

Conductive polymer

A **conductive polymer** is an [organic polymer semiconductor](#), or an [organic semiconductor](#). Roughly, there are two classes-- the [Charge transfer complexes](#) and the conductive polyacetylenes. The latter include [polyacetylene](#) itself as well as [polypyrrole](#), [polyaniline](#), and their derivatives.

Most commercially produced [organic polymers](#) are [electrical insulators](#). Conductive organic polymers often have extended [delocalized bonds](#) (often composed of [aromatic](#) units). At least locally, these create a band structure similar to [silicon](#), but with localized states. When [charge carriers](#) (from the addition or removal of [electrons](#)) are introduced into the conduction or valence bands (see below) the [electrical conductivity](#) increases dramatically. Technically almost all known conductive polymers are [semiconductors](#) due to the band structure and low electronic mobility. However, so-called zero [band gap](#) conductive polymers may behave like [metals](#). The most notable difference between conductive polymers and inorganic [semiconductors](#) is the [mobility](#), which until very recently was dramatically lower in conductive polymers than their [inorganic](#) counterparts, though recent advancements in [molecular self-assembly](#) are closing that gap.

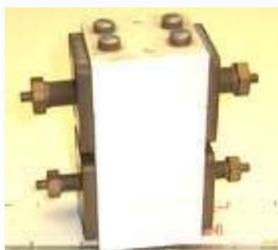
Delocalization can be accomplished by forming a [conjugated](#) backbone of continuous overlapping [orbitals](#). For example, alternating single and double carbon-carbon [bonds](#) can form a continuous path of overlapping [p orbitals](#). In [polyacetylene](#), but not in most other conductive polymers, this creates [degeneracy](#) in the frontier molecular orbitals (the highest occupied and lowest unoccupied [orbitals](#) named [HOMO and LUMO](#) respectively). This leads to the filled ([electron](#) containing) and unfilled bands ([valence](#) and [conduction bands](#) respectively) resulting in a [semiconductor](#).

However, conductive polymers generally exhibit very low conductivities. In fact, as with inorganic [amorphous semiconductors](#), conduction in such relatively disordered materials is mostly a function of "[mobility gaps](#)" with [phonon](#)-assisted hopping, [polaron](#)-assisted [tunnelling](#), etc. between localized states and not band gaps as in [crystalline](#) semiconductors.

In more ordered materials, it is not until an electron is removed from the valence band ([p-doping](#)) or added to the conduction band ([n-doping](#), which is far less common) does a conducting polymer become highly conductive. [Doping](#) (p or n) generates [charge carriers](#) which move in an [electric field](#). Positive charges ([holes](#)) and negative charges ([electrons](#)) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity in crystalline materials.

In contrast, typically "doping" in the polyacetylene-derived conductive polymers involves actually oxidizing the compound. Conductive organic polymers associated with a protic solvent may also be "self-doped". [Melanin](#) is the classic example of both types of doping, being both an oxidized polyacetylene and likewise commonly being hydrated.

History



voltage-controlled switch, an organic polymer electronic device from 1974. Now in the Smithsonian.

See [An Overview of the First Half-Century of Molecular Electronics](#) by Noel S. Hush, *Ann. N.Y. Acad. Sci.* 1006: 1–20 (2003)}

In 1963, Australians DE Weiss and coworkers reported ^[1] high conductivity in oxidized iodine-doped [polypyrrole](#), a polyacetylene derivative. They achieved the quite low resistance of 1.0 ohm/cm. In a series of detailed papers, they also described the effects of doping with iodine on conductivity, the conductivity type (n or p), and electron spin resonance studies on polypyrrole. The same authors noted an Australia patent application (5246/61, June 5, 1961) for conducting polypyrrole. In 1965 ^{[2] [3]}, the Australian group reached resistances as low as .03 ohm/cm with other conductive polymers. This is roughly equivalent to present-day efforts. This extensive work was "lost" until recently. E.g., Diaz *et al.* ^[4] are often wrongly credited with discovering conductive polypyrrole in 1979.

In an "active" solid-state device, a current or voltage controls current flow. In 1974, as a "proof of concept" for their version of the now-accepted model of conduction in such materials, [John McGinness](#) and his coworkers built and reported ^[5] a voltage-controlled organic-polymer switch. This device used [melanin](#)-- here, a self-doped mixed copolymer of oxidized [polyacetylene](#), [polypyrrole](#) and [polyaniline](#). It is now in the Smithsonian's collection of early electronic devices. In the "ON" state, this material has almost metallic conductivity. As Hush notes, this device also exhibited [negative differential resistance](#), now a well-characterized hallmark of electronically-active organic materials. Though in a major journal and (e.g.) the subject of a contemporary news article ^[6] in the journal *Nature*, this work was also "lost" until similar devices emerged decades later.

It is unclear if the Nobel committee in awarding the 2000 Nobel prize in chemistry considered these earlier works. See [Nobel Prize controversies](#).

Nobel Prize

In a virtual reprise of Weiss' *et al's* earlier work with polypyrrole, in 1977 Shirakawa and coworkers reported ^[7] high conductivity in similarly oxidized, iodine-"doped" polyacetylene. This work eventually resulted in the award to them of the 2000 Nobel prize in Chemistry. According to the citation, this was "*For the discovery and development of conductive polymers*" ^[8].

Chemistry

Common classes of organic conductive polymers include [poly\(acetylene\)s](#), [poly\(pyrrole\)s](#), [poly\(thiophene\)s](#), [poly\(aniline\)s](#), [poly\(fluorene\)s](#), [Poly\(3-hexylthiophene\)](#), [polynaphthalenes](#), [poly\(p-phenylene sulfide\)](#), and [poly\(para-phenylene vinylene\)s](#). Classically, these linear backbone polymers are known as polyacetylene, polyaniline, etc. "blacks" or "melanins". The [melanin](#) pigment in animals is generally a mixed copolymer of [polyacetylene](#), [polypyrrole](#), and [polyaniline](#). Some fungal melanins are pure polyacetylene.

Doping

In silicon semiconductors, a few of the silicon atoms are replaced by electron rich (e.g., [phosphorus](#)) or electron-poor (e.g. [boron](#)) atoms to create [n-type](#) and [p-type semiconductors](#), respectively. **In contrast, there are two primary methods of doping a conductive polymer, both through an oxidation-reduction ([redox](#)) process. (1) The first method, chemical doping, involves exposing a polymer, such as [melanin](#) (typically a [thin film](#)), to an [oxidant](#) (typically [iodine](#) or [bromine](#)) or [reductant](#) (far less common, but typically involves [alkali metals](#)). (2) The second is [electrochemical](#) doping in which a polymer-coated, working [electrode](#) is suspended in an [electrolyte](#) solution in which the polymer is [insoluble](#) along with separate counter and reference electrodes. An [electric potential difference](#) is created between the electrodes which causes a charge (and the appropriate counter [ion](#) from the [electrolyte](#)) to enter the polymer in the form of electron addition (n doping) or removal (p doping). Polymers may also be self-doped, e.g., when associated with a protonic solvent such as water or an alcohol.**

The reason n doping is so much less common is that [Earth's atmosphere](#) is [oxygen](#)-rich, which creates an [oxidizing](#) environment. **An electron-rich n doped polymer will react immediately with elemental oxygen to de-dope (re-oxidize to the neutral state) the polymer. Thus, chemical n doping has to be done in an environment of [inert gas](#) (e.g., [argon](#)).** Electrochemical n doping is far less common in research, because it is much more difficult to exclude oxygen from a [solvent](#) in a sealed [flask](#); therefore, although very useful, there are likely to be no commercialized n doped conductive polymers.

Electroluminescence

Electroluminescence and photoconductivity in organic compounds has been known since the early 1950's. However, the very poor conductivity of such materials limited current flow and thus light output. In contrast, the increased current flow through conductive polymers and improvements in their efficiency has led to the rapid development of practical polymer-based light emitting devices ([OLEDs](#)) and organic [photovoltaic](#) devices.

Properties

The biggest advantage of conductive polymers is their processibility. Conductive polymers are also [plastics](#) (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability [elasticity](#), etc.) of plastics with the high electrical conductivities of a doped conjugated polymer.

Physics

In addition to "switching", an increase in conductivity can also be accomplished in a [field effect transistor](#) (organic FET or [OFET](#)), or by [irradiation](#) (originally-demonstrated in the 1960's ^[9]). Strong [coupling](#) can also occur between electrons and [phonons](#) (mechanical oscillations such as heat vibrations, particles of sound) since both are constrained to travel along the polymer backbone.

Applications of conducting polymers

Electroluminescence (light emission) in organic compounds has been known since the early 1950's, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. ^[10] **In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doped anthracene.** ^[11] and <http://www.iitk.ac.in/scdt/doc/Organic%20Semiconductors.pdf>). **In some cases, similar [light emission](#) is observed when a [voltage](#) is applied to a thin layer of a [conductive organic polymer film](#). The increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This has led to the development of [flat panel displays using OLEDs, solar panels and optical amplifiers](#).**

Polyaniline

Polyaniline (PANI) is a [conducting polymer](#) of the [semi-flexible rod polymer](#) family. It was discovered in 1934 as **anilin black**. Polyaniline also exists naturally as part of a mixed copolymer with [polyacetylene](#) and [polypyrrole](#) in some [melanins](#).

Oxidation states

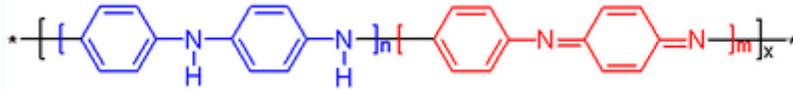


Figure 1. Main polyaniline structures $n+m = 1$, $x =$ degree of polymerization

Polymerized from the [aniline monomer](#), polyaniline can be found in one of five distinct [oxidation](#) states ^[1]:

- leucoemeraldine
- protoemeraldine
- emeraldine
- nigraniline
- pernigraniline

In *figure 1* x equals half the [degree of polymerization](#) (DP). Leucoemeraldine with $n = 1$, $m = 0$ is the fully reduced state. Pernigraniline is the fully oxidized state ($n = 0$, $m = 1$) with [imine](#) links instead of [amine](#) links. **The emeraldine ($n = m = 0.5$) form of polyaniline, often referred to as emeraldine base (EB), is either neutral or only partially reduced or oxidized. Emeraldine base is regarded as the most useful form of polyaniline due to its high stability at room temperature, compared to the easily oxidized leucoemeraldine and the easily degraded pernigraniline. Additionally, the emeraldine base polyaniline can function as a [semiconductor](#) when doped by a protic [acid](#).**

Synthesis

A tried and tested method for the synthesis of polyaniline is by **(1) oxidative polymerization with ammonium peroxydisulfate as an oxidant**. The components are both dissolved in 1 M [hydrochloric acid](#) and slowly (the reaction is very exothermic) added to each other. The polymer precipitates as small particles and the reaction product is a [dispersion](#). **(2) The electrochemical method was discovered in 1862 as a test for the determination of small quantities of aniline**. A two stage model for the formation of emeraldine base is proposed. In the first stage of the reaction the pernigraniline PS salt oxidation state is formed. In the second stage pernigraniline is [reduced](#) to the emeraldine salt as aniline monomer gets oxidized to the [radical cation](#). In the third stage this radical cation couples with ES salt. This process can be followed by [light scattering](#) analysis which allows the determination of the absolute [molar mass](#). According to one study ^[2] in the first step a DP of 265 is reached

with the DP of the final polymer at 319. 19% of the final polymer is made up of [in situ](#) form aniline radical cation.

Properties

Polyaniline exists as bulk films or as [dispersions](#). A recurring problem with these dispersions is [particle aggregation](#) which limits possible applications. A 2006 study ^[3] proposes a strategy to prevent aggregation based on a model for [nucleation](#) and aggregate formation.

The model identifies two nucleation modes for particle formation, one by so-called homogeneous nucleation forming long elongated [nanofibers](#) and very stable dispersions that can last for months. The other nucleation mode is by heterogeneous nucleation taking place on any alien body available in the reactor such as the surface of the reactor wall forming not elongated fiber but granular [coral](#)-like material. With polyaniline, formation by secondary nucleation also takes place on the nanofibers itself. In the study, heterogeneous nucleation is predominant when the reaction medium is stirred or when the reaction temperature is lowered. With both reaction conditions [SEM](#) imagery display nanofibers covered in a layer of coral like granules. The granules act as contact points for a nanoscale glue to link the particles together, causing aggregation. The explanation offered for the suppression of homogeneous nucleation is that this requires a local concentration gradient prior to the onset of nucleation which is destroyed by stirring or by low temperature.

References

1. [^] [Synthesis, processing and material properties of conjugated polymers](#) W. J. Feast et al. *Polymer* Volume 37 Number 22 pp. 5017-5047, **1996**
2. [^] [Absolute Molecular Weight of Polyaniline](#) Harsha S. Kolla, Sumedh P. Surwade, Xinyu Zhang, Alan G. MacDiarmid, and Sanjeev K. Manohar *J. Am. Chem. Soc.*; **2005**; 127(48) pp 16770 - 16771; (Communication) DOI: 10.1021/ja055327k [Abstract](#)
3. [^] [Shape and Aggregation Control of Nanoparticles: Not Shaken, Not Stirred](#) Dan Li and Richard B. Kaner *J. Am. Chem. Soc.*; **2006**; 128(3) pp 968 - 975; (Article) DOI: 10.1021/ja056609n [Abstract](#)

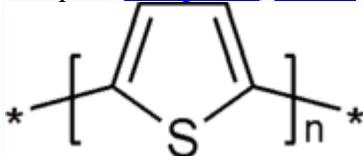
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Polythiophene

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The monomer repeat unit of unsubstituted polythiophene.

Polythiophenes (PTs) result from the [polymerization](#) of [thiophenes](#), a [sulfur heterocycle](#), that can become [conducting](#) when [electrons](#) are added or removed from the [conjugated \$\pi\$ -orbitals](#) via [doping](#).



Polythiophenes demonstrate interesting optical properties resulting from their conjugated backbone, as demonstrated by the [fluorescence](#) of a substituted polythiophene solution under UV irradiation.

The study of polythiophenes has intensified over the last three decades. **The maturation of the field of conducting polymers was confirmed by the awarding of the 2000 Nobel Prize in Chemistry to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa “for the discovery and development of conductive polymers.”** The most notable property of these materials, [electrical conductivity](#), results from the delocalization of electrons along the polymer backbone – hence the term “synthetic metals”. But, conductivity is not the only interesting property resulting from electron delocalization. **The optical properties of these materials respond to environmental stimuli, with dramatic color shifts in response to changes in [solvent](#), [temperature](#), [applied potential](#), and binding to other molecules. Both color changes and conductivity changes are induced by the same mechanism—twisting**

of the polymer backbone, disrupting conjugation—making conjugated polymers attractive as sensors that can provide a range of optical and electronic responses.

Mechanism of conductivity and doping

Electrons are delocalized along the conjugated backbones of conducting polymers, usually through overlap of π -orbitals, resulting in an extended π -system with a filled valence band. By removing electrons from the π -system (“p-doping”), or adding electrons into the π -system (“n-doping”), a charged unit called a bipolaron is formed (see Figure 1).

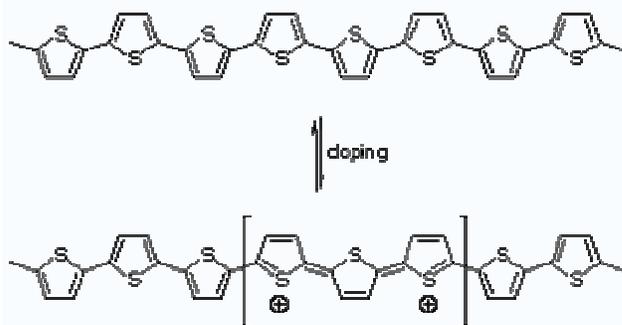


Figure 1. Removal of two electrons (p-doping) from a PT chain produces a bipolaron.

Doping is performed at much higher levels (20–40%) in conducting polymers than in semiconductors (<1%). The bipolaron moves as a unit up and down the polymer chain, and is responsible for the macroscopically observed conductivity of the polymer. For some samples of poly(3-dodecylthiophene) doped with iodine, the conductivity can approach 1000 S/cm.¹⁸¹ (In comparison, the conductivity of copper is approximately 5×10^5 S/cm.) Generally, the conductivity of PTs is lower than 1000 S/cm, but high conductivity is not necessary for many applications of conducting polymers (see below for examples).

Simultaneous oxidation of the conducting polymer and introduction of counterions, p-doping, can be accomplished electrochemically or chemically. During the electrochemical synthesis of a PT, counterions dissolved in the solvent can associate with the polymer as it is deposited onto the electrode in its oxidized form. **Doping may be conducted as:** 1) By doping the polymer as it is synthesized, a thick film can build up on an electrode—the polymer conducts electrons from the substrate to the surface of the film. 2) Alternatively, a neutral conducting polymer film or solution can be doped post-synthesis.

P doping more common than n-doping:

Reduction of the conducting polymer, n-doping, is much less common than p-doping. An early study of electrochemical n-doping of poly(bithiophene) found that the n-doping levels are less than those of p-doping, the n-doping cycles were less efficient, the number of cycles required to reach maximum doping was higher, and the n-doping process appeared to be kinetically limited, possibly due to counterion diffusion in the polymer.^[9]

A variety of reagents have been used to dope PTs. [Iodine](#) and [bromine](#) produce high conductivities^[8] but are unstable and slowly evaporate from the material.^[10] [Organic acids](#), including [trifluoroacetic acid](#), [propionic acid](#), and [sulfonic acids](#) produce PTs with lower conductivities than iodine, but with higher environmental stabilities.^{[10][11]}

Oxidative polymerization with [ferric chloride](#) can result in doping by residual [catalyst](#),^[12] although [matrix-assisted laser desorption/ionization mass spectrometry](#) (MALDI-MS) studies have shown that poly(3-hexylthiophene)s are also partially halogenated by the residual oxidizing agent.^[13] Poly(3-octylthiophene) dissolved in [toluene](#) can be doped by solutions of ferric chloride hexahydrate dissolved in [acetonitrile](#), and can be cast into films with conductivities reaching 1 S/cm.^[14] Other, less common p-dopants include [gold trichloride](#)^[15] and [trifluoromethanesulfonic acid](#).^[16]

Structure and optical properties

Conjugation length and chromisms

The extended π -systems of conjugated PTs produce some of the most interesting properties of these materials—their optical properties. As an approximation, the conjugated backbone can be considered as a real-world example of the “electron-in-a-box” solution to the [Schrödinger equation](#); however, the development of refined models to accurately predict [absorption](#) and [fluorescence](#) spectra of well-defined oligo(thiophene) systems is ongoing.^[17] **Conjugation relies upon overlap of the π -orbitals of the aromatic rings, which, in turn, requires the thiophene rings to be coplanar (see Figure 2, top).**

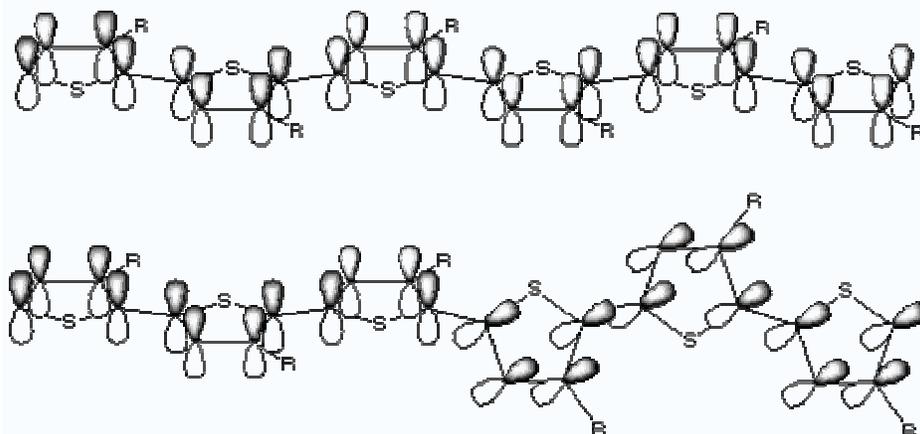


Figure 2. Conjugated π -orbitals of a coplanar and a twisted substituted PT.

The number of coplanar rings determines the conjugation length—the longer the conjugation length, the lower the separation between adjacent energy levels, and the longer the absorption wavelength. Deviation from coplanarity may be permanent, resulting from mislinkages during synthesis or especially bulky side chains; or temporary, resulting from changes in the environment or binding. This twist in the backbone reduces the conjugation length (see Figure 2, bottom), and the separation between energy levels is increased. This results in a shorter absorption wavelength.

Determining the maximum effective conjugation length requires the synthesis of regioregular PTs of defined length. The absorption band in the visible region is increasingly red-shifted as the conjugation length increases, and the maximum effective conjugation length is calculated as the saturation point of the red-shift. Early studies by ten Hoeve *et al.* estimated that the effective conjugation extended over 11 repeat units,^[18] while later studies increased this estimate to 20 units.^[19] More recently, Otsubo *et al.* synthesized 48-^[20] and 96-mer^[21] oligothiophenes, and found that the red-shift, while small (a difference of 0.1 nm between the 72- and the 96-mer), does not saturate, meaning that the effective conjugation length may be even longer than 96 units.^[21]

A variety of environmental factors can cause the conjugated backbone to twist, reducing the conjugation length and causing an absorption band shift, including solvent, temperature, application of an electric field, and dissolved ions. The absorption band of poly(3-thiophene acetic acid) in aqueous solutions of poly(vinyl alcohol) (PVA) shifts from 480 nm at pH 7 to 415 nm at pH 4. This is attributed to formation of a compact coil structure which can form hydrogen bonds with PVA upon partial deprotonation of the acetic acid group.^[22] Chiral PTs showed no induced circular dichroism (ICD) in chloroform, but displayed intense, but opposite, ICDs in chloroform–acetonitrile mixtures versus chloroform–acetone mixtures.^[23] Also, a PT with a chiral amino acid side chain^[24] displayed moderate absorption band shifts and ICDs, depending upon the pH and the concentration of buffer.^[25]

Shifts in PT absorption bands due to changes in temperature result from a conformational transition from a coplanar, rodlike structure at lower temperatures to a nonplanar, coiled structure at elevated temperatures. For example, poly(3-(octyloxy)-4-methylthiophene) undergoes a color change from red–violet at 25 °C to pale yellow at 150 °C. An isosbestic point (a point where the absorbance curves at all temperatures overlap) indicates coexistence between two phases, which may exist on the same chain or on different chains.^[26] Not all thermochromic PTs exhibit an isosbestic point: highly regioregular poly(3-alkylthiophene)s (PATs) show a continuous blue-shift with increasing temperature if the side chains are short enough so that they do not melt and interconvert between crystalline and disordered phases at low temperatures.^[citation needed]

Finally, PTs can exhibit absorption shifts due to application of electric potentials (electrochromism),^[27] or to introduction of alkali ions (ionochromism).^[28] These effects will be discussed in the context of applications of PTs below.

Regioregularity

The asymmetry of 3-substituted thiophenes results in three possible couplings when two monomers are linked between the 2- and the 5-positions. These couplings are:

- 2,5', or head–tail (HT), coupling
- 2,2', or head–head (HH), coupling
- 5,5', or tail–tail (TT), coupling

These three diads can be combined into four distinct triads, shown in Figure 3.

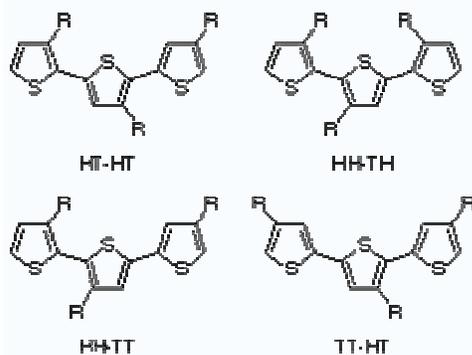


Figure 3. The four possible triads resulting from coupling of 3-substituted thiophenes.

The triads are distinguishable by NMR spectroscopy, and the degree of regioregularity can be estimated by integration.^{[29][30]}

Elsenbaumer *et al.* first noticed the effect of regioregularity on the properties of PTs. A regiorandom copolymer of 3-methylthiophene and 3-butylthiophene possessed a conductivity of 50 S/cm, while a more regioregular copolymer with a 2:1 ratio of HT to HH couplings had a higher conductivity of 140 S/cm.^[31] Films of regioregular poly(3-(4-octylphenyl)thiophene) (POPT) with greater than 94% HT content possessed conductivities of 4 S/cm, compared with 0.4 S/cm for regioirregular POPT.^[32] PATs prepared using Rieke zinc formed “crystalline, flexible, and bronze-colored films with a metallic luster.” On the other hand, the corresponding regiorandom polymers produced “amorphous and orange-colored films.”^[33] Comparison of the thermochromic properties of the Rieke PATs showed that, while the regioregular polymers showed strong thermochromic effects, the absorbance spectra of the regioirregular polymers did not change significantly at elevated temperatures. This was likely due to the formation of only weak and localized conformational defects.^[citation needed] Finally, Xu and Holdcroft demonstrated that the fluorescence absorption and emission maxima of poly(3-hexylthiophene)s occur at increasingly lower wavelengths (higher energy) with increasing HH dyad content. The difference between absorption and emission maxima, the Stokes shift, also increases with HH dyad content, which they attributed to greater relief from conformational strain in the first excited state.^[34]

Solubility

Unsubstituted PTs are conductive after doping, and have excellent environmental stability compared with some other conducting polymers such as [polyacetylene](#), but are [intractable and soluble only in solutions like mixtures of arsenic trifluoride and arsenic pentafluoride](#).^[35] However, in 1987 examples of organic-soluble PTs were reported. Elsenbaumer *et al.*, using a [nickel](#)-catalyzed [Grignard](#) cross-coupling, synthesized two soluble PTs, poly(3-butylthiophene) and poly(3-methylthiophene-'co'-3'-octylthiophene), which could be cast into films and doped with iodine to reach conductivities of 4 to 6 S/cm.^[36] Hotta *et al.* synthesized poly(3-butylthiophene) and poly(3-hexylthiophene) electrochemically^[37] (and later chemically^[38]), and characterized the polymers in solution^[39] and cast into films.^[40] The soluble PATs demonstrated both thermochromism and solvatochromism (see [above](#)) in chloroform and 2,5-dimethyltetrahydrofuran.^[41]

Also in 1987, Wudl *et al.* reported the syntheses of water-soluble sodium poly(3-thiophenealkanesulfonate)s.^[42] In addition to conferring water solubility, the pendant [sulfonate](#) groups act as counterions, producing self-doped conducting polymers. Substituted PTs with tethered [carboxylic acids](#),^[43] [acetic acids](#),^[44] amino acids,^[24] and [urethanes](#)^[45] are also water-soluble.

More recently, poly(3-(perfluorooctyl)thiophene)s soluble in [supercritical carbon dioxide](#)^[46] were electrochemically and chemically synthesized by Collard *et al.*^[47] Finally, unsubstituted oligothiophenes capped at both ends with thermally-labile alkyl esters were cast as films from solution, and then heated to remove the solubilizing end groups. [Atomic force microscopy](#) (AFM) images showed a significant increase in long-range order after heating.^[48]

Synthesis

PTs can be synthesized electrochemically, by applying a potential across a solution of the monomer to be polymerized, or chemically, using [oxidants](#) or [cross-coupling](#) catalysts. Both methods have their advantages and disadvantages.

Electrochemical synthesis

In an electrochemical polymerization, a potential is applied across a solution containing thiophene and an [electrolyte](#), producing a conductive PT film on the [anode](#).^[citation needed] Electrochemical polymerization is convenient, since the polymer does not need to be isolated and purified, but it produces structures with varying degrees of structural irregularities, such as [crosslinking](#).

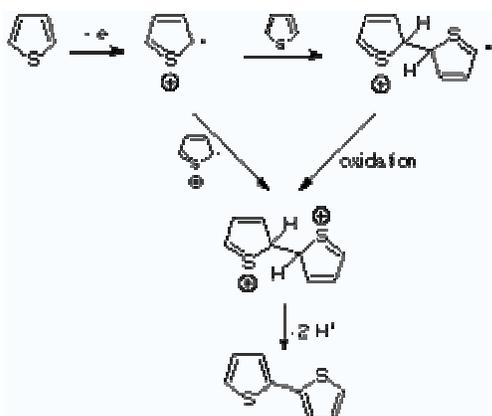


Figure 4. Initial steps in the electropolymerization of thiophenes.

As shown in Figure 4, oxidation of a monomer produces a radical cation, which can then couple with a second radical cation to form a dication dimer, or with another monomer to produce a radical cation dimer. A number of techniques including in situ video microscopy,^[49] cyclic voltammetry,^[50] photocurrent spectroscopy,^[51] and electrochemical quartz crystal microbalance measurements,^[52] have been used to elucidate the nucleation and growth mechanism leading to deposition of polymer onto the anode. Deposition of long, well-ordered chains onto the electrode surface is followed by growth of either long, flexible chains, or shorter, more crosslinked chains, depending upon the polymerization conditions.

The quality of an electrochemically prepared PT film is affected by a number of factors. These include the electrode material, current density, temperature, solvent, electrolyte, presence of water, and monomer concentration.^[2] Two other important but interrelated factors are the structure of the monomer and the applied potential. The potential required to oxidize the monomer depends upon the electron density in the thiophene ring π -system. Electron-donating groups lower the oxidation potential, while electron-withdrawing groups increase the oxidation potential. Thus, 3-methylthiophene polymerizes in acetonitrile and tetrabutylammonium tetrafluoroborate at a potential of about 1.5 V vs. SCE (saturated calomel electrode), while unsubstituted thiophene polymerizes at about 1.7 V vs. SCE. Steric hindrance resulting from branching at the α -carbon of a 3-substituted thiophene inhibits polymerization.^[53] This observation leads to the so-called “polythiophene paradox”: the oxidation potential of many thiophene monomers is higher than the oxidation potential of the resulting polymer. In other words, the polymer can be irreversibly oxidized and decompose at a rate comparable to the polymerization of the corresponding monomer.^[citation needed] This remains one of the major disadvantages of electrochemical polymerization, and limits its application for many thiophene monomers with complex side groups.

Chemical synthesis

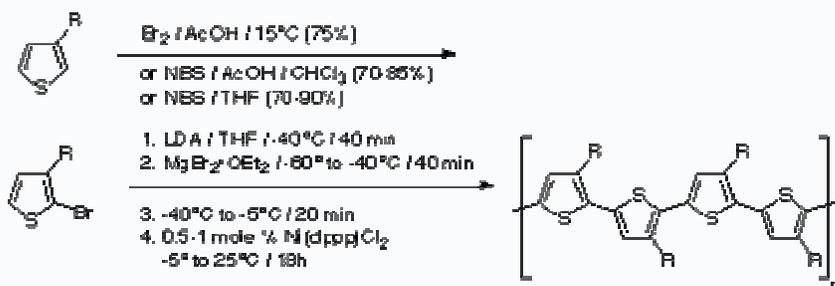
Chemical synthesis offers two advantages compared with electrochemical synthesis of PTs: a greater selection of monomers, and, using the proper catalysts, the ability to synthesize perfectly regioregular substituted PTs. While PTs may have been chemically

synthesized by accident more than a century ago,^[54] the first planned chemical syntheses using metal-catalyzed polymerization of 2,5-dibromothiophene were reported by two groups independently in 1980. Yamamoto *et al.* used magnesium in tetrahydrofuran (THF) and nickel(bipyridine) dichloride, analogous to the Kumada coupling of Grignard reagents to aryl halides.^[55] Lin and Dudek also used magnesium in THF, but with a series of acetylacetonate catalysts (Pd(acac)₂, Ni(acac)₂, Co(acac)₂, and Fe(acac)₃).^[56]

Later developments produced higher molecular weight PTs than those initial efforts, and can be grouped into two categories based on their structure. Regioregular PTs can be synthesized by catalytic cross-coupling reactions of bromothiophenes, while polymers with varying degrees of regioregularity can be simply synthesized by oxidative polymerization.

The first synthesis of perfectly regioregular PATs was described by McCullough *et al.* in 1992.^[57] As shown in Figure 5 (top),

McCullough method:



Rieke method.

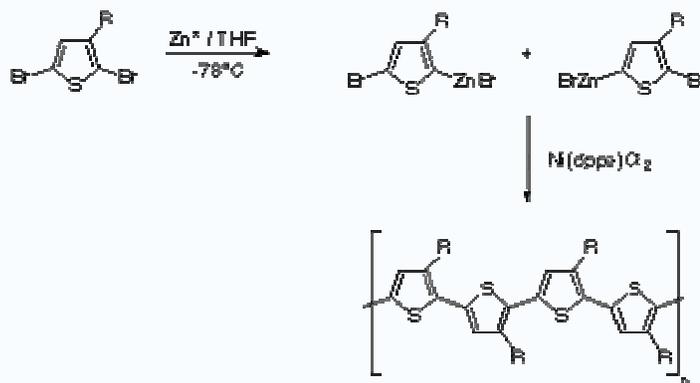


Figure 5. Cross-coupling methods for preparing regioregular PATs.

selective bromination produces 2-bromo-3-alkylthiophene, which is followed by transmetalation and then Kumada cross-coupling in the presence of a nickel catalyst. This method produces approximately 100% HT–HT couplings, according to NMR spectroscopy analysis of the diads. In the method subsequently described by Rieke *et al.* in 1993,^[58] 2,5-dibromo-3-alkylthiophene is treated with highly reactive “Rieke zinc”^[59] to form a mixture of organometallic isomers (Figure 5, bottom). Addition of a catalytic

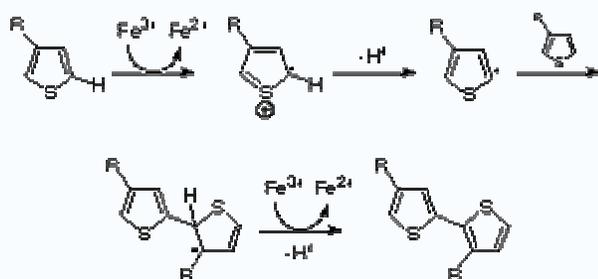
amount of Pd(PPh₃)₄ produces a regiorandom polymer, but treatment with Ni(dppe)Cl₂ yields regioregular PAT in quantitative yield.^[60]

While the McCullough and Rieke methods produce structurally homogenous PATs, they require low temperatures, the careful exclusion of water and oxygen, and brominated monomers. In contrast, the oxidative polymerization of thiophenes using ferric chloride described by Sugimoto in 1986 can be performed at room temperature under less demanding conditions.^[61] This method has proven to be extremely popular; H.C. Stark's antistatic coating Baytron P is prepared on a commercial scale using ferric chloride (see below).^[62]

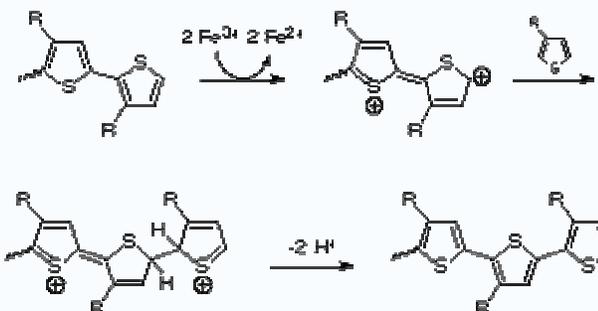
A number of studies have been conducted in attempts to improve the yield and quality of the product obtained using the oxidative polymerization technique. In addition to ferric chloride, other oxidizing agents, including ferric chloride hydrate, copper perchlorate, and iron perchlorate have also been used successfully to polymerize 2,2'-bithiophene.^[63] Slow addition of ferric chloride to the monomer solution produced poly(3-(4-octylphenyl)thiophene)s with approximately 94% H-T content.^[32] Precipitation of ferric chloride in situ (in order to maximize the surface area of the catalyst) produced significantly higher yields and monomer conversions than adding monomer directly to crystalline catalyst.^{[64][65]} Higher molecular weights were reported when dry air was bubbled through the reaction mixture during polymerization.^[66] Exhaustive Soxhlet extraction after polymerization with polar solvents was found to effectively fractionate the polymer and remove residual catalyst before NMR spectroscopy.^[29] Using a lower ratio of catalyst to monomer (2:1, rather than 4:1) may increase the regioregularity of poly(3-dodecylthiophene)s.^[67] Andreani *et al.* reported higher yields of soluble poly(dialkylterthiophene)s in carbon tetrachloride rather than chloroform, which they attributed to the stability of the radical species in carbon tetrachloride.^[68] Higher-quality catalyst, added at a slower rate and at reduced temperature, was shown to produce high molecular weight PATs with no insoluble polymer residue.^[69] Laakso *et al.* used a factorial design to determine that increasing the ratio of catalyst to monomer increased the yield of poly(3-octylthiophene), and claimed that a longer polymerization time also increased the yield.^[70]

The mechanism of the oxidative polymerization using ferric chloride has been controversial. Sugimoto *et al.* did not speculate on a mechanism in their 1986 report.^[61] In 1992, Niemi *et al.* proposed a radical mechanism, shown in Figure 6(top).

Radical:



Carbocation:



Radical cation:

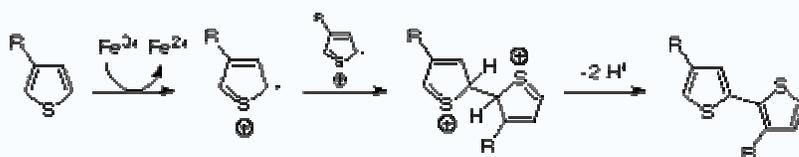


Figure 6. Proposed mechanisms for ferric chloride oxidative polymerizations of thiophenes.

They based their mechanism on two assumptions. First, since they observed polymerization only in solvents where the catalyst was either partially or completely insoluble (chloroform, toluene, carbon tetrachloride, pentane, and hexane, and not diethyl ether, xylene, acetone, or formic acid), they concluded that the active sites of the polymerization must be at the surface of solid ferric chloride. Therefore, they discounted the possibilities of either two radical cations reacting with each other, or two radicals reacting with each other, “because the chloride ions at the surface of the crystal would prevent the radical cations or radicals from assuming positions suitable for dimerization.”^[71] Second, using 3-methylthiophene as a prototypical monomer, they performed quantum mechanical calculations to determine the energies and the total atomic charges on the carbon atoms of the four possible polymerization species (neutral 3-methylthiophene, the radical cation, the radical on carbon 2, and the radical on carbon 5).



Since the most negative carbon of the neutral 3-methylthiophene is also carbon 2, and the carbon with the highest odd electron population of the radical cation is carbon 2, they

concluded that a radical cation mechanism would lead to mostly 2–2, H–H links. They then calculated the total energies of the species with the radicals at the 2 and the 5 carbons, and found that the latter was more stable by 1.5 kJ/mol. Therefore, the more stable radical could react with the neutral species, forming head-to-tail couplings as shown in Figure 6 (top).

Andersson *et al.* offered an alternative mechanism in the course of their studies of the polymerization of 3-(4-octylphenyl)thiophene with ferric chloride, where they found a high degree of regioregularity when the catalyst was added to the monomer mixture slowly. They concluded that, given the selectivity of the couplings, and the strong oxidizing conditions, the reaction could proceed via a carbocation mechanism (Figure 6, middle).^[32]

The radical mechanism was directly challenged in a short communication in 1995, when Olinga and François noted that thiophene could be polymerized by ferric chloride in acetonitrile, a solvent in which the catalyst is completely soluble. Their analysis of the kinetics of thiophene polymerization also seemed to contradict the predictions of the radical polymerization mechanism.^[72] Barbarella *et al.* studied the oligomerization of 3-(alkylsulfanyl)thiophenes, and concluded from their quantum mechanical calculations, and considerations of the enhanced stability of the radical cation when delocalized over a planar conjugated oligomer, that a radical cation mechanism analogous to that generally accepted for electrochemical polymerization was more likely (Figure 6, bottom).^[73] Given the difficulties of studying a system with a heterogeneous, strongly oxidizing catalyst that produces difficult to characterize rigid-rod polymers, the mechanism of oxidative polymerization is by no means decided. However, the radical cation mechanism shown in Figure 6 is generally accepted as the most likely route for PT synthesis.

Applications

A number of applications have been proposed for conducting PTs, including field-effect transistors,^[74] electroluminescent devices, solar cells, photochemical resists, nonlinear optic devices,^[75] batteries, and diodes. In general, there are two categories of applications for conducting polymers. 1) **Static applications rely upon the intrinsic conductivity of the materials, combined with their ease of processing and material properties common to polymeric materials.** 2) **Dynamic applications utilize changes in the conductive and optical properties, resulting either from application of electric potentials or from environmental stimuli.**

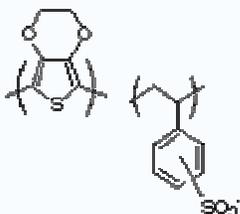


Figure 7. PEDOT-PSS (Baytron-P).

Example of static applications:

Example of a static application: H.C. Stark's [poly\(3,4-ethylenedioxythiophene\)-poly\(styrene sulfonate\) \(PEDOT-PSS\)](#) product Baytron P (Figure 7) has been extensively used as an antistatic coating (as packaging materials for electronic components, for example). **AGFA coats 200 m × 10 m of photographic film per year with Baytron because of its antistatic properties.** The thin layer of Baytron is virtually transparent and colorless, prevents electrostatic discharges during film rewinding, and reduces dust buildup on the negatives after processing.

Example of dynamic Application: PEDOT can also be used in dynamic applications where a potential is applied to a polymer film. 1) The electrochromic properties of PEDOT are used to manufacture windows and mirrors which can become opaque or reflective upon the application of an electric potential.^[27]

Widespread adoption of [electrochromic windows](#) could save billions of dollars per year in [air conditioning costs](#).^[76] 2) Finally, [Phillips](#) has commercialized a [mobile phone](#) with an electrically switchable PEDOT mirror ([image](#)).

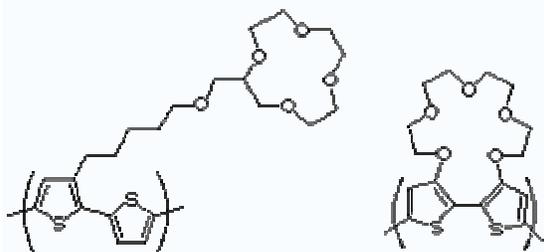


Figure 8. Ionoselective PTs reported by Bäuerle (left) and Swager (right).

3) **The use of PTs as sensors responding to an analyte has also been the subject of intense research.** In addition to [biosensor applications](#), PTs can also be functionalized with synthetic receptors for detecting metal ions or [chiral molecules](#) as well. PTs with pendant^[77] and main-chain^[28] [crown ether](#) functionalities were reported in 1993 by the research groups of Bäuerle and Swager, respectively (Figure 8). [Electrochemically](#) polymerized thin films of the Bäuerle pendant crown ether PT were exposed to millimolar concentrations of [alkali](#) cations (Li, Na, and K). The current which passed through the film at a fixed potential dropped dramatically in [lithium](#) ion solutions, less so for sodium ion solutions, and only slightly for [potassium](#) ion solutions. The Swager main chain crown ether PTs were prepared by chemical coupling and characterized by [absorbance spectroscopy](#). Addition of the same alkali cations resulted in absorbance shifts of 46 nm (Li), 91 nm (Na), and 22 nm (K). The size of the shifts corresponds to the ion-binding preferences of the corresponding crown ether, resulting from a twist in the conjugated polymer backbone induced by ion binding.

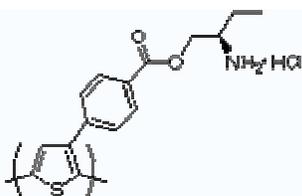


Figure 9. Chiral PT synthesized by Yashima and Goto.

In the course of their studies of the optical properties of chiral PTs,^{[78][79][80][81]} Yashima and Goto found that a PT with a chiral primary [amine](#) (Figure 9) was sensitive to chiral amino [alcohols](#), producing mirror-image-split ICD responses in the π -transition region.^[82] This was the first example of chiral recognition by PTs using a chiral detection method ([CD spectroscopy](#)). This distinguished it from earlier work by Lemaire *et al.* who used an achiral detection method ([cyclic voltammetry](#)) to detect incorporation of chiral [dopant](#) anions into an electrochemically polymerized chiral PT.^[83]

References

1. [^] Street, G. B.; Clarke, T. C. *IBM J. Res. Dev.* **1981**, *25*, 51–57.
2. ^{^ a b} Schopf, G.; Koßmehl, G. *Adv. Polym. Sci.* **1997**, *129*, 1–166.
3. [^] Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738. DOI:10.1021/cr00012a009
4. [^] Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205. DOI:10.1021/cr950257t
5. [^] McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93–116.
6. [^] Reddinger, J. L.; Reynolds, J. R. *Adv. Polym. Sci.* **1999**, *145*, 57–122.
7. [^] McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574. DOI:10.1021/cr9801014
8. ^{^ a b} McCullough, R. D.; Tristramnagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910–4911. DOI:10.1021/ja00064a070
9. [^] Mastragostino, M.; Soddu, L. *Electrochim. Acta* **1990**, *35*, 463–466. DOI:10.1016/0013-4686(90)87029-2
10. ^{^ a b} Lopenen, M. T.; Taka, T.; Laakso, J.; Väkiparta, K.; Suuronen, K.; Valkeinen, P.; Österholm, J. E. *Synth. Met.* **1991**, *41*, 479–484. DOI:10.1016/0379-6779(91)91111-M
11. [^] Bartus, J. *J. Macromol. Sci., Chem.* **1991**, *A28*, 917–924.
12. [^] Qiao, X. Y.; Wang, X. H.; Mo, Z. S. *Synth. Met.* **2001**, *122*, 449–454.
13. [^] McCarley, T. D.; Noble, C. O.; DuBois, C. J.; McCarley, R. L. *Macromolecules* **2001**, *34*, 7999–8004. DOI:10.1021/ma002140z
14. [^] Heffner, G. W.; Pearson, D. S. *Synth. Met.* **1991**, *44*, 341–347. DOI:10.1016/0379-6779(91)91821-Q
15. [^] Abdou, M. S. A.; Holdcroft, S. *Synth. Met.* **1993**, *60*, 93–96. DOI:10.1016/0379-6779(93)91226-R
16. [^] Rudge, A.; Raistrick, I.; Gottesfeld, S.; Ferraris, J. P. *Electrochim. Acta* **1994**, *39*, 273–287. DOI:10.1016/0013-4686(94)80063-4
17. [^] Bässler, H. Electronic Excitation. In *Electronic Materials: The Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: Weinheim, Germany 1998. ISBN 3-527-29438-4
18. [^] ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887–5889. DOI:10.1021/ja00015a067
19. [^] Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.*, *48*, 379–384.

20. [^] Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998**, *63*, 8632–8633. DOI:[10.1021/jo981541y](https://doi.org/10.1021/jo981541y)
21. ^{^ a b} Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286–5287. DOI:[10.1021/ja034333i](https://doi.org/10.1021/ja034333i)
22. [^] de Souza, J. M.; Pereira, E. C. *Synth. Met.* **2001**, *118*, 167–170. DOI:[10.1016/S0379-6779\(00\)00453-7](https://doi.org/10.1016/S0379-6779(00)00453-7)
23. [^] Goto, H.; Yashima, E.; Okamoto, Y. *Chirality* **2000**, *12*, 396–399.
24. ^{^ a b} Andersson, M.; Ekeblad, P. O.; Hjertberg, T.; Wennerström, O.; Inganäs, O. *Polym. Commun.* **1991**, *32*, 546–548.
25. [^] Nilsson, K. P. R.; Andersson, M. R.; Inganäs, O. *J. Phys.: Condes. Matter* **2002**, *14*, 10011–10020.
26. [^] Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141–2144. DOI:[10.1021/ma00034a012](https://doi.org/10.1021/ma00034a012)
27. ^{^ a b} Heuer, H. W.; Wehrmann, R.; Kirchmeyer, S. *Adv. Funct. Mater.* **2002**, *12*, 89–94. DOI:[10.1002/1616-3028\(20020201\)12:2<89::AID-ADFM89>3.0.CO;2-1](https://doi.org/10.1002/1616-3028(20020201)12:2<89::AID-ADFM89>3.0.CO;2-1)
28. ^{^ a b} Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214–12215. DOI:[10.1021/ja00078a090](https://doi.org/10.1021/ja00078a090)
29. ^{^ a b} Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039–3045. DOI:[10.1021/ma00089a022](https://doi.org/10.1021/ma00089a022)
30. [^] Diaz-Quijada, G. A.; Pinto, B. M.; Holdcroft, S. *Macromolecules* **1996**, *29*, 5416–5421. DOI:[10.1021/ma960126+](https://doi.org/10.1021/ma960126+)
31. [^] Elsenbaumer, R. L.; Jen, K.-Y.; Miller, G. G.; Eckhardt, H.; Shacklette, L. W.; Jow, R. "Poly (alkyl thiophenes) and Poly (substituted heteroaromatic vinylenes): Versatile, Highly Conductive, Processible Polymers with Tunable Properties." In *Electronic Properties of Conjugated Polymers* (Eds: Kuzmany, H.; Mehring, M.; Roth, S.), Springer, Berlin, **1987**. ISBN 0-387-18582-8
32. ^{^ a b c} Andersson, M. R.; Selse, D.; Berggren, M.; Järvinen, H.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J. E. *Macromolecules* **1994**, *27*, 6503–6506. DOI:[10.1021/ma00100a039](https://doi.org/10.1021/ma00100a039)
33. [^] Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233–244. DOI:[10.1021/ja00106a027](https://doi.org/10.1021/ja00106a027)
34. [^] Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457–4460. DOI:[10.1021/ma00069a009](https://doi.org/10.1021/ma00069a009)
35. [^] Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2–9. DOI:[10.1021/ar00121a001](https://doi.org/10.1021/ar00121a001)
36. [^] Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169–174. DOI:[10.1016/0379-6779\(86\)90020-2](https://doi.org/10.1016/0379-6779(86)90020-2)
37. [^] Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212–215. DOI:[10.1021/ma00167a038](https://doi.org/10.1021/ma00167a038)
38. [^] Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.* **1988**, *26*, 267–279. DOI:[10.1016/0379-6779\(88\)90243-3](https://doi.org/10.1016/0379-6779(88)90243-3)
39. [^] Hotta, S. *Synth. Met.* **1987**, *22*, 103–113. DOI:[10.1016/0379-6779\(87\)90528-5](https://doi.org/10.1016/0379-6779(87)90528-5)
40. [^] Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79–87. DOI:[10.1016/0379-6779\(87\)90573-X](https://doi.org/10.1016/0379-6779(87)90573-X)
41. [^] Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071–1078.
42. [^] Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858–1859. DOI:[10.1021/ja00240a044](https://doi.org/10.1021/ja00240a044)
43. [^] Englebienne, P.; Weiland, M. *Chem. Commun.* **1996**, 1651–1652. DOI:[10.1039/cc9960001651](https://doi.org/10.1039/cc9960001651)

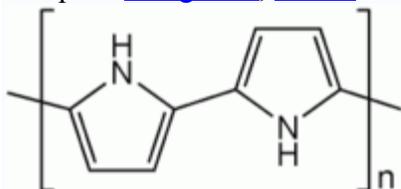
44. [^](#) Kim, B. S.; Chen, L.; Gong, J. P.; Osada, Y. *Macromolecules* **1999**, *32*, 3964–3969. DOI:[10.1021/ma981848z](https://doi.org/10.1021/ma981848z)
45. [^](#) Jung, S. D.; Hwang, D. H.; Zyung, T.; Kim, W. H.; Chittibabu, K. G.; Tripathy, S. K. *Synth. Met.* **1998**, *98*, 107–111.
46. [^](#) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945–947.
47. [^](#) Li, L.; Counts, K. E.; Kurosawa, S.; Teja, A. S.; Collard, D. M. *Adv. Mater.* **2004**, *16*, 180–183.
48. [^](#) Murphy, A. R.; Fréchet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597.
49. [^](#) Lukkari, J.; Tuomala, R.; Ristimäki, S.; Kankare, J. *Synth. Met.* **1992**, *47*, 217–231.
50. [^](#) Lukkari, J.; Kankare, J.; Visy, C. *Synth. Met.* **1992**, *48*, 181–192.
51. [^](#) Lukkari, J.; Alanko, M.; Pitkänen, V.; Kleemola, K.; Kankare, J. *J. Phys. Chem.* **1994**, *98*, 8525–8535.
52. [^](#) Visy, C.; Lukkari, J.; Kankare, J. *Synth. Met.* **1997**, *87*, 81–87.
53. [^](#) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706–6714.
54. [^](#) Meyer, V. Ber. Deutsch. Chem. Ges. 1883, *16*, 1465–1478.
55. [^](#) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9–12.
56. [^](#) Lin, J. W. P.; Dudek, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2869–2873.
57. [^](#) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70–72.
58. [^](#) Chen, T. A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462–3463.
59. [^](#) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445–1453.
60. [^](#) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088.
61. [^](#) ^{a,b} Sugimoto, R.; Taketa, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635–638.
62. [^](#) Jonas, F.; Heywang, G.; Schmidtberg, W.; Heinze, J.; Dietrich, M. [U.S. Patent 5,035,926](#), **1991**.
63. [^](#) Ruckenstein, E.; Park, J. S. *Synth. Met.* **1991**, *44*, 293–306.
64. [^](#) Bizzarri, P. C.; Andreani, F.; Della Casa, C.; Lanzi, M.; Salatelli, E. *Synth. Met.* **1995**, *75*, 141–147.
65. [^](#) Fraleoni-Morgera, A.; Della Casa, C.; Lanzi, M.; Bizzarri, P. C. *Macromolecules* **2003**, *36*, 8617–8620. DOI:[10.1021/ma0348730](https://doi.org/10.1021/ma0348730)
66. [^](#) Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J.; Haider, M. I. *Synth. Met.* **1991**, *41*, 825–830.
67. [^](#) Qiao, X. Y.; Wang, X. H.; Zhao, X. J.; Liu, J.; Mo, Z. S. *Synth. Met.* **2000**, *114*, 261–265.
68. [^](#) Andreani, F.; Salatelli, E.; Lanzi, M. *Polymer* **1996**, *37*, 661–665.
69. [^](#) Gallazzi, M. C.; Bertarelli, C.; Montoneri, E. *Synth. Met.* **2002**, *128*, 91–95.
70. [^](#) Laakso, J.; Järvinen, H.; Skagerberg, B. *Synth. Met.* **1993**, *55*, 1204–1208.
71. [^](#) Niemi, V. M.; Knuutila, P.; Österholm, J. E.; Korvola, J. *Polymer* **1992**, *33*, 1559–1562.
72. [^](#) Olinga, T.; François, B. *Synth. Met.* **1995**, *69*, 297–298.
73. [^](#) Barbarella, G.; Zambianchi, M.; DiToro, R.; Colonna, M.; Iarossi, D.; Goldoni, F.; Bongini, A. *J. Org. Chem.* **1996**, *61*, 8285–8292.
74. [^](#) Garnier, F. Field-Effect Transistors Based on Conjugated Materials. In *Electronic Materials: The Oligomer Approach* (Eds: Müllen, K.; Wegner, G.), Wiley-VCH, Weinheim, **1998**. ISBN [3-527-29438-4](#)
75. [^](#) Harrison, M. G.; Friend, R. H. Optical Applications. In *Electronic Materials: The Oligomer Approach* (Eds: Müllen, K.; Wegner, G.), Wiley-VCH, Weinheim, **1998**. ISBN [3-527-29438-4](#)
76. [^](#) Rosseinsky, D. R.; Mortimer, R. J. *Adv. Mater.* **2001**, *13*, 783–793.

77. [^](#) Bäuerle, P.; Scheib, S. *Adv. Mater.* **1993**, *5*, 848–853.
78. [^](#) Goto, H.; Okamoto, Y.; Yashima, E. *Chem. Eur. J.* **2002**, *8*, 4027–4036.
79. [^](#) Goto, H.; Okamoto, Y.; Yashima, E. *Macromolecules* **2002**, *35*, 4590–4601.
80. [^](#) Goto, H.; Yashima, E. *J. Am. Chem. Soc.* **2002**, *124*, 7943–7949.
81. [^](#) Sakurai, S.; Goto, H.; Yashima, E. *Org. Lett.* **2001**, *3*, 2379–2382.
82. [^](#) Yashima, E.; Goto, H.; Okamoto, Y. *Macromolecules* **1999**, *32*, 7942–7945.
83. [^](#) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988**, 658–661.

Polypyrrole

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 Polypyrrole

A **Polypyrrole (PPy)** is a chemical compound formed from a number of connected [pyrrole](#) ring structures. For example a tetrapyrrole is a compound with four pyrrole rings connected. **Polypyrroles are conducting polymers of the rigid-rod polymer host family**, all basically derivatives of [polyacetylene](#). Polypyrrole was the first of this key family of compounds to show high conductivity.

In a series of papers in 1963, DE Weiss and coworkers reported [\[1\]](#) high-conductivity (up to 1 S/cm) in iodine-doped oxidized polypyrrole. While too early and thus eventually "lost", this anticipated by many years the Nobel-prize-winning discovery of high-conductivity in similarly iodine-doped and oxidized [polyacetylene](#), as well as [John McGinness' et als](#) report of a high-conductivity "ON" state in the putative first organic electronic device [\[2\]](#).

Polypyrroles are also called pyrrole blacks or polypyrrole blacks. Polypyrroles also exist naturally, especially as part of a mixed copolymer with [polyacetylene](#) and [polyaniline](#) in some [melanins](#).

In 2006, scientists from Brown University published work on a fast-charging and discharging battery chemistry based on polypyrroles. [3]

Polyacetylene

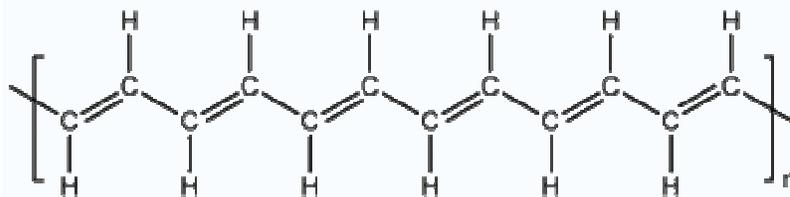
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Polyacetylene (IUPAC name: polyethyne) is an [organic polymer](#) with the repeat unit $(C_2H_2)_n$. The high electrical conductivity discovered for these polymers in the 1970's accelerated interest in the use of [organic compounds](#) in [microelectronics](#). Polyacetylenes are also known where the H atoms are replaced with [alkyl](#) groups.

Structure of polyacetylene

The polymer consists of a long chain of [carbon](#) atoms with alternating single and [double bonds](#) between them, each with one [hydrogen](#) atom. Schematically the structure of polyacetylene is shown below.



A segment of *trans*-polyacetylene.

One distinguishes *trans*-polyacetylene, with all double bonds in the [trans](#) configuration, from *cis*-polyacetylene, with all double bonds in the [cis](#) configuration. Each hydrogen atom could be replaced by a [functional group](#).

Preparation

Acetylene polymerizes in a similar fashion to [ethylene](#): the [polymerization](#) can be effected with anionic, cationic, and radical [initiators](#). Polyacetylene is generally not prepared by polymerizing [acetylene](#), which is a highly flammable gas that uncontrollably [oligomerizes](#) at high concentrations. The most common synthesis utilize [ring-opening](#) polymerization ("ROMP") of molecules like [cyclooctatetraene](#) and substituted derivatives thereof.^{[1][2][3]} Depending on the method of preparation, some polyacetylenes are also called acetylene black or polyacetylene black.^[*citation needed*]

Conductivity and the Nobel Prize

As prepared with a [Ziegler-Natta catalyst](#), with high levels of [catalyst](#), the polyacetylene is a silver, non-conductive film. It was shown in 1976 that oxidation of this material with [iodine](#) results in a 10^8 -fold increase in conductivity. The conductivity of this doped material approaches the conductivity of the best available conductor, [silver](#). This was one of the first known examples of a conductive organic polymer.^[4] The [Nobel Prize in Chemistry](#) in 2000 was awarded to [Alan J. Heeger](#), [Alan G MacDiarmid](#), and [Hideki Shirakawa](#) for this work.

Naturally occurring “polyacetylene”

Some [fungal melanins](#) have been described as polyacetylene.^[citation needed]

References

1. [^] Jozefiak, T. H.; Ginsburg, E. J.; Gorman, C. B.; Grubbs, R. H.; Lewis, N. S. "Voltammetric Characterization of Soluble Polyacetylene Derivatives Obtained from the Ring-Opening Metathesis Polymerization (ROMP) of Substituted Cyclooctatetraenes" *Journal of the American Chemical Society* 1993; volume 115, pages 4705-4713. DOI:[10.1021/ja00064a035](https://doi.org/10.1021/ja00064a035)
2. [^] Gorman, C. B. Ginsburg, E. J.; [Grubbs](#), R. H. "Soluble, Highly Conjugated Derivatives of Polyacetylene from the Ring-Opening Metathesis Polymerization of Monosubstituted Cyclooctatetraenes: Synthesis and the Relationship Between Polymer Structure and Physical Properties" *Journal of the American Chemical Society* 1993, volume 115, pages 1397-1409. DOI:[10.1021/ja00057a024](https://doi.org/10.1021/ja00057a024)
3. [^] Langsdorf, Brandi, L.; Zhou, Xin; Lonergan, Mark C., "Kinetic Study of the Ring-Opening Metathesis Polymerization of Ionically Functionalized Cyclooctatetraenes" *Macromolecules*, 2001, volume 34, pages 2450-2458. DOI:[10.1021/ma0020685](https://doi.org/10.1021/ma0020685)
4. [^] Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H., "Synthesis of Highly Conducting Films of Derivatives of Polyacetylene, (CH)_x," *J. Am. Chem. Soc.* 1978, 100, 1013-15. DOI:[10.1021/ja00471a081](https://doi.org/10.1021/ja00471a081)



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The Nobel Prize in Chemistry 2000

BACK

The Nobel Prize in Chemistry 2000



The Royal Swedish Academy of Sciences has awarded the Nobel Prize in Chemistry for 2000 jointly to **Alan J. Heeger, Alan G. MacDiarmid** and **Hideki Shirakawa** "for the discovery and development of conductive polymers".



Alan G. MacDiarmid
Professor at the University of Pennsylvania,
Philadelphia. USA.

Hideki Shirakawa
Professor Emeritus,
University of Tsukuba. Japan.

Alan J. Heeger
Professor at the University of California
at Santa Barbara. USA.

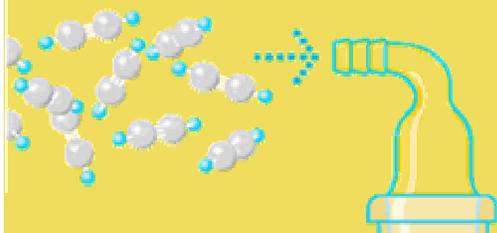
Electrically conductive plastic

Alan Heeger, Alan MacDiarmid and Hideki Shirakawa have been awarded the Nobel Prize in Chemistry for showing how plastic can be made to conduct electric current. This surprising discovery has radically altered our view of plastic as a material. Conductive polymers today constitute a growing research field of great significance to chemists and physicists alike.



Plastics that imitate metals

Plastics are *polymers*, molecules formed of many identical units bound to each other like pearls in a necklace. For a polymer to be electrically conductive it must "imitate" a metal – the electrons in the bonds must be freely mobile and not bound fast to the atoms. One condition for this is that the polymer consists of alternate single and double bonds, termed conjugated double bonds. *Polyacetylene* is the simplest possible conjugated polymer. It is obtained by polymerisation of acetylene, shown to the left.



A surprise with a silver lining...

At the beginning of the 1970s Shirakawa was studying the polymerisation of acetylene. In his reaction vessel polyacetylene appeared in the form of an unremarkable black powder. On one occasion a visiting researcher accidentally added *one thousand times* more catalyst than usual. Imagine the researchers' surprise when a beautiful silvery film formed on the surface of the liquid in the vessel. The obvious question was: "If the plastic film shines like a metal, can it conduct electricity, too?"

Doping raises molecule performance

By analogy with semiconductor technology one speaks of *doping* the polymer when it is subjected to oxidation with

iodine vapour. The more electrons are removed, the higher the degree of doping and the greater the conductivity.

While polyacetylene can be persuaded to conduct current as well as many metals do, this material is unfortunately no good for practical use. Its conductivity drops rapidly in contact with air. This has led to the development of more stable, conjugated polymers, e.g. polypyrrol, polyaniline and polythiophene.

