Phys. Technol. 16 (1985). Printed in Northern Ireland

MOLECULAR ELECTRONICS: 3

ELECTRICALLY CONDUCTING POLYMERS

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The first experiments on electrically conducting polymers began thirty years ago. Efforts since then to enhance their conductivity for use as active electrical components have led to the discovery of a promising new group of materials, although many practical difficulties remain

Plastics, or thermoplastic polymers as they should be called, are made up of long chain molecules. It is these chains which give them their attractive processing and mechanical properties. To have materials which are processible by the low-temperature moulding techniques used for common thermoplastics, but which, once processed, will display appreciable electrical conductivity, is an exciting idea. Unfortunately, such materials do not yet exist. The attraction of conducting polymers lies not just in a simple combination of polymer processing with high electrical conductivity. Rather, these materials may be a totally new class of materials and their properties and potential should be judged accordingly.

To understand the differences between this novel group of materials and the more conventional ones, it is instructive to examine the development of the field through its history. This history is dominated by one polymer, polyacetylene. There are two reasons for this: it was the first of these materials to be produced in a usable form, and it also shows fascinating anomalies in its electrical behaviour. Once the field became firmly established other polymers were synthesised, but these have not yet been subjected to the same intense scrutiny.

This article will outline the history of conducting

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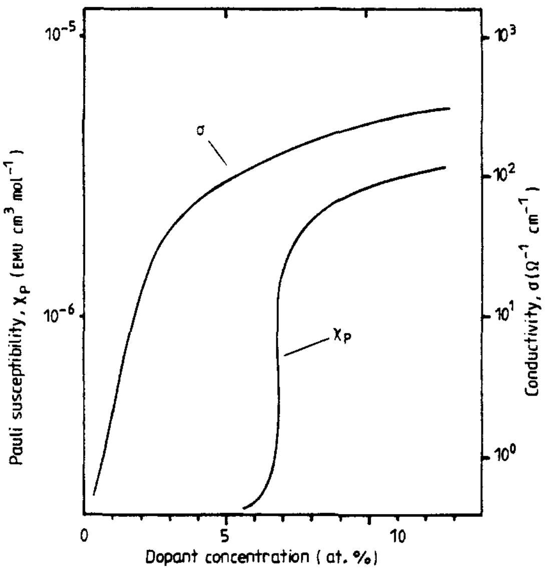


Figure 1 Relationship of electrical conductivity and magnetic susceptibility to dopant concentration.

polymers, review some proposed applications and attempt to assess their future.

Background

Conducting polymers have been around since the latter half of the last century. Indeed many of the 'new' conducting polymers are prepared by synthetic routes which are decades old but which were discarded at the time of their original discovery because they only produced black, intractable powders. The first step on their route to scientific respectability came in the 1950s when Natta polymerised acetylene using the catalyst which is used to produce polyethylene and polypropylene. He too obtained a black, intractable powder, but it was sufficiently pure to be properly characterised. It was at this point that physics entered the field of conducting polymers.

Twenty years earlier it had been postulated that an infinitely long chain of carbon atoms, joined by alternating single and double bonds, would be electrically conducting. Each carbon atom in the chain possesses four electrons in its outer shell. Two of these electrons are used to form the σ bonds which make up the polymer chain, the third electron is used to bond to the hydrogen atom which is attached to each carbon atom and the final electron occupies a p_z orbital which forms the π double bond. These π orbitals were envisaged as being delocalised along the chain to form a one-dimensional band. Since each orbital possessed only one electron this band would be half-filled, and thus metallic. The material would be a metal along the chain, and an insulator across it.

Alternative theories suggested that the energy required to effect this structural reorganisation was prohibitive, and that some bond alternation would remain. This residual bond alternation causes a gap to be formed in the middle of the band and the material would be a semiconductor. The polyacetylene Natta produced was a semiconductor. If it had been a thermoplastic this would have been an exciting discovery, but the lack of any form of processibility meant that the polymer was of no interest to anyone.

The real breakthrough came in 1971 with a means of making thin films of the polymer. These films were grown on surfaces wetted by a very concentrated solution of the same catalyst used by Natta. Films are far better than powders both for the investigation of fundamental properties and for applications. Even though it turned out that these films were in fact fibrillar materials made up of 20 nm fibres and two-thirds void space, a critical advance had been made. Conducting polymers became a hot scientific field of research. The final part of their elevation to scientific respectability came in 1976 with the discovery that oxidation and reduction could increase the conductivity of these films up to metallic levels, with conductivities of 1000 Ω^{-1} cm^{-1} being reported. Since the conductivity of the pristine material was around 10^{-9} Ω^{-1} cm^{-1}, the conductivity of polyacetylene could be varied over 12 orders of magnitude, from insulator, through semiconductor, to metal.

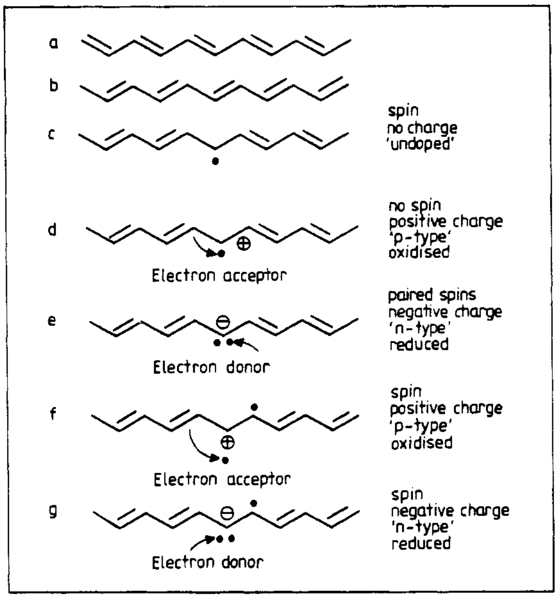
Polyacetylene properties

As understanding of this material increased, differences between it and conventional semiconductors and metals became apparent. Doping, as the redox modification became known, was carried out at the per cent rather than the parts per million level used on conventional semiconductors. High conductivities were achieved by large numbers of charge carriers moving slowly. Also, polyacetylene showed an anomalous relationship between its spin and charge (figure 1). As the level of doping was increased the conductivity rose steeply up to about 1% doping, rising only moderately as the concentration of dopant was increased further. Pristine polyacetylene possessed a moderate concentration of free spins which were all but wiped out at the 1% doping level, reappearing only when the dopant level rose beyond 6%. In the intervening regime then, the charge carrier, present in high concentration, showed no magnetic susceptibility. Put another way, it was not electrons and holes which provided the charge carriers.

Investigation and theory soon discovered that the reason for this apparent anomaly stemmed from the structure of polyacetylene (figure 2) and its remaining bond alternation. The nature of the backbone means that it is a planar zigzag, a, and transposition of the single and double bonds gives an apparently identical structure, b. It can readily be seen that to join one form to another requires a discontinuity with an electron which does not take part in a π bond, as shown in figure 2c. In fact, experiments and calculations suggest that this electron is delocalised over some 14 or so carbon atoms. This delocalised electron is the cause of the magnetic susceptibility of pristine polyacetylene; it has spin but no effective charge, and sits mid-way in the band gap. It is known as a soliton and can, in principle, move up and down the polymer chain. Its position within the band gap (figure 3) makes it easier to remove than electrons within the valence band. Thus on oxidation it is these mid-gap electrons which are removed first, causing a decrease in spin concentration and the formation of charge carriers, d. Similarly, on reduction the extra electrons added go into the mid-gap states to pair off with the existing electrons to give no apparent spin concentration and form charge carriers, e.

These processes continue until the original spins are used up. The processes of oxidation and reduction are then forced to break π bonds and form both spins and charge simultaneously, f and g. These spin–charge pairs are known as polarons. This change in mechanism takes place at around 6% doping and can also be viewed as a saturation concentration of solitons (at 14 carbons atoms each, 6% concentration would fill the chain). Naturally the occurrence of solitons with their interesting spin–charge relationships caused interest in the physics community and a large percentage of the work carried out in the field over the last seven years has been concerned with the mechanisms of conduction through the various doping regimes (0–1%, 1–6% and above 6%).

Figure 2 Structures of polyacetylene. **a** and **b**, undisturbed chain; **c**, soliton; **d**, positive soliton; **e**, negative soliton; **f**, positive polaron; **g**, negative polarons.



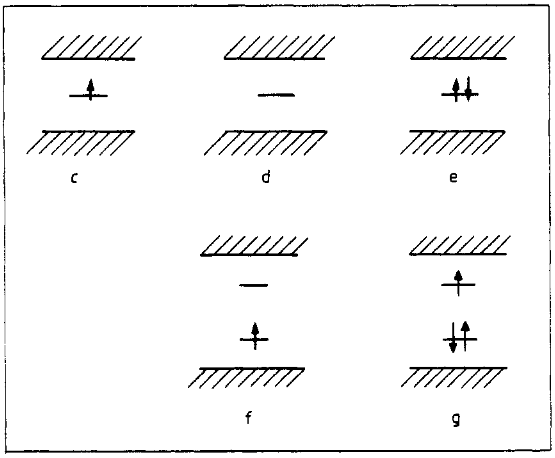


Figure 3 Band diagrams of solitons and polarons.

Stability

The original doping experiments were often carried out with oxidising and reducing agents which were easily available (i.e. on the laboratory shelf). As the process of 'doping' became better understood, many of the early dopants were discarded. For example, an early favourite was iodine: if polyacetylene was exposed to iodine vapour, its conductivity rapidly rose to low metallic levels. Unfortunately, prolonged exposure or even just leaving doped films around in an inert atmosphere caused a slow decay of the electrical properties. The reason for this effect lies in the fact that the iodide ion, formed by the redox doping process, is a strong nucleophile and attacks the positive charge carrier to form a covalent chemical bond. Other favourite oxidants (p-type dopants) had similar problems.

Curiously enough, the n-type material was more stable under similar conditions, since the equivalent reducing agents usually contained alkali metals as the counter cation. This problem of degradation can, however, be overcome. It is the dopant counter ion which reacts with the polymer chain. It is therefore necessary to use ions which do not undergo this chemical reaction. Unfortunately, such ions were not formed in chemical redox reactions, but they can be incorporated into the polymer by electrochemical methods. If two pieces of polyacetylene are placed in an electrolyte solution (e.g. lithium perchlorate in propylene

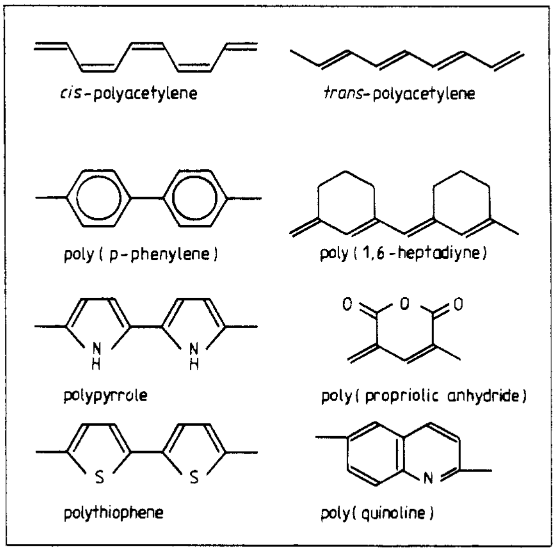


Figure 4 Structures of conducting polymers.

carbonate) and a voltage applied, then one piece is oxidised (p-doped) and the other is reduced (n-doped). It is the electric current which causes the doping, and the counter ions are supplied from the electrolyte. A suitable choice of electrolyte can therefore produce stable doped polyacetylene.

Since doping is a redox reaction, it follows that atmospheric oxygen can dope polyacetylene. In fact it gives rise to the same drawback as iodine, but to a much higher degree. If left in an atmosphere of oxygen polyacetylene rapidly degrades as the doping reaction is followed by chemical reaction. Thus all investigations must be carried out in the absence of oxygen.

The success of the early work on polyacetylene caused an increase in synthetic work aimed at producing new conducting polymers. The basic prerequisite for electrical conductivity (or at least the capacity for electrical conductivity on oxidation and reduction) is a conjugated structure. There are two basic families of conjugated organic polymers, polyenes and polyaromatics. Some typical structures of both types are shown in figure 4. Polyacetylene is the simplest polyene. It is unique in that the double and single bonds can be interchanged with no change in energy of the structure. In poly(1,6-heptadiyne) and poly(propiolic anhydride), for instance, such a rearrangement places the charge carrier on non-equivalent carbon atoms. Polyacetylene is thus the only polymer which can support the solitonic charge transport mechanism; the others can only support the polaronic mechanisms.

Beyond this basic requirement of a conjugated structure, other criteria have been discovered. Early work attempted to produce substituted polyacetylenes which might be more processible than the parent polymer. It was quickly found that while a substituted polyacetylene is indeed more processible, it is also a much poorer conductor of electricity. The second requirement of the structure is, then, that substituents should be avoided. The one exception to this rule appears to be fluorine, which may well have beneficial effects on the electrical properties.

Prospective uses

A variety of uses have been suggested for polyacetylene, both using the material as a replacement for conventional materials and in more novel applications. As the fundamental understanding of the material progressed, these latter applications have grown in interest and probably represent a better view of the future of this material. For example, although the prospect of a lightweight metallic conductor was attractive, it was rapidly discounted. The ultimate conductivities which could be obtained with polyacetylene were 1000 times lower than those of commonly used metals and the material was highly susceptible to oxidative degradation.

Next in line for investigation came the replacement of conventional semiconductors. Since polyacetylene displays electrical properties similar to amorphous semiconductors, it was inevitable that attempts would be made to use it in simple devices. However, since the counter ions used in p- and n-type materials are both mobile and capable of reacting with one another, work on p–n junctions has largely been abandoned. Instead, polyacetylene has been investigated as the active semiconductor in Schottky diodes.

It was quickly discovered that pristine polyacetylene has a work function of around 4.5 eV. This means that a blocking contact is obtained with metals like aluminium, and therefore the majority of data published is on aluminium:polyacetylene Schottky diodes. Several points are worth noting from these results. Firstly, the forward to back ratio of these diodes is typically 100. Compared with gold:n-silicon values of 10^{10}, this is abysmal. Secondly, derivation of the barrier height by the standard thermionic emission model gives a value which is twice that expected from the straight difference in the work functions of aluminium and polyacetylene. Although this may be explained by a high concentration of recombination centres in the depletion region, it is indicative of the general problem of applying standard theories to this novel group of materials. A final point is that the diode characteristics decay with time under reverse bias, although they recover if left at zero bias. A probable explanation for this effect is the diffusion of the dopant ion under the applied electric field.

Several groups of workers have attempted the construction and characterisation of a photovoltaic cell utilising a conducting polymer semiconductor. They were inspired by the close match of the absorption spectrum of polyacetylene to that of the solar spectrum and to date all published work has been on this polymer. Very little success has been obtained with heterojunctions against conventional semiconductors such as n-silicon and n-cadmium sulphide. Schottky devices, however, look remarkably attractive at first sight. Efficiency values in the range 0.1 to 1% are quoted if allowance is made for the energy loss through the thin blocking contact. These efficiencies are low but are coupled to a cheap production process. This has enabled at least one worker to predict a cost of $0.1 per peak watt for a polyacetylene solar cell, well within the US Department of Energy goal for 1986.

There are, however, several limitations to this use of conducting polymers. The first of these is their susceptibility to atmospheric oxidation, particularly strong in the case of polyacetylene, which has the most desirable electronic properties for this application. The second stems from the need to 'dope' the materials lightly to achieve the correct conductivity. The dopants typically used are capable of further chemical reactions with the doped chain and it is probable that these reactions are more facile with the chain in its photoexcited state.

Batteries

Perhaps the most promising (and fashionable) application of conducting polymers is in rechargeable batteries. The ability of conducting polymers to function as charge-storage materials is a function of their high charge-carrier concentration. Their application in electrochemical devices came about as a result of the experiments mentioned earlier, designed to separate out the two sequential processes which take place during doping, i.e. removal or addition of an electron to the polymer chain followed by the provision of a counter ion to balance the resulting charge difference. In chemical doping the same molecule carries out both functions, doing neither properly. Electrochemical doping provides a route to incorporate more stable dopant counter ions. In early electrochemical doping experiments it was discovered that the electrochemical potential of the doped material varied with doping concentration, hence it is possible to dope to a predetermined level by applying a specific voltage. What was soon apparent was that the cells which were constructed to carry out the doping experiments could also be used as batteries. Early work at the University of Pennsylvania was quickly taken up by industry both in America and Europe, and other polymers have been included in batteries with varying success. In polyacetylene, which is the most fully studied system, it is possible to obtain energy and power densities which are comparable with current commercial systems, and so the concept of a 'plastic' battery has been much discussed. However, there are still several problems facing the application of polyacetylene and the other conducting polymers to battery systems.

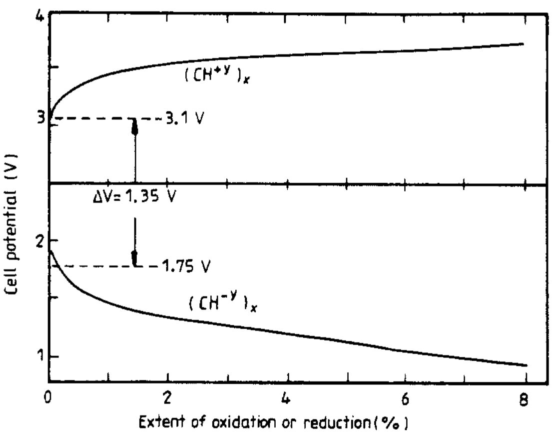


Figure 5 Electrochemical potential of p- and n-doped polyacetylene as a function of a percentage oxidation or reduction.

The polyacetylene battery system can best be characterised by the plot of electrochemical potential against percentage of oxidation or reduction (in effect, dopant concentration) shown in figure 5. This plot was obtained firstly by doping to known levels and then measuring the open-circuit voltage. In fact the voltage was found to decrease on standing, possibly due to the attainment of an equilibrium distribution of dopant counter ions. More recently a similar plot has been obtained using electrochemical voltage spectroscopy. In this technique, the voltage applied to the test cell is incrementally increased or decreased and the current flow measured. When the current flow drops below a preset limit the voltage is changed again; the current passed is integrated and provides a measure of the increase in the dopant level for that voltage change. The time required for this experiment (several days) underlines the problems of attaining equilibrium in these systems. The large initial current is a result of the large surface area of these materials (polyacetylene has an average surface area of $50\,m^2\,g^{-1}$). The surface layer contains a high proportion of easily lost dopant counter ions. If electricity is to flow from the electrode to do work, the counter ions must also move out of the electrode to maintain electrical neutrality and once this surface layer is lost the counter ions must diffuse from the bulk of the material. Even though the distance to be travelled is only around 10 nm, the low diffusion coefficients reported limit the current and hence the continuous power density of the resultant cell. Also, it can be seen from figure 5 that as the dopant concentration decreases, i.e. the cell is discharged, the voltage falls by 0.8–0.9 V. Neither of these problems have stopped the enthusiastic development of 'plastic batteries'.

Of particular interest is recent work on the use of conducting polymers in aqueous systems. It is a commonly held belief among chemists that carbonium ions and carbanions are unstable in water. This adds to the oxidative degradation problems already mentioned. In recent work reported from the University of Pennsylvania, however, polyacetylene has been oxidised by molecular oxygen in an aqueous solution of potassium tetrafluoroborate. It would appear from this experiment that the presence of a sufficiently strong counter ion can stabilise the polyacetylene to oxidative degradation.

This work has been extended to the application of polyacetylene in a fuel cell. In this apparatus, oxygen is bubbled over polyacetylene immersed in aqueous tetrafluoroborate solution. This causes the polyacetylene to become p-doped. The polyacetylene is connected through the external circuit to a lead electrode immersed in the same solution. When the polyacetylene is doped a current flows around the circuit and it undopes. Thus, the polyacetylene is chemically doped and electrochemically undoped to provide energy. Such systems are still in an early stage of characterisation and serve to illustrate the versatility of this group of materials.

Before leaving the electrochemical applications it is necessary to make a final point. The vast majority of work has been carried out on polyacetylene. Other systems are now being developed which show similar electrical properties, coupled to more acceptable stability. These systems must be fully and properly evaluated before the true value of conducting polymer electrochemical systems can be decided.

Future applications and problems

Although conducting polymers undoubtedly represent a novel group of materials, it is important to view the applications described against the comparative youth of the field and paucity of materials. Since the initial breakthrough in producing 'films' of polyacetylene, the majority of work, in both fundamental and application areas, has been carried out on this material. The early literature was characterised by several controversies which can be reasonably attributed to differences in synthetic and experimental techniques. However, several important points are widely agreed upon. The first is that polyacetylene is inherently unstable to oxidative degradation. This means that in applications this polymer must be protected from the natural environment. The second is that the doped polymer usually shows a degradation of properties which is caused by the chemical reaction of the dopant counter ion with the doped chain. This means that the dopant counter ion must be carefully chosen and that most chemical doping systems produce unstable material. The third point is that it still only possesses the minimum of processibility.

Thus it seems likely that 'real world' applications will utilise another of the family of polymers. In particular, systems based on aromatic chain repeat units show much higher stabilities to oxidation. However, the concentration of effort on polyacetylene because of its novel properties and materials advantages means that there is insufficient information to be able to judge these other materials.

The final point that should be made is that no application has yet advanced beyond the laboratory stage. Applications in which the conducting polymer is used simply as a replacement for a conventional material will probably not be successful. It is more likely that new applications based on the unconventional properties of these materials will make them into commercial realities, and with several hundred papers published every year in this field it seems reasonable to say that the challenge of finding these applications has been taken up.

Acknowledgments

The author would like to thank Norman Billingham, Paul Calvert, Jim Feast, Richard Friend and Colin Humphris for help in writing this article. The author would also like to thank BP for permission to publish this article.

Recommended reading

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