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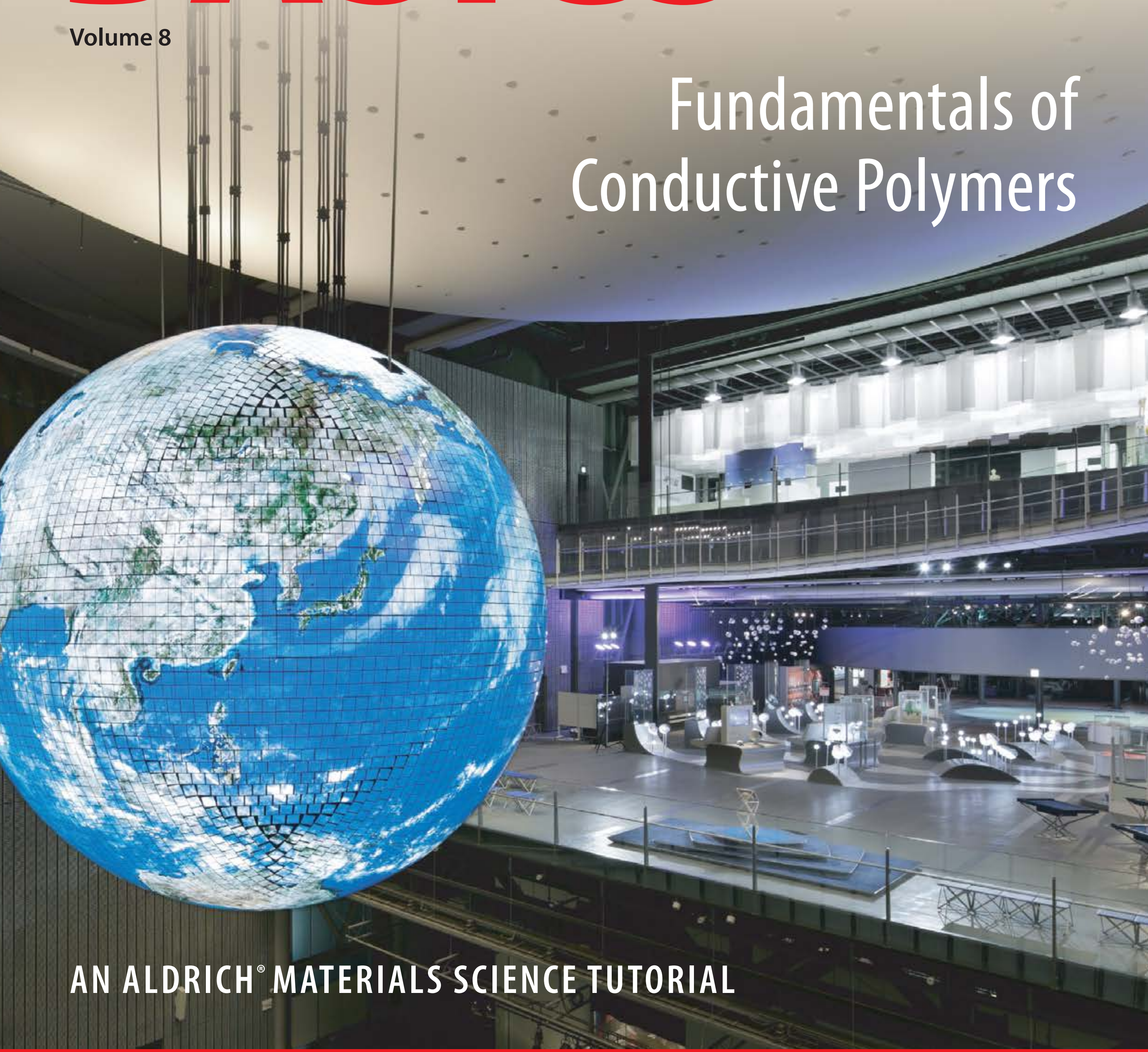
Materials Science

# Material Matters™ BASICS

Volume 8

## Fundamentals of Conductive Polymers



AN ALDRICH® MATERIALS SCIENCE TUTORIAL

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# Introduction

*Material Matters™ Basics,* issued by Sigma-Aldrich Japan, is an excellent reference for researchers who have just started studies in materials science. This Aldrich® Materials Science Tutorial will also assist researchers in other fields who would like to understand the essentials of certain themes in materials science.

Conductive polymers have been in the spotlight since research on them won the Nobel Prize in Chemistry in 2000[1] and have found wide applications in various products. This eighth volume of *Material Matters™ Basics* describes conductive polymers from the viewpoint of their applications to scientific education and introduces actual experimental workshops using conductive polymers. Since *Material Matters™ Basics* is not issued exclusively for specialists of the field, the authors describe the aspects of conductive polymers as easily as possible for readers to be able to appreciate the unique characteristics of the polymers.

What characteristics do conductive polymers have? Electrical conductivity refers to "characteristics related to conducting and directing the flow of electricity" (opposite to insulation characteristics), and a polymer refers to "a molecule that has a very large molecular weight (typically a molecular weight of 10,000 or larger)." Accordingly, conductive polymers literally mean "polymers that can conduct electricity," or in simpler terms, they are "plastics that allow electricity to flow through them." However, the general commonsense view regards polymers as typical insulators similar to materials such as glass. Electric wires are sheathed with a polymer such as polyvinyl chloride (PVC), and the plugs of power supplies are made of a polymer. It was common sense that polymers cannot conduct electricity as metals do because they are insulators, until a conductive polymer was discovered by doping polyacetylene.[2]

# About the Cover

**Geo-Cosmos**, a symbolic display at the National Museum of Emerging Science and Innovation, is the world's first "Earth display" on organic EL panels. It was created based on the desire of the director of the National Museum, Dr. Mamoru Mohri, to share the experience of seeing the Earth in vivid color as seen from outer space with as many people as possible. Visitors will be able to discover different aspects of the present and future Earth according to the data of various scientific observations of Earth provided by scientists and research institutions all over the world.

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# FUNDAMENTALS OF CONDUCTIVE POLYMERS

**Hideki Shirakawa**
Professor Emeritus of the University of Tsukuba
**Kazuaki Hiroki**
Associate Professor of Tsuyama National College of Technology

## History of Conductive Polymer Development

### *Serendipity*

Straight-chain compounds, which consist of alternately linked single bonds and double bonds [-(CH=CH)$_n$-], are called conjugated polyenes; physicists as well as chemists have long been interested in them. From early on, synthetic organic chemists knew a phenomenon in which with increases in the conjugate number (n), the maximum of the absorption spectrum shifts to longer wavelength region (bathochromic effect), and simultaneously, the absorbance increases (hyperchromic effect). In linear polyenes with larger conjugate numbers, single bonds get shorter while double bonds are longer. It is expected that a bond is intermediate between single and double bonds for an infinitely long conjugated polyene where the lengths of single and double bonds tend to be equal. In this state, an infinite number of π (pi) orbitals form continuous energy states (i.e., energy bands). The bonding orbitals, consisting of an infinite number of π electrons occupy the lower half of the bands (valence band) adjacent to the upper half of the empty band (conduction band), which is a characteristic band structure corresponding to metals. Accordingly, some of the π electrons are excited from the valence band to the conduction band even at normal temperature (energy corresponding to normal temperature), thus exhibiting electrical conductivity. This is why infinitely long conjugated polyenes became a popular topic of scientific conversation as a metal model or a free electron model. Later, however, it was theoretically demonstrated that the molecular structure allowing the bond alternation is more energetically stable by taking σ (sigma) electrons as well as π electrons into consideration, negating the metallic model.

Solid-state physicists tend to explain the total energy of a molecule as the sum of electron energy and lattice energy. For example, the lattice of a conjugated polyene is regarded as a property associated with the positions of the carbon atoms that form its linear chain, and when the lattice spacing (the length of a carbon-carbon bond) is uniform, lattice energy will be at a minimum. On the other hand, since electrons have a strong tendency to form pairs of opposite-spin electrons, chemical bonds with diverse bond lengths allow lower electron energy. In other words, lattice energy and electron energy have conflicting characteristics. In particular, a linear molecule consisting of a one-dimensional arrangement of carbon-carbon bonds, such as a conjugated polyene, has markedly weak binding force in the other two dimensional directions. Accordingly, a decrease in electron energy determines the total energy of the molecule by contributing to offsetting the disadvantage of an energy increase that causes lattice deformation (which induces bond alternation). Bond alternation causes a gap ($\Delta Eg$) between the valence band and the conduction band, and the magnitude of the gap varies depending on the degree of the bond alternation. When the gap is small ($\leq 1.5$ eV), the molecule becomes a semiconductor; when the gap is large ($>1.5$ eV), the molecule becomes an insulator.

Conjugated polyenes with larger conjugate numbers exhibit remarkably poor solubility to any solvent. Accordingly, it was extremely difficult to synthesize molecules corresponding to infinitely long conjugated polyenes to demonstrate their bond alternative characteristics. Finally, in 1958, G. Natta et al. reported the synthesis of a polymer[3] corresponding to an infinitely long conjugated polyene by a catalytic polymerization of acetylene using the Ziegler-Natta catalyst, which is a well-known catalyst for polymerization of polyethylene and polypropylene.

In the latter half of the 1960s, Shirakawa, one of the winners of the 2000 Nobel Prize in Chemistry with A. J. Heeger and A. MacDiarmid was studying the polymerization reaction of acetylene with the aid of the Ziegler-Natta catalyst at the Tokyo Institute of Technology. Initially, he did not intend to create conductive polymers, but mainly intended to investigate the mechanism of polyacetylene polymerization reaction.[4] Researchers in those days could only produce a black powder of polyacetylene no matter what they tried. The substance was insoluble in any solvent and unmeltable at high temperatures. Neither heating nor dissolving in solvent softened the polymer. It could not be formed into arbitrary shapes and generally lacked the merits of a plastic, to the extent that one would be hard-pressed to find a use for it.[5]

Around 1967, however, a polyacetylene thin film, which nobody had been able to create, was synthesized almost by chance when a visiting scientist who had joined the Ikeda group of the Tokyo Institute of Technology expressed his wish to try synthesizing polyacetylene. Shirakawa, who was then a member of the group, taught the visiting scientist a normal catalytic recipe and allowed him to perform an experiment. After a while, the visiting scientist reported to him that the experiment had failed. What Shirakawa saw when he went to examine the result of the reaction was a black film on the surface of the catalyst solution. A black film had been formed instead of polyacetylene powder. Moreover, the pressure gauge indicated almost no acetylene had been polymerized. The experiment had not achieved its original purpose, so it had clearly "failed."

Shirakawa did not want to repeat the same failure, so he performed a detailed analysis of the black film. Then, things changed drastically. The black film was without a doubt a polyacetylene film. Shirakawa started experiments to intentionally create a polyacetylene film. In the course of investigating polyacetylene formation conditions, he found that polyacetylene film tends to form in a catalytic solution more concentrated than the conventional solution. Specifically, he hypothesized that the wrong units had been used to measure the concentration of the catalytic solution. The visiting scientist might have mistakenly measured the concentration using mols instead the mmols called for in the recipe. That is 1,000 times stronger than the original recipe! The amazing part of this discovery is that the visiting scientist mistakenly did what common-sense chemists would never have thought of doing. Then Shirakawa saw the value of the experiment, which otherwise might have been regarded as a mere failure. That is why this incident is regarded as an example of serendipity.

Thus, polyacetylene films were successfully synthesized, and experiments associated with its synthesis were repeated. In the course of the study, they observed that polyacetylene films show a metallic sheen. Seeing the sheen, Shirakawa thought that the film might conduct electricity. This is the second moment of serendipity in this discovery. Certainly, the Kambara and Hatano group of the Tokyo Institute of Technology had originally been studying polyacetylene powder and discovered that it is a polymeric organic semiconductor. However, the inspiration that electrically insulating polymers might conduct electricity under a special condition plowed the way to the discovery of doped polyacetylene as the world's first electrically conductive polymer.

Although polyacetylene in the form of a film had been discovered, the journey was far from over. The measured electrical resistivity and band gap of undoped polyacetylene films were exactly in the ranges of those for semiconductors or insulators.

$1.0 \times 10^4$ ohm·cm and 0.56 eV for *trans* form of polyacetylene;

$2.4 \times 10^8$ ohm·cm and 0.93 eV for *cis* form of polyacetylene.

In addition, for better or for worse, no researchers were interested in the reported research achievements and no competing researchers appeared.[6]

However, another wonderful opportunity came to Shirakawa. An inorganic chemist, MacDiarmid of the University of Pennsylvania, became interested in polyacetylene, this humble organic polymer that possesses a metallic sheen. In 1976, Shirakawa was invited to the University of Pennsylvania and started research in cooperation with MacDiarmid and Heeger, a solid-state physicist. As part of their research, they proposed chemical doping, which creates holes to move along the polymer main chain, by adding a trace amount of electrophilic halogen atoms (initially, bromine molecules were used, and later, iodine). Chemical doping brought about a surprising result. The electrical conductivity of polyacetylene jumped to a level 10 million times higher than that of conventional polyacetylene, and subsequent study achieved electrical conductivities of several thousand S/cms, which is comparable to those of typical metals. Thus, the conductive polymer polyacetylene was born.

Polyacetylene, the first conductive polymer had a great impact on the scientific world and drew attention as one of the greatest discoveries in the world. Shirakawa called it "modern-day alchemy,"[6] and it is no exaggeration to call it that. After its creation, various studies were conducted on the synthesis and application of polyacetylene. A research team at BASF reported that they synthesized polyacetylene with electrical conductivity on the order of $10^5$ S/cm by using silicon oil as a solvent and aging the catalyst solution at high temperature. However, to our knowledge, no one else has reported success in obtaining the same result. In addition, studies on the expected applications of polyacetylene seem to have encountered difficulty caused by its low environmental stability at ambient conditions. Given this situation, it is interesting to note that more than 30 years ago, researchers were conducting studies that seem to have predicted the present circumstances regarding batteries. Shirakawa et al. made prototypes of organic thin film solar cells based on polyacetylene and Akira Yoshino of Asahi Kasei Corporation, who is now known as the inventor of the lithium-ion battery, was researching polyacetylene as a material for electrodes in batteries.

# Characteristics of Conductive Polymers

Conductive polymers such as polyacetylene are synthesized with electrical properties ranging from insulators to semiconductors. They are converted from semiconductors to conductors (becoming electrically conductive polymers) by a doping process, which will be described later. Then, what makes electrically conductive polymers represented by polyacetylene differ from general-purpose polymers such as polyethylene? The answer is the difference in their molecular structure.

Polyethylene (**Figure 1**) and polyacetylene (**Figure 2**) seem to have a similar structure. However, the main chain of polyethylene molecule consists only of single bonds, strong σ bonds, whereas that of polyacetylene has a conjugated structure, in which alternate single and double bonds (σ and π bonds, respectively) repeatedly continue. This conjugated structure is a decisive factor in its electrical conductivity.

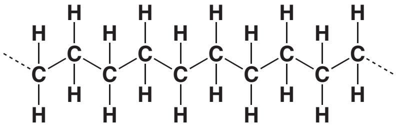


**Figure 1**. Molecular Structure of Polyethylene

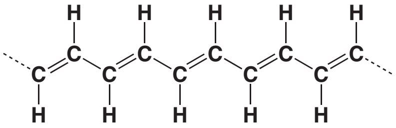


**Figure 2.** Molecular Structure of Polyacetylene (*Trans* Form)

As shown in **Figure 3**, every carbon atom forming the main chain of polyacetylene (*trans* form) has a *p* orbital (also called a π orbital) occupied by a π electron. In other words, π electrons are considered to be arranged in one dimension. However, since each π electron simultaneously belongs to two adjacent π orbitals to contribute to the formation of a double bond, it cannot move freely resulting in the π electron localization. Therefore polyacetylene is an insulator or, at best, a semiconductor.

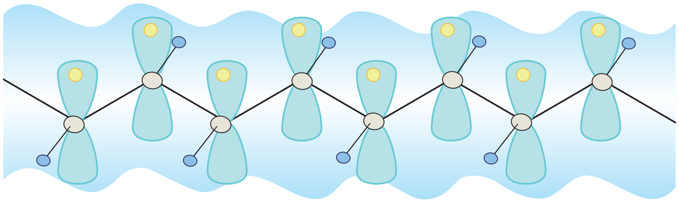


**Figure 3**. *p* Orbitals and π Electrons in Polyacetylene

Imparting electrical conductivity to the polymer requires a process (or reaction) called doping, specifically chemical doping. The actual process of doping is an addition of a small amount of a reagent shown in **Table 1** (including acceptors which tend to readily accept electrons and donors which tend to readily donate electrons). Chemical doping induces electrical conductivity in the polymers.

**Table 1.** Types of Dopants

| **Dopant Types** | |
|---|---|
| **Acceptor** | |
| Halogen | $Br_2$, $I_2$, ICl, $ICl_3$ |
| Lewis acid | $PF_5$, $AsF_5$, $BF_3$, $SO_3$ |
| Proton acid | HCl, $H_2SO_4$, $HClO_4$ |
| Transition metal halide | $FeCl_3$, $FeBr_3$, $SnCl_4$ |
| Organic compound | TCNE, TCNQ, DDQ, Various amino acids |
| Electrochemical doping | $ClO_4^-$, $BF_4^-$, $PF_6^-$, $AsF_6^-$ |
| **Donor** | |
| Alkaline metal | Li, Na, K, Rb, Cs |
| Alkaline earth metal | Be, Mg, Ca |
| Electrochemical doping | $Li^+$, $Na^+$, $K^+$, $R_4N^+$, $R_4P^+$($R=CH_3$, $C_6H_5$, etc.) |

Doping can also be carried out in an electrochemical manner by applying a voltage between a positive and negative electrode made of conductive polymer in an electrolytic solution containing an electrolyte ($D^+A^-$). Acceptor doping occurs at the positive electrode, and donor doping occurs at the negative electrode.

An addition of acceptor or donor induces electrical conductivity of the conjugated polymers. The acceptor extracts π electrons from the conjugated polymer to form positive charge carriers (holes) and the donor supplies electrons to the conjugated polymer to form negative charge carriers.

The *trans* form of polyacetylene may have two isomeric structures with an ascending double bond (here called phase A) and with a descending double bond (here called phase B). The two conjugated structures are symmetric with each other and cannot be distinguished in energy. This system is termed a degenerated state. Among the different kinds of conjugated polymers, only the *trans* form of polyacetylene has this structure.

ESR measurement has revealed that the *trans* form of polyacetylene has $3 \times 10^{19}$ spin/g of unpaired electrons. On the other hand, no unpaired electrons are observed in the carefully synthesized *cis* form of polyacetylene, and a *cis* form of polyacetylene synthesized at low temperature irreversibly turns into the *trans* form of polyacetylene by thermal isomerization. Accordingly, it is considered that an isolated π electron forms between phase A and B by a rearrangement of the conjugation during the thermal isomerization. In other words, a stabilized state where an isolated unpaired π electron exists in the boundary of the two phases is induced. The isolated π electron is called a neutral soliton. Since the isolated π electrons have no electric charge, they do not act as charge carriers. However, they exhibit higher reactivity than paired π electrons so that they tend to react with acceptors to form negatively charged solitons or with donors to form positively charged solitons, contributing to inducing electrical conductivity in polyacetylene (**Figure 4**).

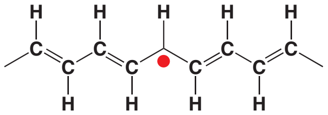


**Figure 4.** Unpaired Electrons (Neutral Solitons) Created in *Trans* Form of Polyacetylene with Degenerated Structure

Conjugated polymers other than the *trans* form of polyacetylene are nondegenerate systems, in which extraction or rearrangement of π electrons produces two structures with different energy states. For example, in a poly (*p*-phenylene), when an acceptor dopant extracts π electrons from its double bonds, the bonds are rearranged to convert from a stable benzenoid structure (phase A) into a quinoid structure (phase B), a higher-energy state. Since the conversion into phase B requires energy equivalent to the energy difference between two states, limited domains are turned into phase B to create polarons (**Figure 5**).

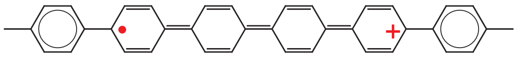


**Figure 5.** Positive Polarons Created in Poly (*p*-phenylene) with Nondegenerate Structure

In the acceptor doping process, the acceptor extracts isolated π electrons from a polaron to form a positively charged bipolaron that has two positive charges, and the donor doping supplies an electron to form a negatively charged bipolaron having two negative charges (**Table 2** and **Figure 6**).

The doping process not only converts the electrical conductivity from an insulator level to a conductor level, it also brings about various physical property changes such as color and size in the conductive polymers. Thus, the doping process is what makes the diversity of applications of the conductive polymers possible.

**Table 2.** Types of Charge Carriers in Conductive Polymers

| **Electric Charge** | **Number of Charges** | **Spin** |
|---|---|---|
| Soliton Charge Carriers | | |
| Neutral | 0 | 1/2 |
| Positive | +1 | 0 |
| Negative | -1 | 0 |
| Polaron Charge Carriers | | |
| Positive | +1 | 1/2 |
| Negative | -1 | 1/2 |
| Bipolaron Charge Carriers | | |
| Positive | +2 | 0 |
| Negative | -2 | 0 |

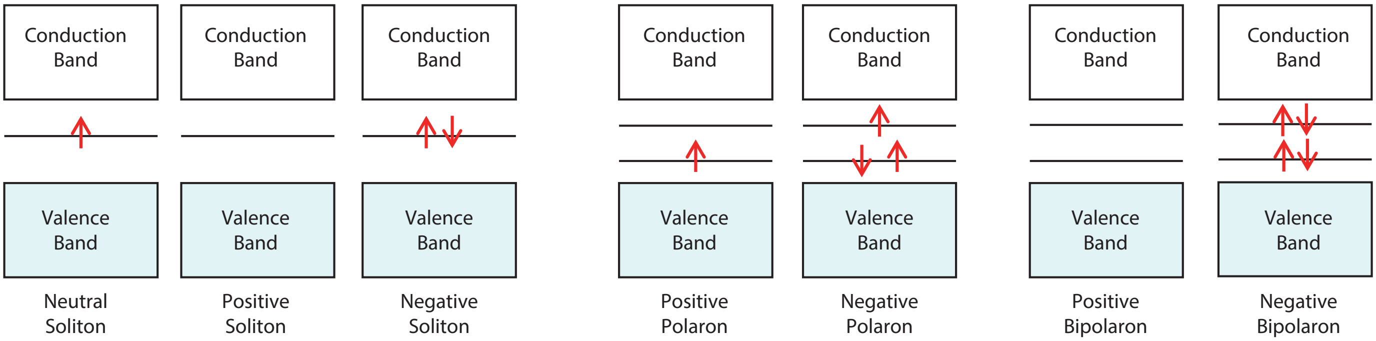


**Figure 6.** Energy Level Diagram of Charge Carriers

As seen in **Figure 7**, for example, when iodine is added to polyacetylene as a dopant, iodine removes π electrons in the polymer main chain and leaves holes there. To explain this in more visual terms, polyactyelene before doping can be considered as a crowded train in which passengers are so packed they cannot move. Passengers in the train are equivalent to the electrons in polyacetylene. If some passengers get off (i.e., π electrons are removed by a dopant), space is created for nearby passengers to move into first. The newly vacated space is then available for the remaining passengers to move into. As a result, passengers can move as a whole. Electrons also move in this manner. When a voltage is applied to the polyacetylene, holes and electrons move successively; thus, electric current flows (**Figure 8**).

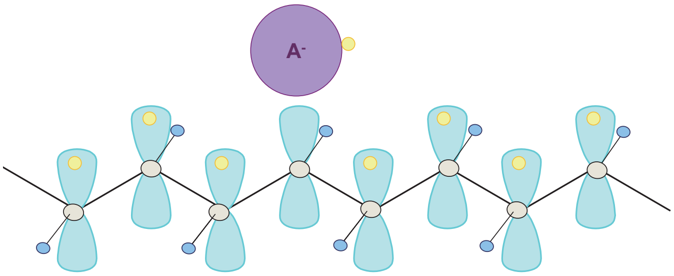


**Figure 7**. Chemical Doping in Polyacetylene

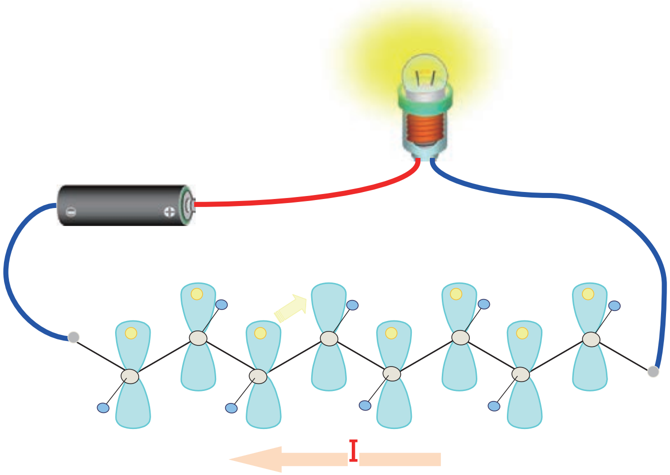


**Figure 8**. Electric Conduction in Polyacetylene

# Evolution of Conductive Polymers

While the potential of polyacetylene has been highly regarded, conductive polymers containing aromatic rings have been developed one after another. Since they have superior air stability, they have been put into practical use. Polyacetylene, a typical aliphatic conjugated compound, tends to induce the electrophilic addition reaction in its double bonds. As a result of the addition reaction, the conjugated system of polyacetylene is cut off, so that its doping susceptibility is easily lost. On the other hand, aromatic conjugated compounds do not have the tendency to induce the addition reaction in their double bonds and are, therefore, more chemically stable than their aliphatic conjugated counterpart.

**Figure 9** shows structures of conductive polymers containing aromatic rings. **Table 3** summarizes the classification of conductive polymers.

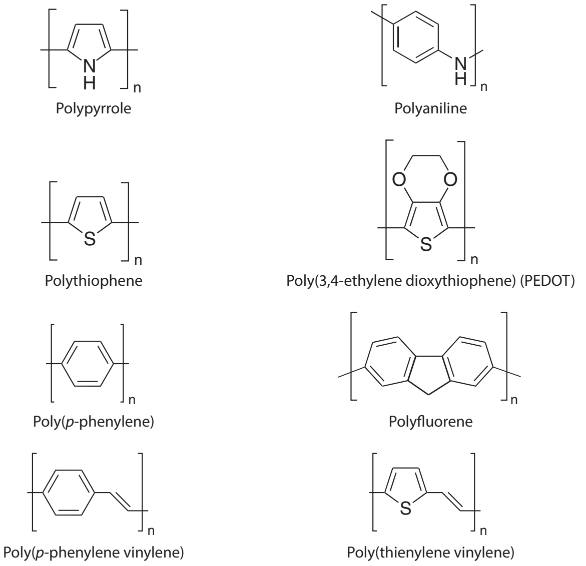


**Figure 9**. Conductive Polymers Containing Aromatic Rings

**Table 3**. Classification of Conductive Polymers

| **Types of Carriers** | |
|---|---|
| Conjugated-system Polymers | Representative Polymer |
| Aliphatic conjugated system | Polyacetylene |
| Aromatic conjugated system | Poly(*p*-phenylene) |
| Mixed-type conjugated system | Poly(*p*-phenylene vinylene) |
| Heterocyclic conjugated system | Polypyrrole, polythiophene, PEDOT |
| Heteroatomic conjugated system | Polyaniline |
| Double-stranded conjugated system | Polyacene (virtual molecule) |
| Two-dimensional conjugated system | Graphene |

In terms of application, polypyrrole (**Aldrich Prod. Nos.** 482552, 577030, 578177, 530573, and 577065) is probably the most common. However, very few people know in what everyday products they encounter polypyrrole. Polypyrrole that has undergone doping with an acceptor is stable (**Aldrich Prod. No.** 482552, etc.). It can be easily synthesized from pyrrole (**Aldrich Prod. No.** 131709) by oxidation polymerization. One of its applications is the solid electrolytic capacitor. Generally, the electrolyte solution in electrolytic capacitors is an ion conductor, so its electric conductivity is low, resulting in its bad frequency characteristics (the impedance increases in the high-frequency region).[7] Use of doped polypyrrole instead of electrolyte solution drastically improves the frequency characteristics and allows small, light-weight, and high-capacity polymer solid electrolytic capacitors to be produced. The polypyrrole-based solid electrolytic capacitors (as backup capacitors used when a power supply suddenly goes off) are superior in noise removal, ripple absorption, and the decoupling effect. Therefore, these capacitors have already been used in many applications, such as cellular phones, notebook computers, handheld games, and portable audio players, and have greatly contributed to the creation of the small, light-weight, and high-performance products that we are using in our everyday lives.

Polyaniline is also easily synthesized from its inexpensive raw material, aniline, by oxidation polymerization. Since the early stage of research on conductive polymers, it has been well studied as the most promising material for practical use. Polyaniline takes four different states depending on the type of treatment applied after its synthesis. However, the only electrically conductive polyaniline is the dark-green emeraldine salt. Heeger et al. used a functional dopant, such as camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA, **Aldrich Prod. No.** 522953) to create polyaniline that is soluble in cresol and xylene while maintaining its electric conductivity. Around the same time, various applications for polyaniline were created in parallel, and research on devices with polyaniline electrodes (i.e., a transistor, a polymeric lithium battery, and a dye-sensitized solar cell) was reported one after another.[8] Polyaniline is also used in products more familiar to us, such as antistatic films and neutralization units in copiers. Various types of polyaniline products are commercially available. They can also be purchased from Sigma-Aldrich (**Aldrich Prod. Nos.** 428329, 476706, 530565, 530689, 556378, 556386, 556459, etc.).

In the 1990s, R. H. Friend et al. of Cambridge University reported on the electroluminescence (EL) of a conductive polymer, polyphenylenevinylene.[9] This report inspired other researchers to research polymeric organic EL materials using conductive polymers. Their research was based on the semiconducting characteristics of undoped conductive polymers, and the term "conjugated polymers" also came into common use. Conductive polymers emit different luminescent colors depending on the design of their molecular structure, that is, the degree of their conjugation length. For example, polyphenylene and polyfluorene emit blue to aqua light, polyphenylene vinylene emits green to orange light, and polythienylenevinylene emits orange to red light. It is possible to produce the three primary colors using only conductive polymers. The details of polymeric organic EL materials, such as device structure, are described in *Material Matters™ Basics Vol. 1: The Fundamentals and Fabrication Technology of Organic EL Devices*[10] and *Material Matters™ Vol. 2, No. 3: Organic Electronics*.[11] Today, organic EL displays using low molecular weight organic EL materials are coming into increasingly wide use. However, it seems that polymeric organic EL materials based mainly on easily processable conductive polymers may be substituted for them sooner or later.

The top runner of the latest conductive polymers is poly(3,4-ethylene dioxythiophene) (PEDOT). Research on PEDOT has been conducted worldwide, and some technical books specializing in PEDOT have been published.[12,13] In a sense, PEDOT, which possesses excellent stability, high electrical conductivity, high hole injection capacity, and flexible doping characteristics, is an ideal conductive polymer. PEDOT/PSS (**Aldrich Prod. Nos.** 768642, 739340, 739332, 739324, 739316, 655201, 483095, and 560596) is a commercially available water or organic-solvent solution in which polystyrenesulfonic acid (PSS) is dispersed in the form of a polymer dopant. It allows conductive polymer films with any desired thickness to be easily produced by spin coating and thereby has carved a new way for organic electronics. In this field, a technology for equalizing the particle sizes of PEDOT to form uniform films has been established.

As described in the above application examples of conductive polymers, PEDOT is finding applications in increasingly wide areas, such as capacitors, transistors, antistatic films, and batteries. In addition, applied research on PEDOT is being performed in incomparable diverse fields[12] associated with devices, such as actuators, sensors, and thermoelectric transducers. For example, in the field of actuators, artificial muscle that is not only strong and flexible, but also electrically conductive is under development by combining mechanically tough double network hydrogel and PEDOT. Thus, so-called hybridization with other functional materials is advancing, which in turn inspires research in this field.

Of particular note is PEDOT's superior hole injection capacity, making it commonly used as a material for the hole injection and transport layer of organic EL devices. In addition, PEDOT/PSS is widely used as a material for the hole transport layer of organic thin film solar cells. The details of their device structure are described in *Material Matters™ Basics Vol. 4: The Fundamentals of Organic Thin Film Solar Cells*.[14] A close look at the device structure reveals that blends of a poly (3-alkylthiophene: P3HT (**Aldrich Prod. Nos.** 445703, 698989, and 698997)) in the polythiophene family and a modified fullerene (phenyl-C61-butyrate methyl ester: PCBM (**Aldrich Prod. Nos.** 684430, 684449, and 684457)) have been widely adopted as materials for the photoelectric conversion layer of organic thin film solar cells. In addition, polythiophene has been regarded as a promising material for organic transistors, and research on it has long been conducted. The details are described in *Material Matters™ Basics Vol. 6: The Fundamentals of Organic Transistors*.[15]

Moreover, PEDOT/PSS, which exhibits low visible light absorption, is expected to be a material able to substitute for indium-tin oxide (ITO), which is absolutely necessary as a transparent electrode material. PEDOT/PSS makes it possible to eliminate the use of toxic lead and the rare metal, indium. Since it is a polymer material, it is also excellent in flexibility and elasticity. It can be used in products for our everyday lives, such as touch panels, and is expected to be used in displays of the future that were once considered to be science fiction, such as flexible electronic paper.

Although it is an excellent material, there also remain issues to be solved regarding PEDOT/PSS. For example, when PSS is used as its dopant, it inevitably develops a light absorption characteristic in the visible light region. It has been reported[16] that substituting polyvinylsulfonic acid (PVS) with no benzene ring for PSS as its dopant suppresses light absorption in the visible light region. In addition, the performance and service life of organic EL devices have been enhanced by lamination. It has been pointed out[17] that the use of PEDOT/PSS for the hole injection layer of organic EL devices may cause the devices to degrade faster than normal because of sulfonic acid, a strong acid. Therefore, dopants for PEDOT and substitute hole transport materials for PEDOT/PSS are under study.[18]

The processing methods of conductive polymers, such as jet printing, spray film formation, and Roll-to-Roll, are essential for application of conductive polymers including PEDOT/PSS to devices, such as organic EL devices, organic solar cells, and electrode materials. These processing methods may serve to create lower-price, higher-performance conductive polymer devices, so various types of research and development on the methods are actively being performed. Particularly, in jet printing technology, some printing devices that can spray PEDOT nanoparticles have been developed and allow nanolevel writing and patterning. This technology will make it unnecessary to rely on large-scale devices, such as deposition apparatuses and photolithography equipment, and will realize printable electronics, bottom-up technology that makes it possible to arrange "necessary quantities" of "necessary materials" in "necessary locations." Simultaneous advancement of printable electronics and conductive polymer technology is sure to bring about a major breakthrough not only in the field of organic electronics, but also in the entire field of electronic devices.

Thus far we have outlined conductive polymers and their applications. Now we move on to another value of conductive polymers—their application in scientific education.

# Application of Conductive Polymers to Scientific Education

Shirakawa has been very interested in assisting children to develop the knowledge, skills and attitudes necessary to become scientifically literate citizens. As part of the activities to promote the value and relevance of science to early childhood education, he has been holding experimental workshops for general people in various places. The National Museum of Emerging Science and Innovation (hereafter, Miraikan) has been playing a great role in the development of experimental programs for the workshops. Since 2003, the National Museum, which is located in Daiba, Tokyo, has invited Shirakawa as a lecturer to hold periodic experimental workshops on conductive polymers under the title of "Message from the Nobel Prize-Winning Scientist in Chemistry: Dr. Hideki Shirakawa and the Science Workshop." The target participants are people of all ages, fifth grade or higher. Experiments with conductive polymers may seem to be difficult; however, conductive polymers actually possess various characteristics that can make chemical experimental workshops very attractive. These characteristics are:

1. They can be synthesized relatively easily.
2. Doping conditions induce drastic changes in their colors and characteristics.
3. Doping induces various physical properties, such as electrical conductivity, electrochromism, and electroluminescence.
4. Their characteristics are all linked directly to various applications.

In addition, experiments using conductive polymers allow people to experience synthesis and application of the polymers at the same time. They are rare materials that can contribute to learning the wonder of the entire spectrum of science in addition to chemistry. In 2012, experimental workshops were held on two themes: "application to transparent loudspeakers"[18] and "application to plastic EL."[19] Hiroki also joined in the development of teaching methods for the experimental workshops[20] as a staff member of the National Museum in cooperation with Shirakawa and colleague science communicators. The following are some examples of the experiments that were performed in the workshops.

# Experiment Notes

## Synthesis of Polypyrrole

The simplest experiment that teaches us about the synthesis of a conductive polymer and its electrical conductivity is the synthesis of polypyrrole by electrochemical polymerization (also known as electrolytic polymerization) (**Figure 10**).

**Figure 10**. Synthesis of Polypyrrole by Electrochemical Polymerization

First, prepare the following (product information follows in **Table 4**):

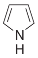
- ITO glass (50 × 50 × 0.50 mm; preferably, 10 Ω/sq or lower): 1
- Stainless plate (50 × 50 × 0.1 mm): 1
- Rubber plate (spacer; 10 × 40 × 2.0 mm): 1
- Plastic clip: 1
- Power supply: 1
- Circuit tester: 1
- Lead wires (with plastic-covered alligator clips attached at the ends): 1 red wire and 1 black wire
- Beaker (500 mL and 300 mL): 1 of each size
- Cellophane tape
- Pure water (distilled water or ion-exchanged water): 150 mL
- Pyrrole solution (2.1 mL of pyrrole, 7.5 g of sodium chloride, and 150 mL of pure water)

**Table 4**. Reagents for Experimental Workshops—Synthesis of Polypyrrole

**ITO Glass**

| Name | Structure | L × W × Thickness | Surface Resistivity | Prod. No. |
|---|---|---|---|---|
| Indium tin oxide coated glass slide, square | $In_2O_3 \cdot (SnO_2)_x$ | 25 × 25 × 1.1 mm | 8-12 Ω/sq | 703192-10PAK |

**Pyrrole Solution**

| Name | Structure | Prod. No. |
|---|---|---|
| Pyrrole, reagent grade |  | 131709-25ML<br>131709-100ML<br>131709-500ML |
| Water, deionized | $H_2O$ | 38796-1L |
| Water, CHROMASOLV®, for HPLC | $H_2O$ | 270733-1L<br>270733-6X1L<br>270733-2.5L<br>270733-4X2.5L<br>270733-4L<br>270733-4X4L<br>270733-18L<br>270733-20L |
| Sodium chloride, ACS reagent | NaCl | S9888-25G<br>S9888-500G<br>S9888-6X500G<br>S9888-1KG<br>S9888-2.5KG<br>S9888-4X2.5KG<br>S9888-5KG<br>S9888-10KG<br>S9888-20KG<br>S9888-25KG<br>S9888-50KG |

### *Experimental Procedure*

1. Put 150 mL of pure water for cleaning into the 300 mL beaker.
2. Put 150 mL of pyrrole solution into the 500 mL beaker.
3. Check the conductivity of the conducting plane (in which electric current flows) of the ITO glass with the circuit tester, and then, put a red seal on it (**Figure 11-1**).

**Figure 11-1**. Check of Conducting Plane on ITO Glass

4. Place the spacer (rubber plate) on the stainless plate (**Figure 11-2**). Stack the ITO glass and the stainless plate so that the conducting plane of the ITO glass faces the stainless plate with the spacer sandwiched between them. Fix them with the plastic clip (**Figure 11-3**).

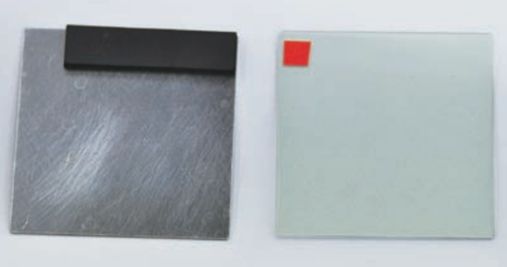


**Figure 11-2**. Placement of Rubber Plate on Stainless Plate

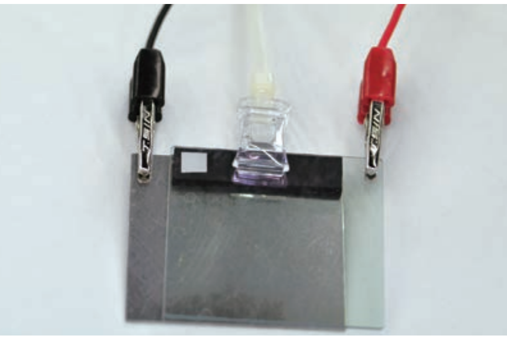


**Figure 11-3**. Attachment of ITO Glass and Stainless Plate and Connection of Lead Wires

5. Connect the lead wires to the terminals of the power supply. Connect one of the lead wires from the positive (+) terminal to the ITO glass, and connect the other lead wire from the negative (-) terminal to the stainless plate (**Figure 11-3**).
6. Immerse the ITO glass and the stainless plate of Step 5 into the pyrrole solution prepared in Step 2 (by 50 to 60 mm).
7. Apply voltage across the ITO glass and the stainless plate (3 V for approximately 1 min.) to induce polymerization.
8. After the polymerization is completed, remove the ITO glass, rinse it with the pure water of Step 1, and dry it.
9. Put two pieces of cellophane tape on the polypyrrole obtained from the polymerization in the arrangement shown in **Figure 11-4**.

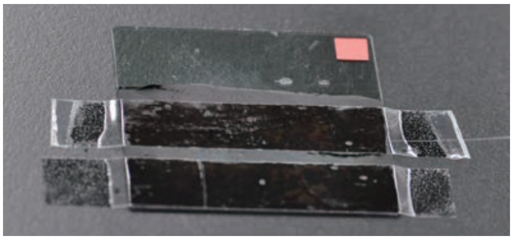


**Figure 11-4**. Fixation of Polypyrrole Thin Film

10. Peel off the polypyrrole film synthesized by the polymerization of Step 7 along with the cellophane tape under it (**Figure 11-5**).

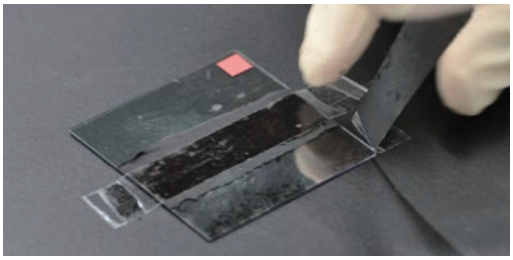


**Figure 11-5**. Peeling of Polypyrrole Thin Film

11. Check the electrical conductivity of the polypyrrole film (**Figure 11-6**).

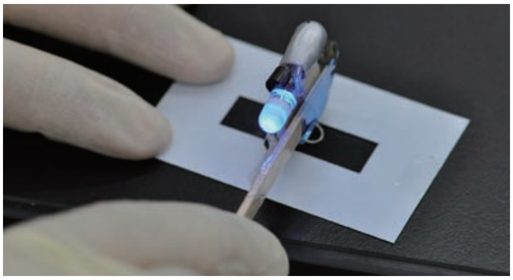


**Figure 11-6**. Check of Electrical Conductivity of Polypyrrole Thin Film Using "Toru-kun"

12. The measurement tool for checking electrical conductivity, "Toru-kun," was devised by Satoshi Saeki, a volunteer of Miraikan. It is a handmade conductivity checker consisting of a light-emitting diode (LED), a transistor, a resistor, and a 3-V button battery. At present, the tool is used by the "Nobel Team" led by his "Nobel Science Show Demonstration Team." When it touches an electric conductor, the LED lights up to indicate to the user that electric current flows in the conductor. A commercially available party toy called a "crystal candle" can substitute for the tool (**Figure 12**).

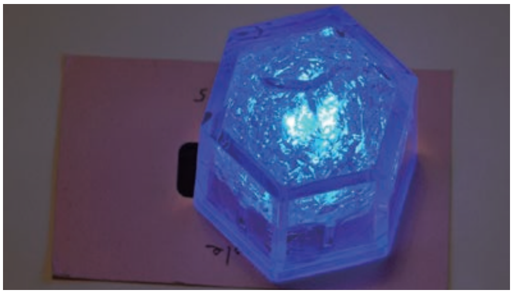


**Figure 12**. Check of Electrical Conductivity of Polypyrrole Thin Film Using Crystal Candle

# Fabrication of an Organic EL Device Using PEDOT

The latest conductive polymer experiment developed by Miraikan is "Let's synthesize a Conductive Plastic!: Application to Plastic EL." This section introduces its experimental procedure.

First, prepare the following (product information follows in **Table 5**):

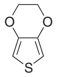
- ITO glass (20 × 50 × 0.50 mm; preferably, 10 Ω/sq or lower): 2
- Stainless plate (30 × 50 × 0.1 mm): 1
- Rubber plate (spacer; 10 × 10 × 1.0 mm): 1
- Plastic clip: 1
- Power supply: 1
- Circuit tester: 1
- Lead wires (with plastic-covered alligator clips attached at the ends): 1 red wire and 1 black wire
- Beaker (200 mL): 1
- Tall beaker (200 mL): 1
- Circular seals (5 mm in diameter; for checking conductivity of the conducting plane and electrodes): 1 red seal and 1 blue seal
- Double-sided tape (25 mm × 25 mm; a square portion of 10 mm × 10 mm needs to be cut out in the middle of it to form a window section in advance)
- Kimwipes®
- Pure water (distilled water or ion-exchanged water): 100 mL
- Ethylene dioxythiophene (EDOT) solution (0.165 mL of EDOT, 0.800 g of lithium perchlorate, and 75 mL of 70% EtOH)
- Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) solution (0.040 g of MEH-PPV and 10 mL of chloroform; it needs to be preserved in a glass weighing bottle)
- Gallium-indium eutectic (Ga/In; approximately 0.050 g)
- Ethanol: a slight amount
- Hair dryer

**Table 5.** Reagents for Experimental Workshops—Fabrication of Organic EL Device Using PEDOT

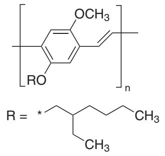
**ITO Glass**

| Name | Structure | L × W × Thickness | Surface Resistivity | Prod. No. |
|---|---|---|---|---|
| Indium tin oxide coated glass slide, rectangular | $In_2O_3 \cdot (SnO_2)_x$ | 75 × 25 × 1.1 mm | 8-12 Ω/sq | 578274-10PAK<br>578274-25PAK |

**Ethylenedioxythiophene (EDOT) Solution**

| Name | Structure | Purity | Prod. No. |
|---|---|---|---|
| 3,4-Ethylenedioxythiophene |  | 97% | 483028-10G |
| Lithium perchlorate, ACS reagent | $LiClO_4$ | ≥95.0% | 205281-5G<br>205281-100G<br>205281-500G |
| Ethyl alcohol, Pure, 200 proof, ACS reagent | $CH_3CH_2OH$ | ≥99.5% | 459844-500ML<br>459844-6X500ML<br>459844-1L<br>459844-6X1L<br>459844-2L<br>459844-2.5L<br>459844-4L<br>459844-4X4L<br>459844-25L<br>459844-200L |

**Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) Solution**

| Name | Structure | Average $M_n$ | Prod. No. |
|---|---|---|---|
| Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] |  | 40,000-70,000 | 541443-250MG<br>541443-1G |
| | | 70,000-100,000 | 541435-1G |
| | | 150,000-250,000 | 536512-1G |
| Chloroform, anhydrous, contains 0.5-1.0% ethanol as stabilizer | $CHCl_3$ | - | 288306-100ML<br>288306-12X100ML<br>288306-1L<br>288306-2L |

**Electron Injection Material**

| Name | Structure | Purity | Prod. No. |
|---|---|---|---|
| Gallium–Indium eutectic | Ga / In | ≥99.99% trace metals basis | 495425-5G<br>495425-25G |

## *Experimental Procedure I: Construction of a Hole Injection Layer*

1. Put 100 mL of pure water for cleaning into the 200 mL beaker.
2. Put 75 mL of EDOT solution into the 200 mL tall beaker.
3. Check the conductivity of the conducting plane of one piece of ITO glass with the circuit tester, and then, put the red seal on it (**Figure 13-1**).
4. Place the spacer (rubber plate) on the stainless plate (**Figure 13-1**).

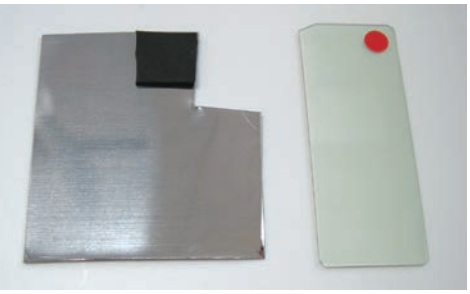


**Figure 13-1**. Check of Conducting Plane on ITO Glass

5. Stack the ITO glass and the stainless plate so that the conducting plane of the ITO glass faces the stainless plate with the spacer sandwiched between them. Fix them with the plastic clip (**Figure 13-2**).

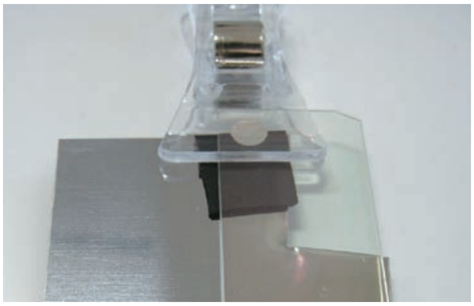


**Figure 13-2**. Attachment of ITO Glass and Stainless Plate

6. Connect the lead wires to the terminals of the power supply. Connect one of the lead wires from the positive (+) terminal to the ITO glass, and connect the other lead wire from the negative (–) terminal to the stainless plate (**Figure 13-3**).

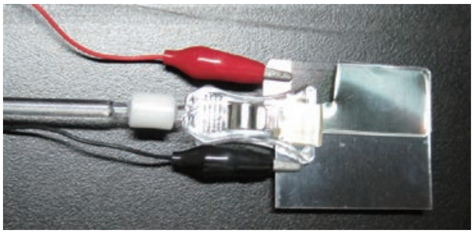


**Figure 13-3**. Connection of Lead Wires

7. Immerse the ITO glass and the stainless plate of Step 6 into the EDOT solution prepared in Step 2 (by approximately 20 mm) (**Figure 13-4**).
8. Apply voltage across the ITO glass and the stainless plate (2 V for approximately 5 sec) to induce polymerization (**Figure 13-4**).

**Figure 13-4**. Electrochemical Polymerization of EDOT

9. After the polymerization is completed, remove the ITO glass, rinse it with the pure water of Step 1, and dry it (**Figure 13-5**).

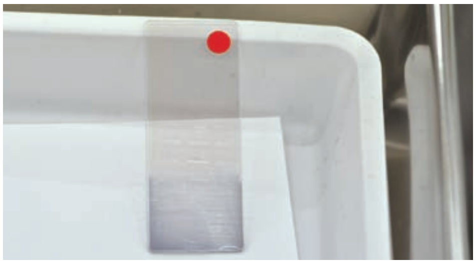


**Figure 13-5**. Drying of PEDOT Thin Film (Hole Injection Layer)

### *Experimental Procedure II:*
### *Construction of a Luminescent Layer*

1. Immerse the ITO glass with the PEDOT thin film that was created by Experimental procedure I into the MEH-PPV solution (by approximately 20 mm) to form a luminescent layer by dip coating (**Figure 14**).

**Figure 14**. Dip Coating with MEH-PPV (Luminescent Layer)

2. Wipe off any MEH-PPV adhering to the glass surface (onto which no ITO is applied) with Kimwipes wet with a small amount of ethanol.

### *Experimental Procedure III:*
### *Preparation for Construction of Electron Injection Layer*

1. Check the conductivity of the conducting plane of the other piece of ITO glass with the circuit tester, and then put the blue seal on the conducting plane (**Figure 15-1**).
2. Put the double-sided tape with a window section on the conducting plane of the ITO glass (**Figure 15-1**).

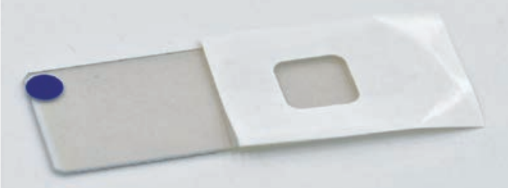


**Figure 15-1**. Check of Conducting Plane on ITO Glass and Application of Double-sided Tape

3. Remove the backing sheet of the double-sided tape, and place approximately 0.05 g of Ga-In eutectic on the central section of the window section (**Figure 15-2**).

**Figure 15-2**. Preparation of Gallium-Indium Eutectic Mixture (Electron Injection Layer)

## *Experimental Procedure IV:*
## *Fabrication of an Organic EL Device*

1. Stick the two pieces of ITO glass used in Experimental Procedures I and II to each other with their conducting planes on the inside (**Figure 16**).

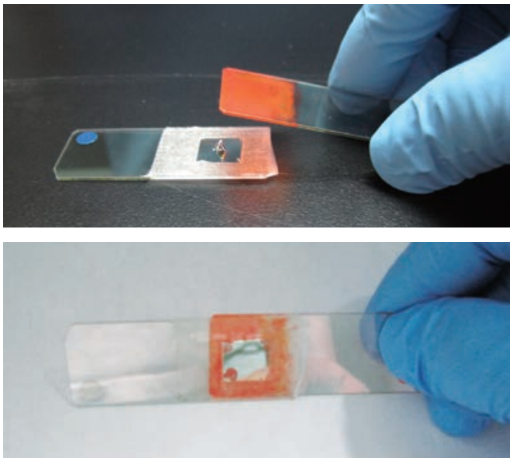


**Figure 16**. Assembly of Organic EL Device

## *Experimental Procedure V:*
## *Luminescence of an Organic EL Device*

1. Connect the positive (+) lead wire to the ITO glass with the red seal on it, and connect the negative (-) lead wire to the ITO glass with the blue seal on it (**Figure 17**).
2. Place the device with the positive (+) ITO glass side facing upward; apply a voltage of approximately 3 V across the device and observe the luminescence of the device while gradually increasing the voltage (**Figure 17**).

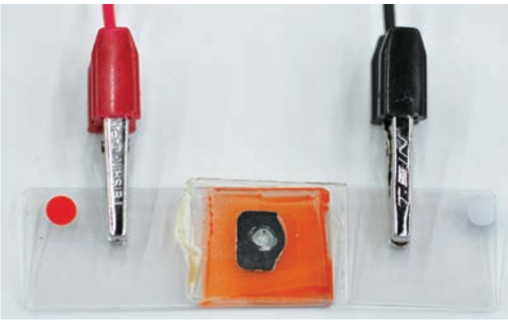


**Figure 17**. Completed Organic EL Device

Development of teaching methods for experimental workshops of organic EL devices based on conductive polymers was the earnest wish of Shirakawa and the staff members of Miraikan who worked on its development. Simple organic EL devices have single-layer structures, in which a luminescent layer is sandwiched between a cathode and an anode (**Figure 18-a**). However, general organic EL devices have multilayer structures in which an injection and a transport layer are constructed for boosting the injection of electrons and holes from electrodes in order to enhance luminescence efficiency (**Figure 18-b**). Conventionally, there were some difficulties in forming luminescent layers and injection layers, in sealing, and in selecting metals for electron injection layers.

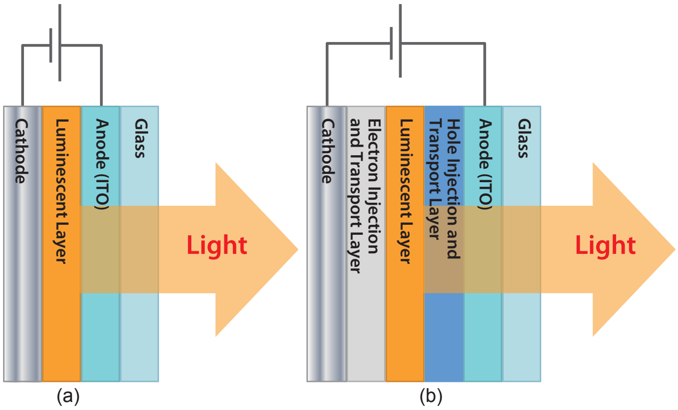


**Figure 18**. Structure of Organic EL Device

The problem with electron injection layers was resolved early on, accelerating the development of teaching methods for the experimental workshops. Film formation is generally performed by deposition of a metal, such as calcium. However, we could not use that kind of film formation method because it requires a special apparatus and takes a long time. When we were looking for another way, Toshihiro Ohnishi of Sumitomo Chemical Co., Ltd. suggested that use of a liquid gallium-indium eutectic (Ga/In) at normal temperature would make it possible to form electron injection layers relatively easily. The eutectic was commercially available from Sigma-Aldrich (**Aldrich Prod. No.** 495425), and we purchased it without difficulty.

The next problem was how to perform sealing. Then, Shirakawa made a suggestion surprising to the staff members of Miraikan. He suggested sealing it with "strong double-sided tape." The electrodes of the device are both made of ITO glass. On its anode, a PEDOT (for its hole injection layer) film is formed followed by a MEH-PPV (for its luminescent layer) film on it. On its cathode, instead of a gallium-indium eutectic coating, a piece of double-sided tape with a square window approximately 1 cm × 1 cm cut out from the tape is put on the ITO glass, and then, gallium-indium eutectic is placed in the window section. Participants in the experimental workshops only have to stick the anode to this cathode, and the thickness of the electron injection layer is determined by the thickness of the double-sided tape. Thus, it is not necessary for the participants to work with a potentially problematic bonding agent.

The final problems were how to form a hole injection layer and a luminescent layer. Initially, we attempted to coat films and managed to assemble the device and succeed in its luminescence. However, the nonuniform film thickness sometimes caused a short circuit and sometimes caused poor contact, resulting in a low chance of success. The problem with the formation of a hole injection layer was resolved by the idea of simplified electrochemical polymerization using a rubber plate proposed by Hiroki. During his days as a visiting researcher at Riken, Hiroki happened to see Taiki Tominaga, a researcher in the same laboratory, using a silicon-rubber thin plate to synthesize high-strength gel. In the simplified electrochemical polymerization, a thin rubber plate sandwiched in-between maintains a constant distance between the conducting plane of the ITO glass and the opposite stainless plate. When voltage is applied to this device while the device is immersed in PEDOT solution, hole injection layers with a certain thickness can be constructed by controlling the electric current and the duration of the immersion. The problem with the formation of a luminescent layer was also finally resolved by adopting the dip coating method. Controlling concentrations of solvent and

MEH-PPV appropriately allowed formation of uniform luminescent layers compared with conventional luminescent layers. Those newly devised methods and ideas made it possible for the staff members of Miraikan to create devices to emit light almost 100% of the time (**Figure 19**).

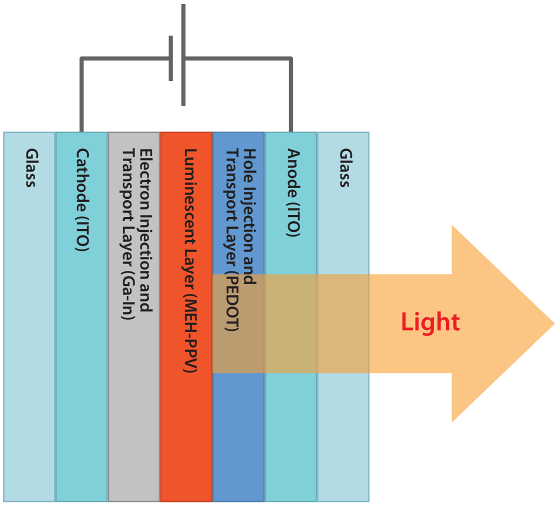


**Figure 19**. Structure of Polymeric Organic EL Device Fabricated in Experimental Workshop

Thus, the experimental program of a polymeric organic EL device without using a deposition apparatus or a spin coater was established. This experiment is interesting in that a conductive polymer, PEDOT, is synthesized by electrochemical polymerization, and another conductive polymer, MEH-PPV, is used for its luminescent layer under the PEDOT hole injection layer.

From each actual experimental workshop, there was always one or two who experienced a failure of their EL device out of the 20 participants. Finally, this year, Shirakawa received news that all the workshop participants successfully fabricated their EL devices. The author (Hiroki) was pleased the value of conductive polymers in science education had finally been realized. Orange luminescent light from MEH-PPV (**Figure 20**) is a warm color and seems to evoke some comforting feeling in the participants.

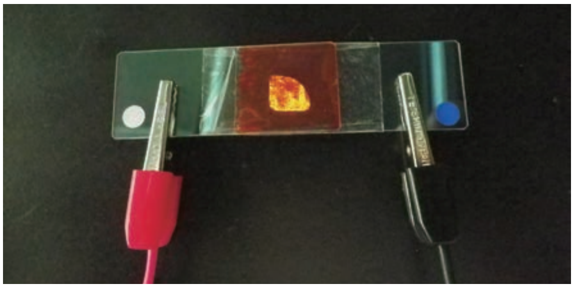


**Figure 20**. Luminescence of Polymeric Organic EL Device

## Conclusions

The science of conductive polymers has advanced remarkably over the 35 years since the result of polyacetylene doping was published in 1977. However, many problems still remain to be resolved. This article described the basic mechanism of electrical conductivity in molecules. However, no real synthesized conductive polymers have an infinite length. The measured electrical conductivity must be caused by carrier transfer from one molecular chain to another. Polyacetylene films have high crystallinity compared with other polymers, but the crystallinity is far from that of single crystals. In spite of that, they exhibit high specific conductance ($1.7 \times 10^5$ S/cm) comparable to that of copper. It is appropriate to regard this value as a contribution from intermolecular conduction rather than intramolecular conduction. However, its mechanism has not been elucidated yet.

Conductive polymers are finding increasingly widespread application, and their application to devices, such as sensors, capacitors, and actuators, is actively being studied. This is because of the fact that they are "polymers," which are superior in processability and may play an important role (particularly in printable electronics) in conjunction with printing technologies. Before long, the day will come when patterning by spraying conductive polymer solution like ink will allow for easy fabrication of complex devices. What kind of benefit can we enjoy when that day has come? One thing that we can be sure of is that conductive polymers will be stealthily playing an important role somewhere in our lives. Conductive polymers will continue to evolve.

The ultimate application of conductive polymers is to use the properties of an individual conjugated molecular chain, such as its semiconductive and conductive properties. The issue is how to do that. Further advances need to be made in "molecular nanoscience and molecular nanotechnology,"[22] such as techniques for dealing with individual conjugated molecular chains to measure their electrical conductivity separately and techniques for synthesizing a single conjugated molecular chain in a desired location.

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(15) *Material Matters™ Basics* Vol. 6: The Fundamentals of Organic Transistors.

(16) http://www.asahikasei-fc.jp/cgi-bin/topics/news/2010/062801/index.html.

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(18) Hitachi Chemical Technical Report No. 51, **2008**.

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(20) http://www.miraikan.jst.go.jp/, "Special Course: Let's synthesize Conductive Plastics (Application to polymeric organic EL devices)".

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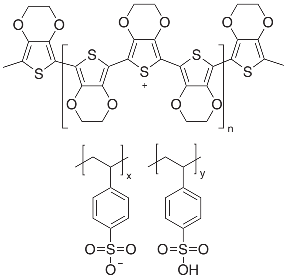
  Mr. Shinji Tanaka and Mr. Akinori Suwada.

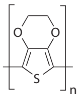
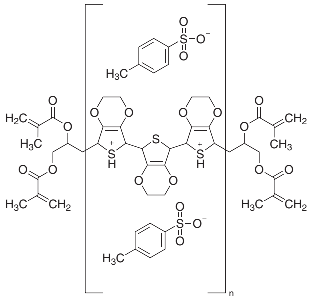
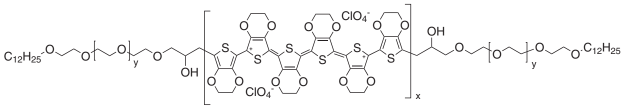
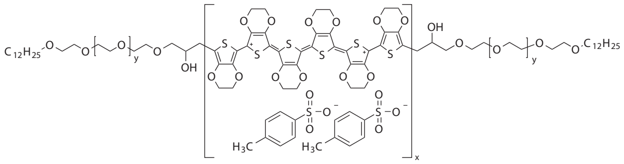
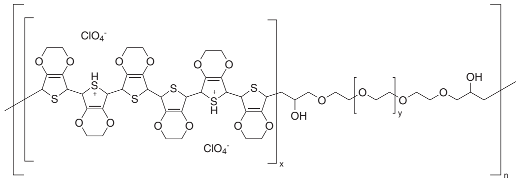
# PEDOT Polymers

## PEDOT:PSS

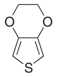
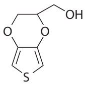
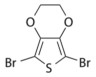
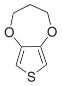
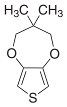
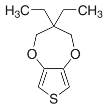


| Description | Sheet Resistance (Ω/sq) | Viscosity | pH | Prod. No. |
|---|---|---|---|---|
| dry re-dispersible pellets | 200-450 | n/a | - | 768618-1G<br>768618-5G |
| 1.0 wt. % in $H_2O$ | 50-120 | 7-12 mPa.s at 22 °C | 1.8-2.2 | 768642-25G |
| 5.0 wt. %, conductive screen printable ink | 50-150 | 50,000-90,000 mPa.s at 22 °C | 1.5-2.0 | 768650-25G |
| 0.8% in $H_2O$, conductive inkjet ink | - | 7-12 cP at 22 °C | 1.5-2.5 | 739316-25G |
| 1.1% in $H_2O$, neutral pH | <100 (>70% visible light transmission, 40 μm wet) | <100 cP at 22 °C | 5-7 | 739324-100G |
| 1.1% in $H_2O$, surfactant-free | <100 (<80% visible light transmission, 40 μm wet) | <100 cP at 22 °C | <2.5 | 739332-100G |
| 0.54% in $H_2O$ | <200 (>90% visible light transmission, 40 μm wet) | <18 cP at 22 °C | <2.7 | 739340-25G<br>739340-100G |
| 3.0-4.0% in $H_2O$ | 1500 (4 point probe measurement of dried coating based on initial 6 μm wet thickness.)<br>500 (4 point probe measurement of dried coating based on initial 18 μm wet thickness.) | 10-30 cP at 20 °C | 1.5-2.5 at 25 °C (dried coatings) | 655201-5G<br>655201-25G |
| 2.8 wt % dispersion in $H_2O$ | - | <20 cP at 20 °C | 1.2-1.8 | 560596-25G<br>560596-100G |

## Other PEDOT Polymers

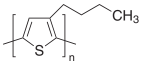
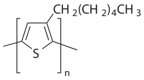
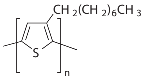
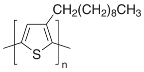
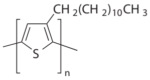
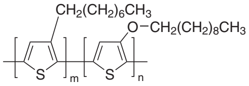
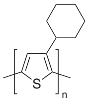
| Name | Structure | Description | Conductivity | Prod. No. |
|---|---|---|---|---|
| Poly(3,4-ethylenedioxythiophene) |  | in $H_2O$, dodecylbenzene sulfonic acid (DBSA) as dopant | - | 675288-25ML |
| Poly(3,4-ethylenedioxythiophene), tetramethacrylate end-capped |  | 0.5 wt. % (dispersion in propylene carbonate), *p*-toluenesulfonate as dopant | 0.1-0.5 S/cm (bulk) | 649813-25G |
| | | 0.5 wt. % (dispersion in nitromethane), *p*-toluenesulfonate as dopant | 0.1-0.5 S/cm (bulk) | 649821-25G |
| Poly(3,4-ethylenedioxythiophene), bis-poly(ethyleneglycol), lauryl terminated |  | 0.6-1.1 wt. %<br>0.8 wt. % (dispersion in propylene carbonate), perchlorate as dopant | 10-45 S/cm (bulk) | 736287-25G |
| |  | 0.6-1.0 wt. % (solid)<br>0.8 wt. % (dispersion in 1,2-dichlorobenzene), *p*-toluenesulfonate as dopant | 0.01-0.05 S/cm (bulk) | 736309-25G |
| | | 0.5-0.9 wt. % (solid concentration)<br>0.7 wt. % (dispersion in nitromethane), *p*-toluenesulfonate as dopant | $10^{-2}$-$10^{-4}$ S/cm (bulk) | 736295-25G |
| Poly(3,4-ethylenedioxythiophene)-*block*-poly(ethylene glycol) solution |  | 1 wt % dispersion in nitromethane, perchlorate as dopant | 0.1-5.0 S/cm (bulk) | 649805-25G |

# EDOT and Related Products

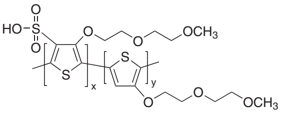
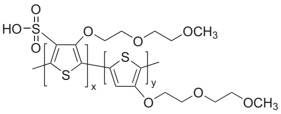
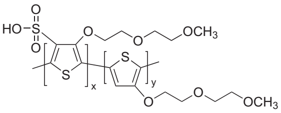
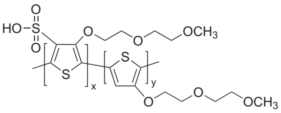
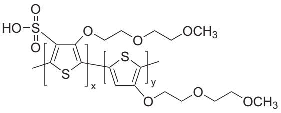
| Name | Structure | Purity | Prod. No. |
|---|---|---|---|
| 3,4-Ethylenedioxythiophene |  | 97% | 483028-10G |
| Hydroxymethyl EDOT |  | 95% | 687553-500MG |
| 2,5-Dibromo-3,4-ethylenedioxythiophene |  | 97% | 759791-5G |
| 3,4-Propylenedioxythiophene |  | 97% | 660485-100MG<br>660485-500MG |
| 3,4-(2,2-Dimethylpropylenedioxy)thiophene |  | 97% | 660523-500MG |
| 3,4-(2′,2′-Diethylpropylene)dioxythiophene |  | 97% | 669210-250MG |

# Polythiophene (PT)

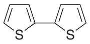
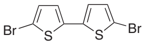
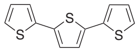
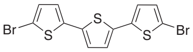
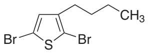
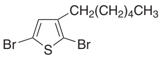
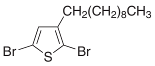
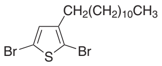
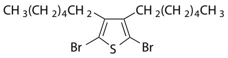
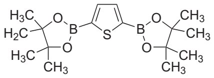
## Poly(3-alkylthiophene) (P3AT)

| Name | Structure | Regioregularity | Mol. Wt. | Prod. No. |
|---|---|---|---|---|
| Poly(3-butylthiophene-2,5-diyl) |  | regioregular | $M_w$ 54,000 (typical) | 495336-1G |
| | | regiorandom | - | 511420-1G |
| Poly(3-hexylthiophene-2,5-diyl) |  | regioregular | average $M_n$ 54,000-75,000 | 698997-250MG<br>698997-1G<br>698997-5G |
| | | regioregular | average $M_n$ 15,000-45,000 | 698989-250MG<br>698989-1G<br>698989-5G |
| | | regioregular | - | 445703-1G |
| | | regiorandom | - | 510823-1G |
| Poly(3-octylthiophene-2,5-diyl) |  | regioregular | $M_n$ ~34,000 | 445711-1G |
| | | regioregular | average $M_n$ ~25,000 | 682799-250MG |
| Poly(3-decylthiophene-2,5-diyl) |  | regioregular | average $M_n$ ~30,000<br>average $M_w$ ~42,000 | 495344-1G |
| Poly(3-dodecylthiophene-2,5-diyl) |  | regioregular | average $M_w$ ~60,000 | 450650-1G |
| | | regioregular | average $M_w$ ~27,000 | 682780-250MG |
| Poly(3-octylthiophene-2,5-diyl-*co*-3-decyloxythiophene-2,5-diyl) |  | - | $M_n$ 8,000<br>$M_w$ 21,000 | 696897-250MG |
| Poly(3-cyclohexylthiophene-2,5-diyl) |  | - | - | 557625-1G |

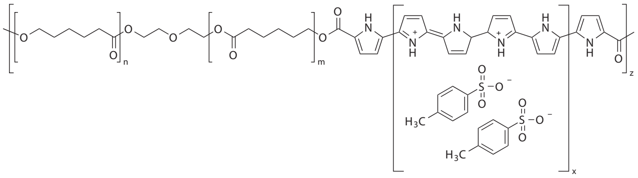
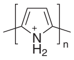
## Other PTs

| Name | Structure | Form | Electronic Properties | Prod. No. |
|---|---|---|---|---|
| Poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl), sulfonated solution |  | liquid | resistivity 500-3,000 Ω-cm<br>work function –5.1-–5.2 eV | 699780-25ML |
| | | liquid | resistivity 25-250 Ω-cm<br>work function –5.1-–5.2 eV | 699799-25ML |
| Plexcore® OC RG-1110 organic conductive ink |  | liquid | resistivity 10-300 Ω-cm | 719110-25ML |
| Plexcore® OC RG-1115 organic conductive ink |  | liquid | resistivity 10-300 Ω-cm<br>work function 4.8 eV | 719129-25ML |
| Plexcore® OC RG-1150 organic conductive ink |  | liquid | resistivity 300-1000 Ω-cm<br>work function 4.8 eV | 719137-25ML |
| Plexcore® OC RG-1155 organic conductive ink |  | liquid | resistivity 300-1000 Ω-cm | 719145-25ML |

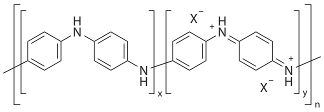
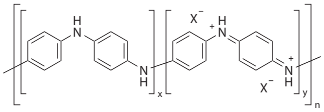
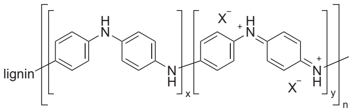
## Thiophene Derivatives

| Name | Structure | Purity | Prod. No. |
|---|---|---|---|
| 2,2′-Bithiophene |  | 97% | 241636-10G |
| 5,5′-Dibromo-2,2′-bithiophene |  | 99% | 515493-1G<br>515493-5G |
| 2,2′:5′,2″-Terthiophene |  | 99% | 311073-1G |
| 5,5″-Dibromo-2,2′:5′2″-terthiophene |  | 97% | 699098-500MG |
| 2,5-Dibromo-3-butylthiophene |  | 96% | 525499-1G<br>525499-5G |
| 2,5-Dibromo-3-hexylthiophene |  | 97% | 456373-5G<br>456373-25G |
| 2,5-Dibromo-3-decylthiophene |  | 97% | 456381-1G<br>456381-5G |
| 2,5-Dibromo-3-dodecylthiophene |  | 97% | 456403-5G |
| 2,5-Dibromo-3,4-dihexylthiophene |  | 97% | 752541-1G<br>752541-5G |
| Thiophene-2,5-diboronic acid bis(pinacol) ester |  | 99%, GC | 776920-1G<br>776920-5G |

## Polypyrrole (PPy)

| Name | Structure | Description | Conductivity | Prod. No. |
|---|---|---|---|---|
| Polypyrrole-*block*-poly(caprolactone) |  | 0.3-0.7 wt. % (dispersion in nitromethane), *p*-toluenesulfonate as dopant | 10-40 S/cm (bulk) | 735817-25G |
| Polypyrrole |  • X organic acid anion | composite with carbon black<br>doped, proprietary organic sulfonic acid as dopant | 30 S/cm (bulk) | 530573-25G |
| | | proprietary organic sulfonic acid as dopant | 10-50 S/cm (pressed pellet) | 577030-5G<br>577030-25G |
| | | coated on titanium dioxide<br>doped, proprietary organic sulfonic acid as dopant | 0.5-1.5 S/cm (pressed pellet, typical) | 578177-10G |
| | | 5 wt % dispersion in $H_2O$, doped, proprietary organic acids as dopant | > 0.005 S/cm (dried cast film) | 482552-100ML |

## Polyaniline (PANI)

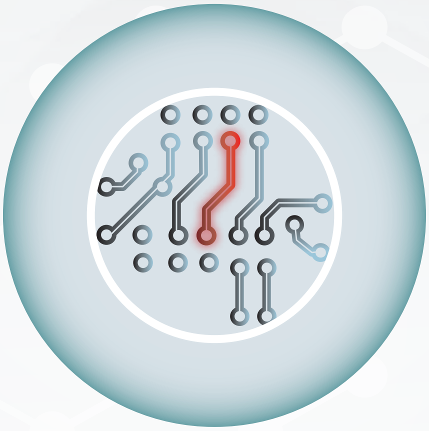
| Name | Structure | Conductivity | Prod. No. |
|---|---|---|---|
| Polyaniline (emeraldine salt), composite (20 wt.% polyaniline on carbon black) |  | 30 S/cm (pressed pellet) | 530565-5G<br>530565-25G |
| Polyaniline (emeraldine salt), composite (30 wt.% polyaniline on nylon) |  | ~ 0.5 S/cm (pressed pellet) | 577073-10G |
| Polyaniline (emeraldine salt) short chain, grafted to lignin, powder |  | 1-2 S/cm (pressed pellet) | 561126-10G |

ALDRICH
Materials Science

# MATERIALS TO DRIVE INNOVATION

## BIOMEDICAL

- Materials for drug delivery, bone and tissue engineering
- PEGs, biodegradable and natural polymers
- Functionalized nanoparticles
- Block copolymers and dendrimers
- Nanoclays



## ELECTRONICS

- Nanowires
- Printed electronics inks and pastes
- Materials for OPV, OFET and OLED
- Nanodispersions
- CNTs and graphene
- Precursors for PVD, CVD and sputtering

## ENERGY

- Electrode and electrolyte materials for batteries and fuel cells
- Hydrogen storage materials, including MOFs
- Phosphors
- Thermoelectrics
- Nanomaterials
- Precursors for nanomaterials and nanocomposites

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