Conducting polymers—Physical concepts and practical applications

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Developments in different fields of applications of conducting polymers, e.g., electrical conductivity, luminescence and non-linear optics, localisation and large scale electronics are discussed. The paper summarises the experience accumulated in the Network NEOME, a network of the European Materials Research Society.

1 Introduction

Conducting polymers have been known for several decades. They did not attract much attention, however, until 1977, when it was reported, that polyacetylene treated with iodine could show conductivity values up to \(10^3\) S/cm (ref. 2), which triggered a world-wide research and publication activity. Iodine-doped polyacetylene is not the only conducting polymer. Figure 1 shows the chemical structure of a family of polymers, which all become conducting upon “doping” with an oxidising or reducing agent.

![Chemical structures of some polymers which become electrically conducting after “doping”](image)

L1: Electrical conductivity
L2: Luminescence and non-linear optics
L3: Localisation
L4: Large scale electronics

Conductivity, luminescence, and localisation are closely related to the conjugated double bonds, which are characteristic of the structure of these polymers (regular alternation of single and double bonds as shown in Fig. 1).

L1: Double bonds are unsaturated bonds. Therefore, they can be easily attacked by chemical methods. This is what happens during the doping procedure. Oxidation removes electrons from the polymer and free sites are created (“holes”), into which other electrons can move so that finally the whole electronic system in the conjugated bonds becomes mobile and hence conducting. Upon reduction, additional electrons are transferred to the polymer. This process also leads to “partially filled bands” and consequently to metal-like conductivity.

L2: Double bonds can be attacked not only chemically but also optically. This implies breaking the double bonds by absorption of light. When the bond is closed again the binding energy is set free and emitted as light. This is the well known phenomenon of luminescence. In a semiconductor optical breaking of bonds is usually accompanied by charge separation: an electron is lifted from a bonding state (in the valence band) into an anti-bonding state (in the conduction band). A positively charged “hole” is left back in the valence band and a negatively charged...
"excess electron" is created in the conduction band. The recombination of hole and electron leads to luminescence. Those electrons and holes, which escape recombination, are the photogenerated charge carriers which lead to photoconductivity.

In addition to the chemical generation of holes and excess electrons (via oxidation or reduction, i.e. doping) and the optical generation (absorption) there is also the possibility of injection from metal electrodes. In this case metal electrodes are evaporated on both sides of a polymer film and an electric field is applied between the electrodes (Fig. 2). The holes are injected and "electroluminescence" is observed. Light emitting diodes are used in displays and in particular, they are the basis of future large, flat and flexible video screens.

L3: In a three-dimensional crystalline semiconductor like silicon or germanium electrons and holes are described as Bloch waves. These are harmonic waves, which are delocalised over all of the crystal volume. The chain-like structure of the polymers leads to strong coupling between electronic excitations and "lattice deformations" (conformation changes of the polymer) and this strong coupling localises the excitations. The coupling is easy to understand: The creation of a hole implies removal of a binding electron, i.e., transformation of a double bond into a single bond. As a consequence, the bond length changes and very often the polymer chain twists. In silicon and germanium conformational changes are of very little importance, because not only the atoms are bound to neighbours on the left hand and the right hand sides, but they are also fixed in their positions from top and bottom and front and back. The localisation of excitations in organic materials can—at least theoretically—be used to localise information and thus it is the basis of "molecular electronics", which would have a much higher integration density than the semiconductor electronics of nowadays.

L4: In addition to the displays and video screens mentioned above, solar cells and other photovoltaic or photochemical solar energy converters are examples of applications in large scale electronics. Optical wave guides based on organic materials also belong to this field. Here advantages over other materials are expected because of the cheaper processability of polymers. Of course, compared to more conventional polymers, polymers with conjugated double bonds are not easily processable, but in comparison to molecular beam epitaxy and electron lithography used for processing other materials even complicated polymer processes are fairly cheap.

2 Conductivity

In most polymers with conjugated double bonds, doping leads to an electrical conductivity between 10 and 100 S/cm. In Fig. 3 the conductivities of some well

Fig. 2—Electroluminescence in polymers. Schematic set-up: a polymer film is sandwiched between two evaporated metal electrodes

Fig. 3—Conductivity chart. The arrow indicates the conductivity regime which can be covered by polymers. The hatched point of the arrow corresponds to samples with "metal-like" conductivity.
known materials are compiled and compared with those of conducting polymers. We see that conjugated polymers cover the whole conductivity range from insulators to metals. The highest conductivity has been obtained in iodine-doped polyacetylene: the group at BASF has reported a value of $1.5 \times 10^5$ S/cm and in a Japanese paper a curve is reproduced reaching as high a value as $9 \times 10^5$ S/cm. So far, however, other groups have not yet succeeded in producing polyacetylene with a conductivity above $3 \times 10^4$ S/cm. (Conductivity of a sample synthesised by BASF has been measured at Bayreuth and a value of $8 \times 10^4$ S/cm has been found). There is general agreement that the value $3 \times 10^4$ S/cm is the “state of the art”, if some care is put into sample preparation. Figure 4 shows how the conductivity of polyacetylene changes by exposure to iodine or AsF$_5$ (the data are reproduced from a relatively early work, so that the curve saturates at about $10^2$ S/cm). Note the large doping concentrations, which are needed for high conductivity: some 5 molar per cents, i.e., one electron is removed from every tenth double bond! Typical doping concentrations for inorganic semiconductors like silicon or germanium are by several orders of magnitude lower!

Figure 5 shows the temperature dependence of the conductivity for various iodine concentrations in polyacetylene. We see that the conductivity drops in all cases if the sample is cooled. According to conventional material classification we would regard this as typical of semiconductors. In today’s solid state physics it is quite common to classify the conducting behaviour by the zero temperature limit rather than by the temperature coefficient: If the conductivity vanishes at $T \rightarrow 0$, we speak of semiconductors, if it stays finite we speak of metals. In crystalline semiconductors the conductivity follows the well known exponential law,

$$\sigma \propto e^{-\Delta E/kT}$$

The temperature dependence of polyacetylene at very low doping concentrations looks similar. At highest doping concentrations, not only the total value of the conductivity increases (because there are many charge carriers), but the curves become more flat also and rather follow the law,

$$\sigma \propto e^{(\Delta E/kT)^{1/4}}$$

which is known from work on amorphous semiconductors and applies to “variable range
hopping. In amorphous semiconductors the electrons do not move in the conduction band; they hop from one defect site to another. In variable range hopping the conductivity also freezes out on cooling, but more slowly than in semiconductors with band conductivity. In Fig. 5 the conductivity stays finite at low temperatures for samples with more than 5% iodine concentration. According to the above terminology these samples are metallic and doping induces a semiconductor-to-metal transition.

On the basis of the behaviour of good metals we are used to an increase in the conductivity as the sample is cooled. This behaviour is due to freeze-out of lattice vibrations and it is well known that collisions between electrons and lattice vibrations limit the conductivity in metals. In variable range hopping, on the contrary, lattice vibrations favour conductivity as they assist in the hopping process. In Fig. 6 we compare the temperature dependence on the conductivity of poorly conducting and a highly conducting sample. The conductivity of the highly conducting sample is nearly independent of the temperature. The sample does not yet quite behave like a good metal, but it resembles a metal in the regime of residual resistance, where the conductivity is limited by collisions with defects rather than lattice vibrations. There are also some reports on polyacetylene samples, in which a negative temperature coefficient of the conductivity has been found at room temperature (maximum of the conductivity at about 200 K).

For technical applications, the temperature dependence of the conductivity is only of minor importance. But the temperature dependence allows one to determine the mechanism of the conductivity and hence to predict theoretical limits. For this theoretical limit of the conductivity, experts have estimated a value of $2 \times 10^7$ S/cm. This limit is by more than two orders of magnitude higher than the room temperature conductivity of copper. This high conductivity would be obtained in (hypothetical) completely perfect polyacetylene single crystals. If there were no defects in the single crystals, the conductivity would only be limited by collisions with lattice vibrations. In these collisions energy and momentum must be conserved. Since electrons can—to a first approximation—move only along the polymer chains, there are—in contrast to conventional three-dimensional metal—only few lattice vibrations, which fulfill the conservation laws in collisions with electrons.

As for applications, today hardly anybody thinks of replacing copper wires by polyacetylene ropes. Polyacetylene exhibits the highest conductivity values and in addition it is of great interest from the viewpoint of basic research and theoretical considerations, but for practical applications less conducting polymers are more important, e.g., polypyrrole, polythiophene, polyphenylene, polyvinylene, and polyaniline. The stability and the processability of these polymers are decisive factors. The conductivities are usually between 1 and 100 S/cm only, but these values are for many purposes sufficient, such as transparent coatings, condensers, packaging materials for sensitive electronic devices,
If the electrons can be displaced easily, as in conjugated double bonds, the polarisability $\alpha$ is large. But in this case polarisability also saturates quickly, because the electrons bump against the chain ends. Additional terms must be added to the polarisability, $p = \alpha E + \beta E^2 + \gamma E^3 + \ldots$ where $\beta$, $\gamma$, etc. are the so-called hyperpolarisabilities. We easily see that in an AC field with large amplitude the polarisation will not be able to quite follow the field. This leads to a distortion of the original oscillation (Fig. 8). The distorted wave
has higher harmonics in its Fourier spectrum, and so we can understand that a non-linear optical material hit by light will emit frequency—doubled and frequency—multiplied light. Frequency multipliers and frequency mixers are important optical devices. Another aspect is the intensity dependence of the index of refraction. This is used in directional couplers in integrated optics: depending on its intensity a signal can travel along the left hand or the right hand branch of a bifurcation. This and similar concepts form the basis of “photonics”, a possible alternative to the electronics of today. Because of their larger non-linear optical effects and because of their better processability, conjugated polymers could be advantageous over conventional (inorganic) non-linear optical materials, if in future some photonics develop.

4 Localisation

As already mentioned, in systems with conjugated double bonds there is a very strong coupling between electronic excitations and the underlying “crystalline lattice of the solid”, i.e., electronic excitations lead to conformational changes. This coupling allows for strong localisation of the excitations and might be useful in information technology for higher density memories and ultra fast switches. This is the basic idea of molecular electronics and there is general agreement, why in its theoretical limits molecular electronics will beat conventional electronics.

Here again polyacetylene is a model substance. Due to the strong electron-lattice coupling, holes and excess electrons in polyacetylene turn into “solitons” — at least within zero approximation.

In the terminology of solid state physics electrons are Bloch waves. These are harmonic waves, which are delocalised all over the solid. If we want to make electron pulses, we have to construct wave packages from harmonic waves. These packages have a finite extension, but if the packages move they “disperse”, because each component travels with a different velocity. Solitons are very special pulses, which do not disperse when moving. This behaviour is schematically shown in Fig. 9 (ref. 4).

Experimentally, it is difficult to decide whether excitations in polyacetylene disperse or do not disperse. But through absorption of light such excitations can be created in polyacetylene (i.e., holes and excess electrons coupled to the lattice) and these excitations can be moved by applying an electric field. All we have to do is to carry out a photoconductivity experiment: evaporate electrodes onto the sample, apply a voltage, illuminate the sample, measure the photocurrent—actually the inverse of the set-up in Fig. 2. If the illumination is very short, e.g., picosecond pulses of an appropriate laser, the temporal decay of the photocurrent can be measured. Under certain circumstances then the velocity of the charge carriers can be estimated (if the distance of displacement = schubweg is known) and from this the mobility. This value of the mobility can be compared to predictions made on the basis of various soliton or non-soliton theories. Figure 10 shows the result of such a measurement. Photocurrent decay times of some picoseconds cannot be determined by electronic means, because all detectors and amplifiers are much slower. Therefore, a so called optical correlation experiment has to be carried out, in which two fast optical switches are put in series and the switches are successively illuminated by two pulses, one retarded with respect to the other by allowing it to run along a somewhat longer optical path. An optical “double-switch” is shown in Fig. 11. The dark fields are strip electrodes and the Si film on the (CH)₅ film [(CH)₅ = polyacetylene] represents the respective switches. The 6 ps decay in Fig. 6 furnishes the desired information on the mobility of the charge carriers. This will not be discussed here in detail. In any case, we see that a fast optical switch can be made from polyacetylene. Fast switching in polyacetylene can be used for data processing—at least on a laboratory
solitons in polyacetylene but solitons in glass fibers. But the discussions on polyacetylene solitons have also cross-fertilised increases in knowledge on glass fiber solitons. The figure compares a message carried by solitons. Through their form-conservation (non-dispersion) solitons can be packed much more closely than wave packages. (That in glass fibers there are solitons instead of wave packages is also due to non-linear optical effects.)

5 Large scale electronics

Large scale applications of conducting polymers have been discussed for quite a long time. During this time the term "large scale" has experienced a remarkable transmutation. Originally, many people associated synthetic metals to plastic shopping bags which—in addition to their plastic properties—would also be electrically conducting. Expectations were in terms of thousands of tons per year and corrugated iron or roofing felt were thought to be competitors. Today we compare conducting polymers (and their semiconducting pristine forms) to, silicon and gallium arsenide and whatever is larger than a finger nail is large scale!

The first semiconductor-oriented request was in the early 1980's and it came from the area of high energy physics. Some colleagues working in this area wanted to build a solid state elementary particle detector and realised that 1 m$^3$ of silicon single crystals would exceed their financial means. They thought of replacing the expensive silicon by the certainly cheaper polyacetylene, which has about the same energy gap between valence and conduction bands. That such a polyacetylene detector would be feasible enough can easily be seen from the decay of the transient photoconductivity in Fig. 10. But ten years ago nobody was willing to take the risk of the development expenses for such a project (and probably even today nobody would be willing either).

**Fig. 10—Decay of photocurrent in polyacetylene after picosecond excitation**

**Fig. 11—Fast optical switch on polyacetylene basis, connected in series to a fast silicon switch (Fig. 10 is the cross-correlation of the responses of the two switches)**

**Fig. 12—Solitons in data transmission. The form conservation (non-dispersion) of the solitons allows for a considerably higher transmission rate**

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**Zo**

**to boxcar**

**Si-film**

**sapphire**

**Au-electrode**

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scale: A British group has reported on pattern recognition by the aid of holograms, which had been stored in polyacetylene films$^{32}$. Since recording a hologram needs only one or two picoseconds and a few picoseconds later the next hologram can be recorded (because of the fast relaxation in polyacetylene) a world record in the data processing rate has been obtained.

Figure 12 shows that solitons are of general use in information technology. In this case we do not look at
At around the same period polycyacetylene-based solar cells were also considered. But when the prices of amorphous silicon suddenly dropped, the interest in polymers for photovoltaics considerably decreased. We can expect that it will revive sooner or later.

As already mentioned, today large scale light emitting devices seem to have the largest potentiality for applications and we dream of video screen several p(;

produce large area all-polymer field effect transistors.32 - 34. An example thereof is schematically shown in Fig. 13. But even such a transistors32 - 34. An example thereof is

(ITO, i ium tin oxide, is today the most common materia for transparent electrodes).

Concluding remarks

This report summarised the experience accumulated in the Network NEOME. NEOME is both a network of the European Materials Research Society (E-MRS) and of the European Strategic Programme for Research and Development in Information Technology (ESPRIT). NEOME is an acronym for “Network of Excellence on Organic Materials for Electronics”. This network consists of 12 nodes distributed over various European countries. The author of this article represents one of the nodes. The paper is based on a talk given at a meeting of the Deutsche Gesellschaft für Galvanotechnik, of which a German version will appear in “Galvanotechnik”.

References