

SEMICONDUCTORS AND SEMIMETALS

TREATISE EDITORS: ROBERT K. WILLARDSON AND EICKE R. WEBER

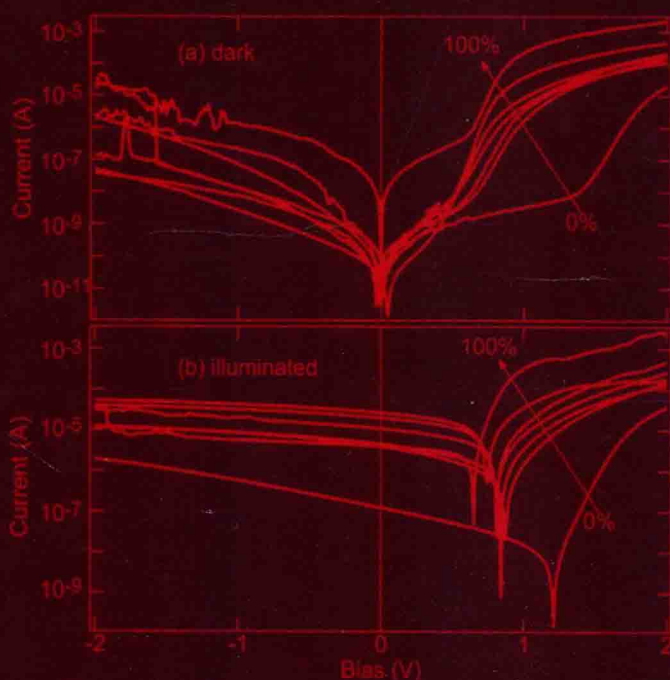
VOLUME 81

CONDUCTING ORGANIC MATERIALS AND DEVICES

SURESH C. JAIN

MAGNUS WILLANDER

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Volume 81

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Conducting Organic Materials and Devices

**SEMICONDUCTORS
AND SEMIMETALS**

Volume 81

Semiconductors and Semimetals

A Treatise

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Finally, we must thank sincerely our children and our wives who provided us unfailing support and help during the preparation of this book.

S.C. Jain
Magnus Willander
Vikram Kumar
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CHAPTER 1

INTRODUCTION

1.1. Advantages of Conducting Polymers

Plastics created a lot of excitement in the 1940s and 1950s. These plastics were insulators. Until the early 1970s the idea that plastics could conduct electricity would have appeared absurd. The first conducting polymer was synthesized in the 1970s. In the early 1970s a graduate student in Shirakawa's laboratory in Tokyo was trying to make polyacetylene from the acetylene gas. Instead of the polyacetylene (which is known to be a dark powder), the student produced a lustrous metallic looking film. The film looked like an aluminum film but stretched like a thin plastic sheet. Accidentally the student had added 1000 times more catalyst than the amount required to produce polyacetylene. Subsequently Shirakawa collaborating with MacDiarmid and Heeger of the University of Pennsylvania could increase the conductivity of the polyacetylene films a billion times by doping it with iodine. The doped films looked like golden metallic sheets. Later more than a dozen organic polymers could be made conducting by appropriate doping. Now plastics with conductivity comparable to that of copper can be easily fabricated. Early work on conducting plastics is described in [1-8].

The semiconducting conjugated polymers can be used as the active layer in LEDs, field effect transistors, solar cells, photodiodes, electrochemical cells and memory devices. They have proved to be of great importance as an active medium in lasers. These devices are being pushed toward commercialization because they can be fabricated by inexpensive techniques, such as spin coating, ink-jet printing, low temperature fiber drawing and screen-printing on the flexible substrates. This leads to a real advantage over the expensive and sophisticated technology used with inorganic materials in the semiconductor industry. The glass and flexible plastic foil make these devices particularly interesting because of the advantages they offer in terms of flexibility, low power, low weight, and low cost. In view of the above advantages, conducting plastics have emerged as a new class of electronic materials. It is possible that by the year 2010, silicon might hit the wall and the conducting polymers may become the major players in the field of semiconductor devices.

The polymers consist of chains, each chain contains C-H or related groups bound together by strong sigma bonds, which provide strength and integrity to the polymer. Inter-chain coupling is small. Therefore the materials are quasi-one dimensional (quasi-1D). The structure allows the dopant atoms or molecules to go in space in-between the chains.

1.2. Early Attempts for Applications

Early work on the conducting polymers has been discussed in the reviews [2,9,10]. Early applications of polymers as processible conductors are also given in these publications. There were attempts to commercialize the conducting polymer products. Two Japanese companies manufactured rechargeable button-cell batteries. The batteries used polyaniline and lithium electrodes. These batteries had a longer lifetime than the nickel-cadmium and lead-acid batteries. However the venture was not successful. A textile manufacturer Milliken and Company in the USA developed a fabric known as Context. Context had conducting polymer polypyrrole interwoven with other common synthetics. This fabric is excellent for camouflage because it fools the radar by making it appear that the signal is going through empty space. Context was approved for use but for a variety of reasons the material was not successful. The annual damage to electronic equipment by electrostatic charges is estimated to be more than \$15 million. At present the protective packaging relies on ionic salts or resins filled with metals or carbon. The conductivity of ionic salts is low and it is unstable. A metal is expensive and heavy. Carbon bits cast off during shipment and can cause contamination. IBM is developing a polyaniline solution, known as PanAquas. If conductivity of PanAquas could be increased, it could replace the lead based solder, which is hazardous. Polymers are good candidates for electromagnetic shielding also. Allied Signals developed a product named Versacon, which was similar in performance to the IBM PanAquas. Several companies incorporated it in paints and coatings. However the volume of sales continued to be too small and Allied had to stop its production. As compared to Versacon, which is in a powder form, PanAquas is a solution and is transparent. Epstein has a patent on a technique to join two pieces of plastics using conducting polymer polyaniline. The pieces to be joined are sprinkled with polyaniline and irradiated with microwaves. Polyaniline absorbs the energy from microwaves, melts and fuses the two pieces together. MacDiarmid and collaborators have made polymer electromechanical mechanisms. The polymers undergo large changes in dimensions with small electric currents. Potentially several microactuators coupled together could be used as artificial muscles.

1.3. Growth and Properties

Monolayer control of thickness of organic films has been obtained using the Langmuir-Blodgett film deposition technique as well as layers grown by self-assembled monolayer from solutions [11]. However the structure of the films grown by these methods cannot be controlled accurately. Since its emergence in the mid-1980s, Organic Molecular Beam Epitaxy (OMBE) has become an important technique for deposition of organic films with monolayer thickness control in atomically clean environments. Extreme chemical and structural control of the films is also obtained. Forrest [11] has written an extensive review on the structure and properties of the films grown by this method.

Typical conductivity values of several polymers are shown in Fig. 1.1. The conductivity of polymers is compared with the conductivity of other solids in Fig. 1.2. It is seen that the maximum conductivity is quite high and close to that of good metals.

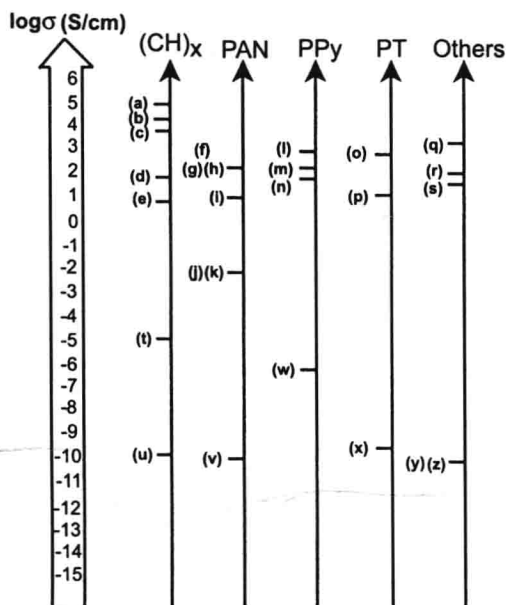


FIG. 1.1. Observed conductivity of several conducting polymers. Low values of conductivity are obtained in the pristine conducting polymers containing high degree of disorder. Conductivity increases with stretching, which aligns the molecular chains of the fiber and produces more ordered regions. The high conductivity under the heading 'Others' is for the sulphuric doped PPV and AsF_5 doped PPP. For more details see Ref. [12] from where the figure has been taken. Note that conductivity close to that of copper has been achieved.

Though conductivity of polyaniline is not as high as that of some other polymers, it is emerging as the material of choice for many applications. It is stable in air and its electronic properties can be easily tailored. It is one of the oldest synthetic polymers, and probably it is the cheapest conducting polymer used in devices. It can be easily fabricated as thin films or patterned surfaces. Polyaniline will never replace the materials which have extremely high conductivity. However, it will be useful for certain specific applications. Andy Monkman has a program to extrude the polymer braids and lay the insulation of the coaxial cables in a single step. The work is supported by a cable company [3]. Properties of polyacetylene are discussed in detail in Chapter 2.

Excitations in conducting polymers consist of localized polarons. The polarons can be singly charged, doubly charged or neutral polaron-exciton [15]. This localization results in large binding energy of the excitons. If there are no quenching centers in the polymer, this localization results in very high luminescence efficiencies. There are no satisfactory theories of conducting polymers. The widely quoted SSH Hamiltonian neglects electron energies. It gives results, which agree with experiments in many cases. Many experiments show discrepancy with the theory by up to 50%. Almost any theory can be defended by using a restricted set of data. In many cases the inconvenient data is dismissed as the product of bad samples by simply ignoring the data altogether. Optical properties are discussed briefly in Chapter 3. More detailed description of individual polymers is given in the chapters on LEDs and solar cells.

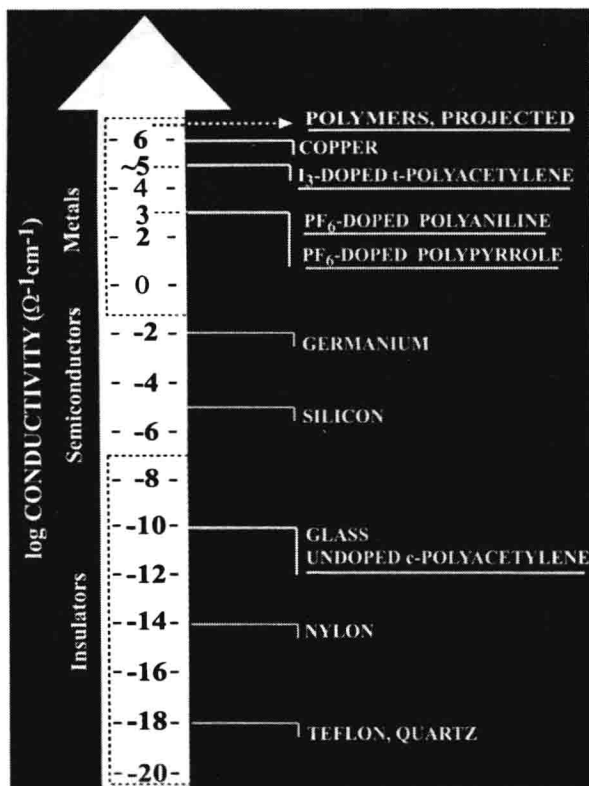


FIG. 1.2. Conductivity of polymers varies over 16 orders of magnitude. Both experiments and theory suggest that ultimate conductivity will be larger than that of copper as shown by the dotted arrow [12,13].

Much of the modeling of devices requires knowledge of the mechanism of the transport of charge carriers in the conducting organics. Because of the importance of transport properties, extensive work has been done on this topic. Transport properties are also discussed in detail in Chapter 3.

1.4. Active Devices

Since the discovery of electroluminescence from organic materials it has been recognized that the conducting polymers are important for fabricating the Organic Light Emitting Diodes (OLEDs). To improve the performance of OLEDs a good understanding of basic device physics is very necessary. Today OLED technology has become a competitor for conventional light sources and display technologies like liquid crystal displays. Displays based on organic semiconductors have already entered the market. Flat panel displays and LEDs, antistatic coatings, electromagnetic shielding, lights for toys, microwave ovens are important applications being pursued now. UNIAX Corporation in Santa Barbara has demonstrated alphanumeric OLED displays [3].

There is a large demand of green, blue and violet Light Emitting Diodes (LEDs) and lasers. These light sources are required for full color displays, laser printers, high-density information storage and for under-water optical communication. By reducing the laser wavelength from the present red to 360 nm the information that can be stored in a compact disc can be increased by a factor 4. These emitters will also be very useful in designing and developing instruments for medical diagnostics and all solid state full color flat panel displays. They will save power by replacing incandescent lamps with LEDs. The quest for blue and green semiconductor light sources has been on for over 30 years. Due to several breakthroughs in the early 1990s, violet, blue and green semiconductor light emitters have become available. During the present decade the evolution and rise of blue and green LEDs and lasers have taken place at an extraordinary pace. The materials and optoelectronic devices emitting light are reviewed in Chapter 4. One of the most spectacular achievements of this decade is the development of the violet, blue and green light emitting diodes, optically pumped lasers and laser diodes. These devices are based on conducting polymers and oligomers, III-Nitrides, and II-VI semiconductors. Work on the properties of organic materials and devices is described in Chapter 4. Organic electroluminescence has bright feature for low cost, lightweight, large area flexible full color flat panel electronic displays. LEDs are discussed in Chapter 4.

Organic solar cells have reached efficiencies exceeding 4%. In fact power conversion efficiencies of organic solar cells have reached an impressive 5%. This has been possible because of the discovery of bulk heterojunction solar cells. Solar cells are discussed in Chapter 5.

First organic thin film transistors were fabricated more than 15 years ago [16]. Very significant improvements have been made in the performance of OFETs. Organic Thin Film Field Effect Transistors (OFETs or OTFTs) are of great interest for both academic and industrial institutions. Several authors have fabricated organic OFETs with performance comparable to the best amorphous silicon transistors. The mobility of the charge carriers is improved considerably. In pentacene transistors mobility of more than $1 \text{ cm}^2/\text{Vs}$ has been obtained. The transistors have application as drivers for flat-panel displays, smart cards, electronic barcodes and in other low cost electronic devices. OFETs are discussed in Chapter 6. The transport of the charge carrier in OFETs has been generally interpreted using the mobility model. The mobility of highly pure and defect free crystals of small molecules follows the same behavior as the inorganic semiconductors. In this case, mobility decreases with temperature. The mobility in OFETs is also discussed in Chapter 6.

CHAPTER 2

POLYACETYLENE

2.1. Structure, Growth, and Properties

2.1.1. STRUCTURE

Polyacetylene is the simplest conducting polymer. The two forms of conducting polyacetylene, known as *trans*-polyacetylene (or *t*-PA) and *cis*-polyacetylene (or *c*-PA), exist. They are shown in Fig. 2.1(a). The bandgap of *t*-PA is about 1.4 eV and that of *c*-PA is 2.0 eV. The *t*-PA is of greater academic and technological interest. It has two degenerate ground states as shown in Figs. 2.1(b) and 2.1(c). The degeneracy of the ground state of *t*-PA plays a significant role in determining the properties of the polymer. Typical polymers with non-degenerate ground states are shown in Table 2.1.

2.1.2. GROWTH AND DOPING OF POLYACETYLENE

The most commonly used method to synthesize the PA is the Shirakawa method. In this method a smooth surface wetted by the Ziegler–Natta catalyst is exposed to the acetylene gas. A film of PA (generally *c*-PA) is produced on the smooth surface. The *c*-PA is converted to the *t*-PA by heating. The process of doping also converts the *c*-PA to the *t*-PA.

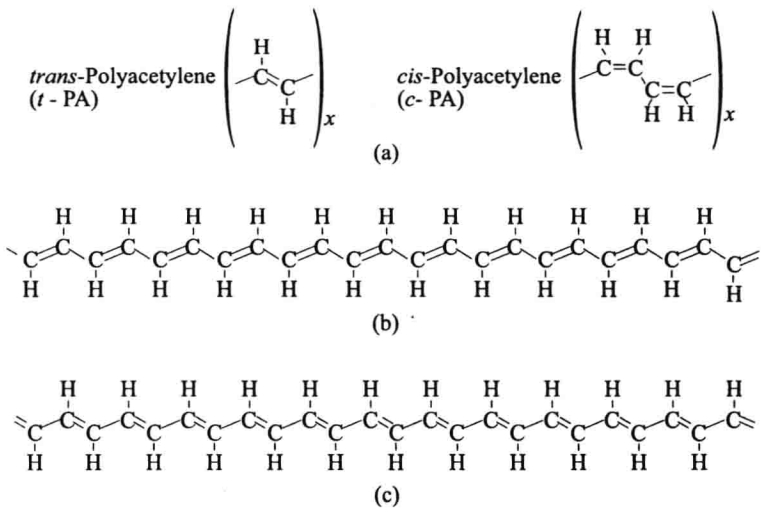


FIG. 2.1. (a) Structure of the *t*-PA and *c*-PA repeat units; (b) and (c): two degenerate ground state configurations of the *t*-PA.