanted for light emitting diodes (LEDs), but are very helpful for the fabrication of power transistors. Alternatively, pyroelectricity is interpreted as the ability of certain materials to generate a temporary voltage when they are heated or cooled.

If the temperature stays constant at its new value, the pyroelectric voltage gradually disappears due to leakage current (the leakage can be due to electrons moving through the crystal, ions moving through the air, current leaking through a voltmeter attached across the crystal, etc)

Lot of polymeres also shows this property and have uses . PVDF and its co polyeres shows Pyro electric properties .

Photo resisists

- Photo resists are radiation sensitive materials.

  - Undergo soe (splicing by overlap extension) when exposed to radiation reaction
- A photoresist is a light-sensitive material used in several processes, such as photolithography and photoengraving,
- to form a patterned coating on a surface. This process is crucial in the electronic industry.

Major process

1. Crosslinking of linear polymer backbone by the light induced
2. Crosslinking of polymer containing photosensitive groups .
3. Polymerization of monomeric materials .
4. Enhancement of solubility by a photo induced molecular rearrangements.
5. Enhancement of solubility by photo effect reduction in molecular weight .

- The process begins by coating a substrate with a light-sensitive organic material.
- A patterned mask is then applied to the surface to block light, so that only unmasked regions of the material will be exposed to light.
- A solvent, called a developer, is then applied to the surface. In the case of a positive photoresist, the photo-sensitive material is degraded by light and the developer will dissolve away the regions that were exposed to light, leaving behind a coating where the mask was placed.

  In the case of a negative photoresist, the photosensitive material is strengthened (either polymerized or cross-linked) by light, and the developer will dissolve away only the regions that were not exposed to light, leaving behind a coating in areas where the mask was not place

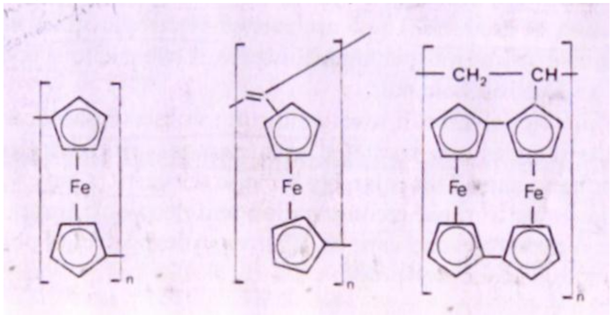
Organometallic polymers

Organometallic polymers are polymers having metallic ions in the structure of polymers.

It helps to improve conductivity and related properties .

- **With transition metals conductivity can achieve**
- **Fero cenylene and ferri cenylene cobinations shows better results**

- Presently m
- any combinations are in reserch



Liquid Crystal Polymer (LCP)

Liquid-crystal polymers are capable of forming regions of highly ordered structure while in the **liquid** phase. However, the degree of order is some what less than that of a regular solid **crystal**.

Liquid Crystal Polymer (LCP) - A relatively unique class of partially crystalline aromatic polyesters based on p-hydroxybenzoic acid and related monomers. Liquid crystal polymers are capable of forming regions of highly ordered structure while in the liquid phase. However, the degree of order is somewhat less than that of a regular solid crystal. Typically LCPs have outstanding mechanical properties at high temperatures, excellent chemical resistance, inherent flame retardancy and good weatherability. Liquid crystal polymers come in a variety of forms from sinterable high temperature to injection moldable compounds.

Today, liquid crystal polymers can be melt processed on conventional equipment at fast speeds with excellent replication of mold details and efficient use of regrind.

Features

Low Warpage , High Heat Resistance , Flame Retardant , High Flow , Low Viscosity , Good Moldability , Good Dimensional Stability , Chemical Resistant , Good Flow , Heat Aging Resistant

Properties

Liquid-crystal polymers are capable of forming regions of highly ordered structure while in the liquid phase. However, the degree of order is somewhat less than that of a regular solid crystal. Typically, LCPs have a high mechanical strength at high temperatures, extreme chemical resistance, inherent flame retardancy, and good weatherability. Liquid-crystal polymers come in a variety of forms from sinterable high temperature to injection moldable compounds. LCPs can be welded, though the lines created by welding are a weak point in the resulting product. LCPs have a high Z-axis coefficient of thermal expansion.

LCPs are exceptionally inert. They resist stress cracking in the presence of most chemicals at elevated temperatures, including aromatic or halogenated hydrocarbons, strong acids, bases, ketones, and other aggressive industrial substances. Hydrolytic stability in boiling water is excellent. Environments that deteriorate the polymers are high-temperature steam, concentrated sulfuric acid, and boiling caustic materials.

Polar and bowlic LCPs are ferroelectrics, with reaction time order-of-magnitudes smaller than that in conventional LCs and could be used to make ultrafast switches. Bowlic columnar polymers possess long, hollow tubes; with metal or transition metal atoms added into the tube, they could potentially form ultrahigh-T_c superconductors.

Uses

Because of their various properties, LCPs are useful for electrical and mechanical parts, food containers, and any other applications requiring chemical inertness and high strength. LCP is particularly good for microwave frequency electronics due to low relative dielectric constants, low dissipation factors, and commercial availability of laminates. Packaging microelectromechanical systems (MEMS) is another area that LCP has recently gained more attention. Superior Properties make them especially suitable for automotive ignition system components, heater plug connectors, lamp sockets, transmission system components, pump components, coil forms and sunlight sensors and sensors for car safety belts.

Disadvantages

- Form weak weld lines
- Highly anisotropic properties
- Drying required before processing
- High cost