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Solitons in polyacetylene

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Abstract

Polyacetylene is presented both as a prototype conducting polymer and as a prototype one-dimensional metal and semiconductor. The concepts of the physics of one-dimensional metals are demonstrated on idealized polyacetylene. A review of the chemical and physical properties of real polyacetylene is given and experimental results on electrical conductivity, magnetic behaviour, optical spectroscopy and photoconductivity are discussed in the context of soliton-like excitations.

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1. Introduction

Electrically conducting polymers have attracted considerable attention in recent years. This is partly due to the fact that dealing with these substances combines, in an almost ideal way, two prime motivations for scientific research: the desire to study novel phenomena and to explain them using elegant theoretical models; and the hope for useful applications.

In materials science one is guided by the idea that new materials can be obtained in much the same way as the generation of a new biological species, namely, by hybridization, i.e. by accumulating onto one product properties that were originally attached to different products. Just as a 'pomato' is expected to bear tomatoes on its branches and potatoes on its roots, so the experts hope that electrically conducting polymers might combine the mechanical properties and chemical variability of organic synthetics with the electrical and optical behaviour of inorganic metals and semiconductors. For this new kind of material the term 'synthetic metals' (synmets) has been coined. Although presently available synthetic metals are no longer as easily processed as conventional polymers and have not yet gained the electrical conductivity of classical metals, there are nevertheless numerous promising proposals for technical applications, such as solar cells with a high energy-harvest factor, high power-density batteries, transparent antistatics and electromagnetic shielding. In the long term, probably on a scale of decades, applications in molecular electronics are considered possible. Appendix 1 presents a collection of some representative references on the applications of synthetic metals.

The novel physical phenomena that can be studied in electrically conducting polymers are related to the one-dimensional character of these substances. The most

attractive of the new theories is the soliton. Some very simple models show that a defect in a one-dimensional chain can bond all the atoms of a chain, as in a three-dimensional solid. This leads to effects such as quantum fluctuations (and waves and solitons). The discussion of these topics was the subject of conferences on low-dimensional physics.

During the last decade a large number of scientists has formed who have been studying conductors with A15 structure (transition metals) via Krogman salts (TTF-TCNQ, molecular crystals), polysulphur nitride ((SN)_x), (CH)_x, one-dimensional π -conjugated systems. They have been presented in the proceedings of the conference given in Appendix 2.

Solitons are kink- or soliton-like structures. Solitons are related to hydrodynamic waves as flood waves to ordinary waves. They are regarded as a superposition of linear and nonlinear waves. In general, waves having different frequencies are not coupled. Therefore, such a wave packet is not stable. On the other hand, does not satisfy a linear differential equation but a nonlinear differential equation. Such a wave packet is stable and occasionally solitary waves are observed. They are dragged through narrow channels and tides.

Similar nonlinear equations occur in many areas of physics. In the latter case solitons are quasi-particles, the soliton is a localized wave in crystals, domain walls in ferroelectrics and for bond defects in polymers. In this case the soliton is a localized wave. When the polymer chain is long, the soliton can be studied. The soliton is a localized wave. Symmetry properties of the soliton are of elementary-particle physics. The soliton is a localized wave. Particle number, pair creation, charges, confinement, etc.

One can easily imagine the soliton as a localized wave. Intellectually very appealing. Publications (which in its annual publications. In the soliton literature the key word 'soliton', 'polyacetylene' and 'soliton' key words occur together.

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attractive of the new theoretical concepts that have been applied to this study is that of the soliton. Some very simple facts, for example, that it is impossible to circumvent a defect in a one-dimensional system or that by changing the length of one chemical bond all the atoms of a chain move (because they are not supported from the sides, as in a three-dimensional solid), have very important consequences, which strongly influence transport phenomena, phase transitions and the nature of excited states. This leads to effects such as the metal-insulator transition (Peierls transition), quantum fluctuations (and perhaps fluctuation superconductivity), charge-density waves and solitons. The discussion of these effects has dominated several topical conferences on low-dimensional physics.

During the last decade or so a community of physicists, chemists and materials scientists has formed whose principal research interest has moved from superconductors with A15 structure (V_3Si , Nb_3Sn , etc., which contain chains of transition metals) via Krogman salts (KCP, well separated platinum chains), charge-transfer salts (TTF-TCNQ, molecular crystals with stacks of planar π -electron systems) and polysulphur nitride $((SN)_x)$ to polymers with conjugated double bonds (polyacetylene, $(CH)_x$, one-dimensional π -electron system). The results of these investigations have been presented in the proceedings of several topical conferences, details of which are given in Appendix 2.

Solitons are kink- or pulse-like excitations of physical systems. By analogy, solitons are related to harmonic excitations (phonons, Bloch waves, magnons) as flood waves to ordinary water waves. At any one time a flood wave can be regarded as a superposition of harmonic waves with different wavelengths. In general, waves having different wavelengths propagate at different velocities. Therefore, such a wave package should quickly disperse. A so-called 'solitary' wave, on the other hand, does not change shape. Just as harmonic waves are solutions of *linear* differential equations, so the solitary waves are solutions of certain *nonlinear* differential equations. Such nonlinear differential equations occur in hydrodynamics, and occasionally solitary waves can be observed in water, for example when ships are tugged through narrow channels or in the estuary of some rivers during the spring tides.

Similar nonlinear equations exist in elementary-particle physics and solid-state physics. In the latter case the concept of solitary waves and their corresponding quasi-particles, the solitons, has proven to be useful for the treatment of dislocations in crystals, domain walls in ferromagnets, phase-slip centres in charge-density waves and for bond defects in polymers. Here we pay special attention to solitons in polyacetylene. In this case the soliton is a defect in the conjugation of double bonds. When the polymer chain is long enough, the spreading of this perturbation along the chain can be studied. The conjugation of double bonds leads to very interesting symmetry properties of this defect and presents a close analogy to some phenomena of elementary-particle physics (existence of solitons and antisolitons, conservation of particle number, pair creation and annihilation, spin-charge inversion, fractional charges, confinement, etc.).

One can easily imagine that the possibility of unusual applications together with intellectually very appealing theoretical concepts has lead to a quickly rising flood of publications (which in itself resembles a soliton!). Figure 1 shows a histogram of annual publications. In the last few years about 6000 papers have been published with the key word 'soliton', 'polyacetylene' appears in 1380 papers; and in 404 papers both key words occur together.

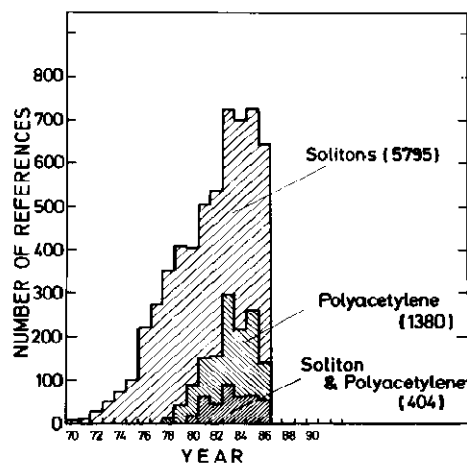


Figure 1. Histogram of annual publications, evaluating the key words 'soliton' and 'polyacetylene' (Source: *Physics Abstracts*, 1 January 1987).

The purpose of this article is (i) to give a fairly general introduction to conductive polymers and to the concept of solitons, (ii) to review arguments for and against the existence (and relevance) of solitons in conductive polymers, and in particular (iii) to report on experiments which may help to illuminate these problems. In what follows we seek to demonstrate that the symmetry properties of solitons are very useful, but point out that there is no experimental means, either now or in the reasonably foreseeable future, to verify their kinematic properties (conservation of shape during motion). In Appendix 3, references to some review papers and general articles on conductive polymers are compiled.

2. Chemical structure and morphology of electrically conducting polymers

It is a common feature of all conducting polymers that the pure substances are electrical insulators. Only after doping (oxidation or reduction) do they become conductors. This insulator-to-metal transition is an interesting phenomenon in itself, which will be discussed in some more detail in the next section. The change in conductivity upon doping is plotted in figure 2. Here the conductivity of polyacetylene is shown as a function of the doping concentration (where 'molar' concentrations refer to a CH group). As can be seen, doping increases the conductivity by seven orders of magnitude and conductivity values as high as some 100 S cm^{-1} are obtained, which is already in the metallic regime. In total a conductivity range of 15 orders of magnitude is available from highly doped samples on the one side to compensated samples, in which the background doping level of pristine samples is neutralized, on the other. This background doping is due to oxygen contamination or residual catalyst. The figure shows examples of acceptor doping with oxidizing agents like bromine, iodine or AsF_5 . However, donor doping with reducing agents (alkaline metals) is also possible and one can continuously cover the whole range from hole-conducting metal via p-type semiconductor, insulator and n-type semiconductor to metal with electron conduction. The enormous doping-induced conductivity change in polyacetylene was first shown in 1977 by Chiang *et al.* [2] and has attracted so much attention that in the years following all topical conferences on low-dimensional

Figure 2. Change of the electrical conductivity of polyacetylene, which behaves like an insulator in the undoped state, already close to those of some crystalline semiconductors: AsF_5 ; \square I_2 ; \triangle Br_2 ; \times S.

systems (see Appendix 2) deal with the change of conductivity values to date (see also Chiang *on Electronic Properties of* $1.5 \times 10^5 \text{ S cm}^{-1}$ [3].)

Meanwhile similar changes in conductivity values have been observed in other extended systems of conjugated polymers, as shown in figure 3. Polyacetylene is a conjugated polymer that can be doped to obtain high conductivity values. At present the study of polyacetylene is only as an impurity in nature, but its completely linear structure makes it, despite the fact it is not yet fully understood, a lattice dynamical calculation in figure 3 can be varied in many ways, be built in and so on. Appendix 3 deals with these polymers.

Systems of conjugated polymers, which have electrical conductivity, they are chemically and biologically relevant molecules. β -carotene has 11 conjugated double bonds. Vitamin A is half a carotene molecule. Retinal is the photosensory

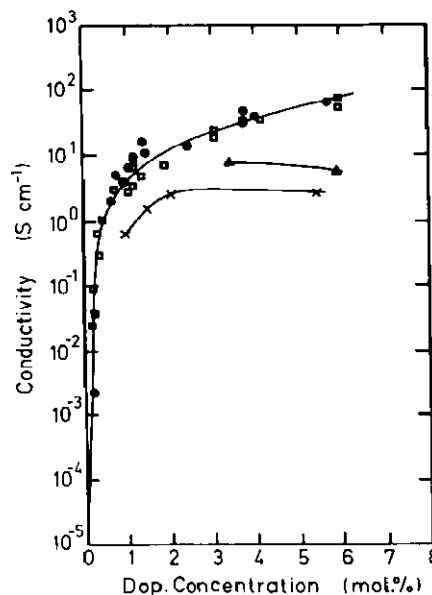


Figure 2. Change of the electrical conductivity of polyacetylene by doping. Pristine material behaves like an insulator; highly doped samples exhibit conductivity values that are already close to those of some metals [1]. D.c. room temperature; *trans*-polyacetylene: ●; AsF_6^- : □; I_3^- : △; Br_3^- : ×; SbF_6^- .

systems (see Appendix 2) devoted sessions to conducting polymers. (The highest conductivity values to date were presented at the International Winter School on Electronic Properties of Polymers, Kirchberg, March 1987, and amount to $1.5 \times 10^5 \text{ S cm}^{-1}$ [3].)

Meanwhile similar changes of the conductivity and comparably high conductivity values have been observed in several other polymers. They are all characterized by extended systems of conjugated double bonds. The most important of these polymers are shown in figure 3. Polydiacetylene is included in this figure, because it is the only conjugated polymer that can be obtained in the form of large single crystals (attempts to obtain high conductivity in this substance have not, however, been very successful). At present the study of polycarbene is not a very realistic prospect, since it is found only as an impurity in natural graphite and in interstellar matter. However, owing to its completely linear structure it does present a very attractive model system, and, despite the fact it is not yet feasible to obtain samples, several band structure and lattice dynamical calculations have already been carried out. All the structures shown in figure 3 can be varied in many ways: side groups can be added, heteroatoms can be built in and so on. Appendix 4 lists some papers on the chemical preparation of these polymers.

Systems of conjugated double bonds are not only important with respect to electrical conductivity, they also play a prime role in biophysics. Some of the biologically relevant molecules with conjugated double bonds are shown in figure 4. β -carotene has 11 conjugated double bonds and is a close relative of polyacetylene. Vitamin A is half a carotene molecule and retinal is a modification of vitamin A. Retinal is the photosensory part of rhodopsin, the pigment of vision: absorption of

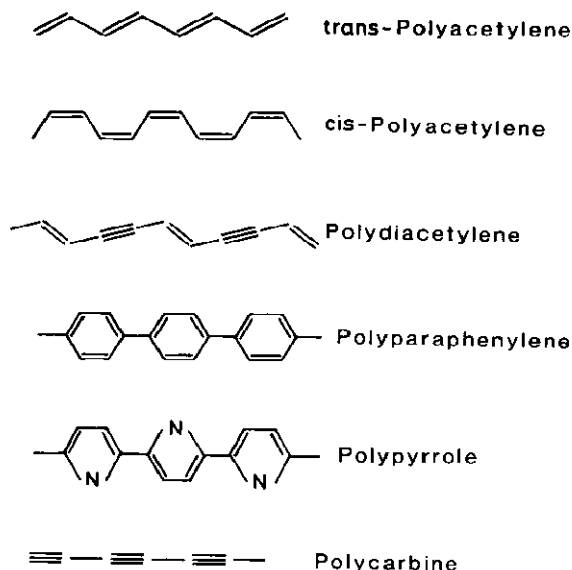


Figure 3. Chemical structure of the most important polymers with conjugated double bonds that are frequently discussed within the context of synthetic metals.

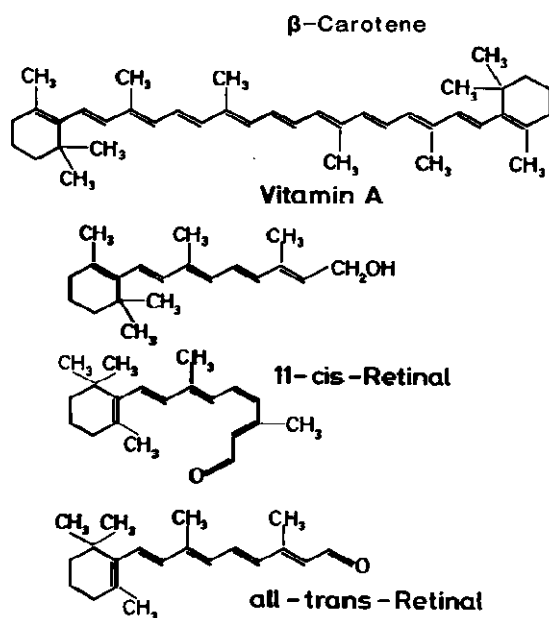


Figure 4. Biologically important macromolecules with conjugated double bonds.

light transforms the bent 1. Clearly physical investigation of biological processes.

2.1

Usually polyacetylene is perhaps *trans*-polyacetylene is our dreams of a one-dimensional zig-zag chain can easily transport an electron each to the solid. The three sp^2 hybrid orbitals forming the chain, the remaining p-orbital 'melts' into a band. In this way a linear chain of orbitals of which is determined by the structure are delocalized in a way very different from is a typical metallic property. It is unstable with respect to a Peierls transition.

The one-dimensional world is a fact that there is a *cis* and a *trans* form. This complicates some, but theory wins by the *trans*-polyacetylene. The high energy investigated much more energy computer search up to April 1971 by 599 on polypyrrole; 181, polyphenylene-vinylene, polyacetylene, partly in order to study other groups, but also to

2.2.1. Samples from Shirakawa

Real polyacetylene (in its form) presents a number of severe problems: irregularity of the growing chains; irregularity of the electron-micrographs of a sample usually obtained when prepared over a solution of the catalyst. Figure 5(a) shows the upper and lower side (*spätzle* side). As a rule one-third of the sample volume is in disorder. In as-grown films, these fibres are much disorder: there are no separated by amorphous regions. well oriented parallel chains. A schematic view of the structure is shown in figure 6. The pointers 1 and 2 indicate transport, which are discussed

light transforms the bent 11-*cis*-retinal into the stretched all-*trans* modification. Clearly physical investigations of conjugated systems can also help to understand biological processes.

2.1. Polyacetylene as a prototype

Usually polyacetylene is regarded as the prototype conductive polymer. Perhaps *trans*-polyacetylene is the substance where nature approaches most closely our dreams of a one-dimensional metal: The CH groups sitting at the corners of the zig-zag chain can easily be imagined to be metal atoms which contribute one electron each to the solid. The carbon orbitals in polyacetylene are sp^2 -hybridized, all three sp^2 hybrid orbitals form σ -bonds to the neighbouring carbon and hydrogen, the remaining p-orbital 'melts' into the conjugated system of double bonds, the π -system. In this way a linear chain of mono-electronic atoms is formed, the principal structure of which is determined by the σ -bonds. The electrons in the conjugated systems are delocalized in a way very similar to that in benzene. Delocalization of electrons is a typical metallic property. A very strongly one-dimensional metal, however, is unstable with respect to a Peierls distortion, which will lead to a metal-to-insulator transition.

The one-dimensional world of polyacetylene suffers a complication owing to the fact that there is a *cis* and a *trans* isomer. Usually we are faced with a mixture of the two forms. This complication often makes the interpretation of experiments cumbersome, but theory wins by exploiting the different symmetry properties of *cis*- and *trans*-polyacetylene. The highly symmetric form of ideal *trans*-polyacetylene has been investigated much more energetically than any other conducting polymer. (A computer search up to April 1987 revealed 1820 publications on polyacetylene, followed by 599 on polypyrrole; polythiophene, 383, polyphenylene, 323, polyaniline, 181, polyphenylene-vinylene, 67.) The present work, too, will deal mainly with polyacetylene, partly in order to allow us to compare our own investigations with those of other groups, but also to complement them.

2.2. Polyacetylene samples

2.2.1. Samples from Shirakawa synthesis

Real polyacetylene (in contrast to the ideal substance of theoretical physicists) presents a number of severe restraints: finite chain length; interactions with neighbouring chains; irregularity of chain orientation. Figure 5 presents two scanning electron-micrographs of a typical Shirakawa polyacetylene film. Such films are usually obtained when polyacetylene is synthesized by blowing acetylene gas over a solution of the catalyst [4]. The films will float on the solution like skin on milk. Figure 5(a) shows the upper side of such a film (*spaghetti* side) and figure 5(b) the lower side (*spätzle* side). As can be seen, the films consist of fibres which fill only about one-third of the sample volume. A typical fibre diameter is some hundred ångström. In as-grown films, these fibres lie completely at random, and even within a fibre there is much disorder: there are microcrystalline domains extending over perhaps 100 Å, separated by amorphous regions. The microcrystalline domains consist, of course, of well oriented parallel chains, but can contain a considerable number of point defects. A schematic view of the morphology of Shirakawa-type polyacetylene is shown in figure 6. The pointers 1 to 4 are to illustrate the various mechanisms of charge transport, which are discussed in §4.

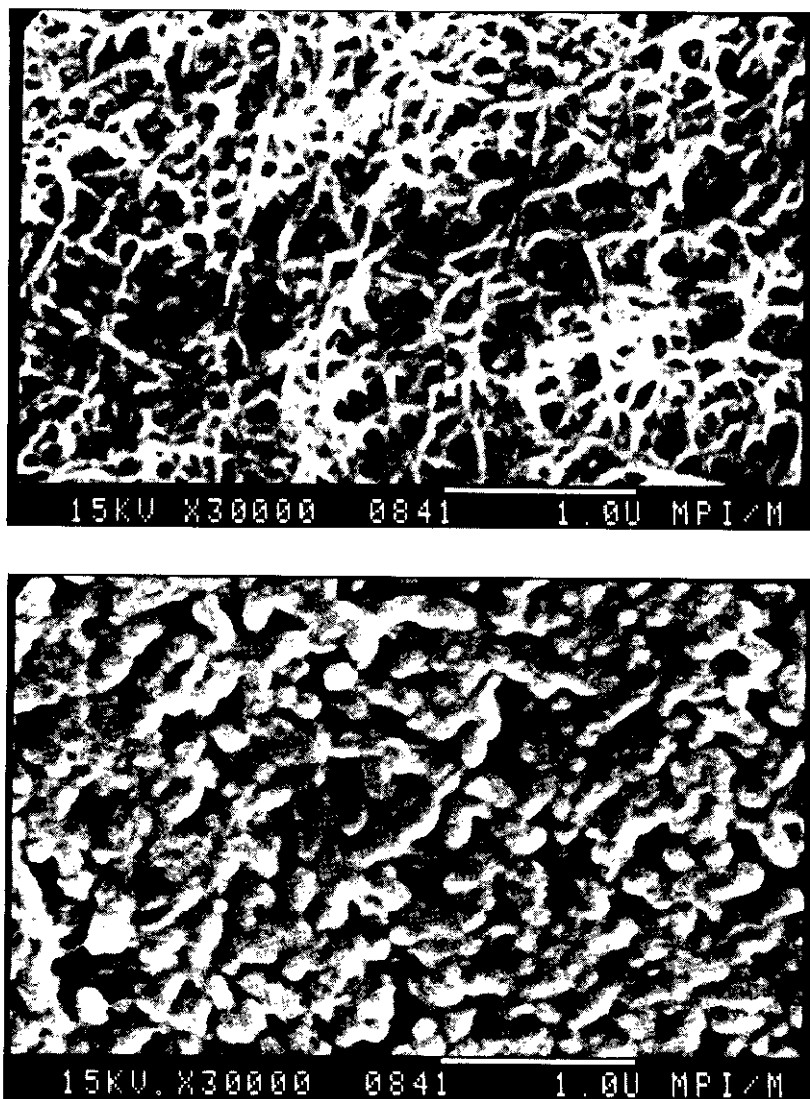


Figure 5. (a) Scanning electron micrograph of a polyacetylene film (*spaghetti* side, i.e. upper side of a film floating on the catalyst solution). The scale mark on the edge corresponds to 1 μm . (b) Lower side (*spätzle* side) of the film shown in (a).

2.2.2. Oriented samples

The morphology of polyacetylene can be changed by using different chemical syntheses or by subsequent treatment, such as stretching or rolling. Single crystals cannot yet be obtained, but at least it is possible to arrange the polymer chains so that they are parallel. Today there are three ways to achieve this:

- (a) cold working after polymerization [5];
- (b) growth on oriented substrates [6]; and
- (c) the Durham-Graz precursor route [7, 8].

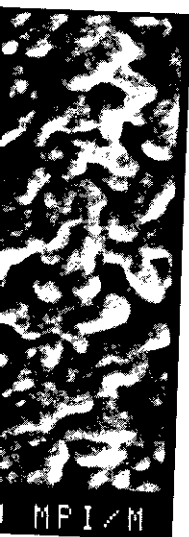


Figure 6. Schematic view

In the precursor route, a solution of the precursor is converted into a film. Conversion factors up to 20 can be obtained without determining the reaction conditions. The resulting films are very dense. The 'rocking curve' of an oriented film shows a high intensity of the reflection.



Figure 7. Scanning electron micrograph



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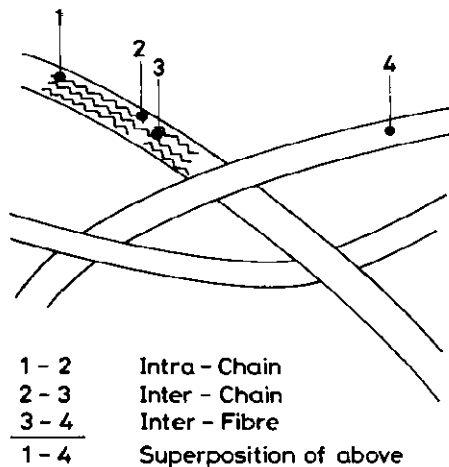


Figure 6. Schematic view of fibrillar structure of Shirakawa-type polyacetylene.

In the precursor route, a soluble precursor polymer is first prepared. By thermal treatment the precursor is converted into polyacetylene. During this conversion, stretching factors up to 20 can be obtained. The temperature at which the conversion is carried out determines the reaction rate and the *cis/trans* ratio of the final product. The resulting films are very dense and show no fibrillar morphology (figure 7). In figure 8 the 'rocking curve' of an oriented Durham-Graz sample is shown. In the rocking curve the intensity of the reflection (101) + (200) (see figure 9) is recorded while the sample



Figure 7. Scanning electron micrograph of oriented Durham-Graz polyacetylene [8].

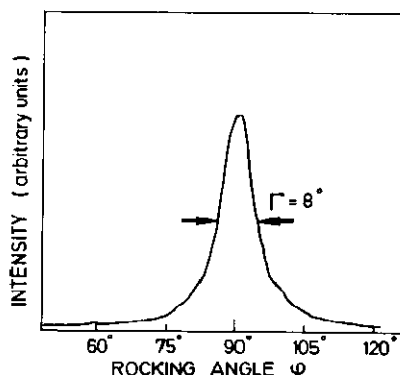


Figure 8. Rocking curve of stretch-oriented *trans*-polyacetylene: reflection (101) + (200). Rotation around an axis perpendicular to stretch direction; electron diffraction (J. Fink and G. Leising, unpublished work).

is rotated around an axis perpendicular to the stretching direction. Maximum intensity is obtained when the stretching direction is perpendicular to the scattering plane. Since the selected reflection is entirely due to chain packing, figure 8 shows that the chains are preferentially oriented parallel to the stretching direction. This result settles—at least for such samples—a controversy which existed in the literature for some time [9–11]. From the width of the rocking curve a misalignment of the polymer chains of $\pm 4^\circ$ can be obtained.

2.3. Crystalline structure and electronic structure of polyacetylene

In figure 9 neutron diffraction patterns of deuterated *cis*- and *trans*-polyacetylene are shown. The data were collected at the Grenoble high-flux reactor [12]. As can be seen, rather sharp reflections are obtained. From the width of the reflections the diameter of the crystallites can be estimated: values of about 100 Å have been calculated. Inspection of the spectra shows that the sharp peaks sit on a broad background structure. The ratio of peak intensity to background intensity is a measure of the crystallinity. This is found to be about 80%. From the position of the sharp reflections the structure of the elementary cell can be deduced. Figures 10(a) and (b) show the elementary cell for *cis*- and *trans*-polyacetylene in a plane perpendicular to the chain axis. Other investigations of the structure of polyacetylene have been carried out by X-ray and electron diffraction. Literature on the crystalline structure of polyacetylene is listed in Appendix 5.

Once the crystalline structure is known, the electronic band structure can be calculated. From the overlap integral of the π -electrons (the electrons in the double bonds) a bandwidth of about 10 eV is obtained along the direction of the polymer chains and of a few tenths of an eV perpendicular to it [13]. As one can see from the indices of the reflections in figure 9, the diffraction pattern is mainly determined by the packing of the polymer chains. The structure along the chains is very difficult to determine. This is especially true for the difference in length of the single and double bonds, which is very important for the calculation of the energy gap opening at the Fermi level arising from bond alternation and which transforms the one-dimensional metal into a one-dimensional semiconductor (Peierls transition). By carefully scanning special regions of the reflection pattern Fincher *et al.* [14] have succeeded in estimating

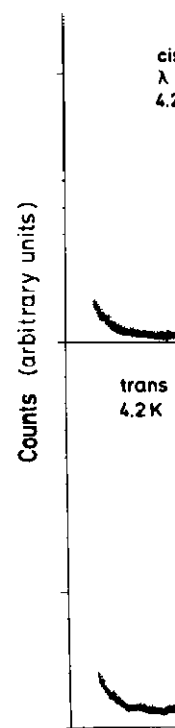


Figure 9. Neutron

this difference in bond length. Neutron diffraction investigations of polyacetylene by rotation spectroscopy, Yan et al. [15] give 0.08 Å. More recently, S

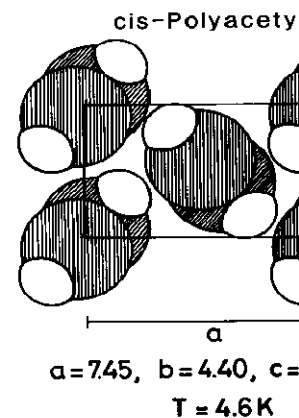


Figure 10. (a) Elementary cell of cis-polyacetylene

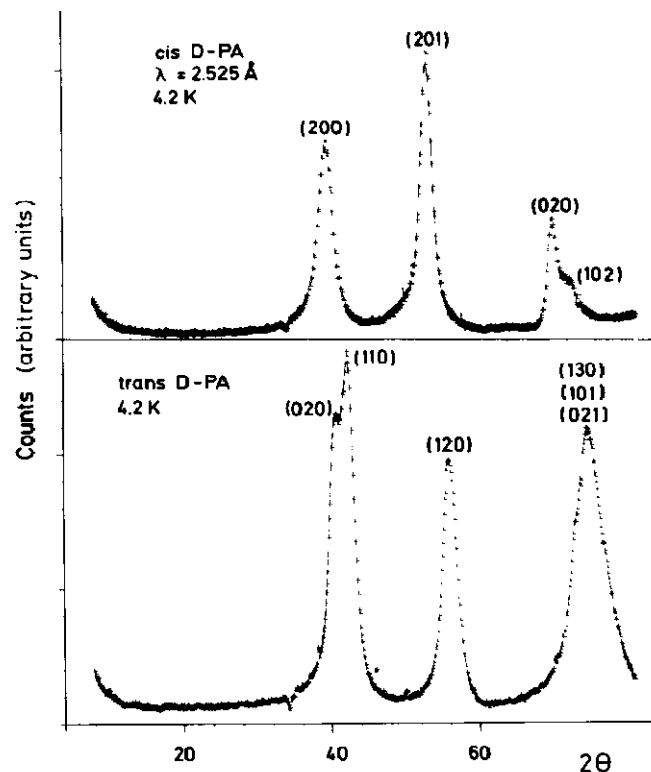


Figure 9. Neutron diffraction patterns of deuterated polyacetylene.

this difference in bond length as 0.06 \AA , which has been confirmed by the electron diffraction investigations of Chien *et al.* [15]. Using nuclear magnetic resonance nutation spectroscopy, Yannoni and Clarke [16] were able to determine this value to be 0.08 \AA . More recently, Springborg [17] has reproduced this experimental result by

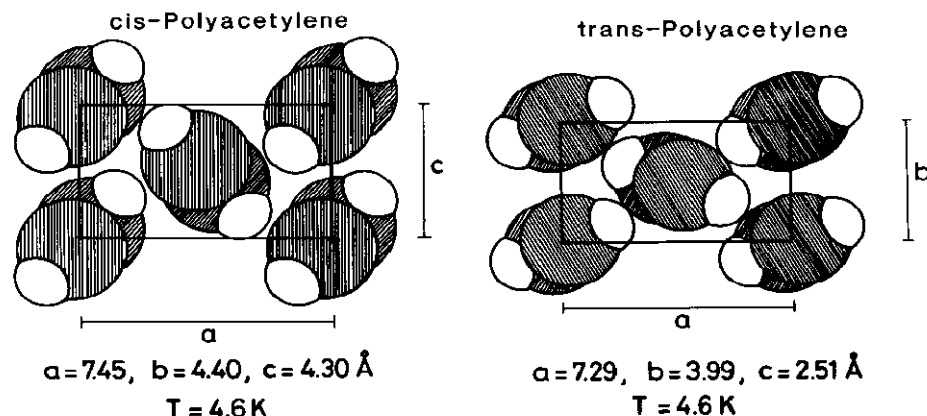


Figure 10. (a) Elementary cell of *cis*-polyacetylene perpendicular to chain direction. (b) Elementary cell of *trans*-polyacetylene perpendicular to chain direction.

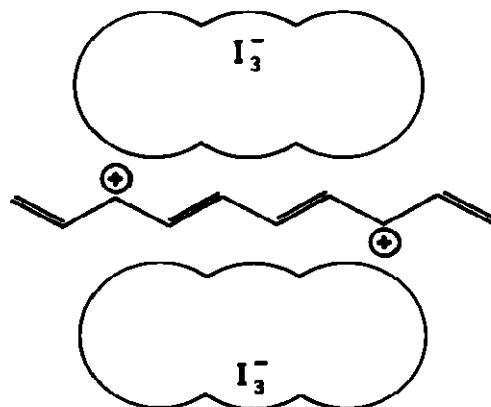


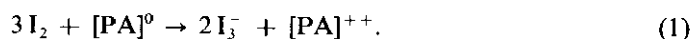
Figure 11. Proposed defect after iodine doping (G. Zerbi, private communication). The electronic shells of iodine are drawn to scale, whereas the polymer is represented by the backbone in order to show the bond defects more clearly.

self-consistent LMTO (linear muffin-tin orbital) calculations (0.086 Å). The value 0.88 Å is close to that one would need in order to explain [13] the optically measured energy gap of 1.4 eV without taking electron correlations into account. Horsch [18] has shown, however, that correlation effects in polyacetylene cannot be ignored. Their neglect would lead to an error of as much as a factor two in the gap energy. Today, this issue is considered to be one of the major controversies in the theoretical treatment of polyacetylene (see the discussion at the end of § 3).

2.4. Doping

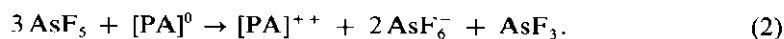
In the most simple case, polyacetylene is doped by exposure to a gaseous reducing or oxidizing agent. Most commonly iodine, bromine or AsF₅ are used, but by now more than one hundred dopants have been successfully applied. Some relevant literature is listed in Appendix 6.

We still know very little about the physical and chemical details of the doping process. Certainly electrical charges are transferred between the dopant and the polymer chain. In the case of iodine doping this will occur by the following reaction:



G. Zerbi (private communication) has suggested that this will lead to entities like that shown in figure 11. The presence of I₃⁻ ions can be verified by Raman scattering [19] and Mössbauer spectroscopy [20, 21]. From the latter we know that in addition to I₃⁻, I₅⁻ is also present. From a quantitative analysis of the Mössbauer spectra the concentrations of the ions can be determined. In figure 12 the relative I₃⁻ content is plotted against the total iodine concentration.

During the reaction with arsenic pentafluoride, AsF₅ is probably split off:



It is often argued that the term 'doping' should not be used in the case of conducting polymers. 'Intercalation' would be more neutral and would, in addition, stress the similarities with intercalated graphite. On the other hand, 'doping' elucidates the relationship between conjugated polymers and inorganic semiconductors: to the extent that conjugated polymers are one-dimensional systems, the doping of silicon

Figure 12. Relative content of I₃⁻ ions determined by Mössbauer spectroscopy.

and of polyacetylene are the same. The concentration within the host lattice is also the same. Accommodating an additional dopant ion requires the occupation of levels there. In the case of such shifts are the same. If the term 'doping' is abandoned, the unity of solid-state physics is restored. Studying conductive polymers is already beyond the one-dimensional case.

Figure 13 shows a series of X-ray diffraction patterns during AsF₅ doping of *cis*-polyacetylene (arrows) vanish and the emittance from pristine *cis*- or pristine *trans*-polyacetylene diffraction pattern. Because the pattern is not well resolved, there is no clear distinction between *cis* or *trans*.

The *trans* isomer (zig-zag structure) of polyacetylene. The usual Shirai structure (meander structure). The *trans* isomer annealing at 150–200°C (at 150°C) is clear. Doping also transforms *cis* to *trans*. Many authors assume that the doping is sufficient to induce a conformational change. Samples would be *trans*-polyacetylene are listed in Appendix 7.

The structural changes during the change of the chain conformation of point defects. The effective conjugation length can be inferred from the change of the Raman spectra. In these investigations the same doping). The Raman line at 1500 cm⁻¹ of the double bond; that at 1300 cm⁻¹. Both lines are resonance enhanced.

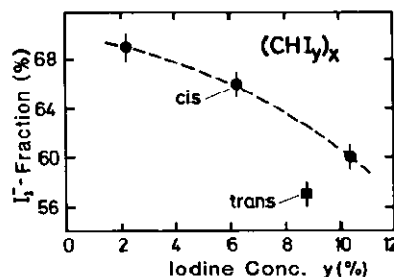


Figure 12. Relative content of I_3^- ions as a function of the total iodine concentration, determined by Mössbauer spectroscopy [20].

and of polyacetylene are the same physical phenomenon. In both cases the electron concentration within the host is changed and the effect of the dopant ion is neglected. Accommodating an additional electron (or hole) within the host will not only change the occupation of levels there, it might also shift the energy levels themselves. Extreme cases of such shifts are the solitonic and polaronic states discussed in the next section. If the term 'doping' is abandoned, this relationship will become blurred, some of the unity of solid-state physics will become masked and it will become less evident that studying conductive polymers will also help our understanding classical semiconductors. It is known that doping also affects the packing of polymer chains, but this effect is already beyond the one-dimensional approximation.

Figure 13 shows a series of neutron diffraction patterns, which have been recorded during AsF_5 doping of *cis*-polyacetylene. One can clearly see the pristine structure (arrows) vanish and the emergence of new peaks [12]. No matter whether one starts from pristine *cis*- or pristine *trans*-polyacetylene, doping leads to the same final diffraction pattern. Because the reflections resulting from order along the chain are not well resolved, there is no direct evidence for the isomeric state of the end product (*cis* or *trans*).

The *trans* isomer (zig-zag chain) is the thermodynamically stable form of polyacetylene. The usual Shirakawa method, however, leads primarily to the *cis* isomer (meander structure). The *cis* isomer can be transformed into the *trans* isomer by annealing at 150–200°C (at room temperature this transformation occurs only slowly). Doping also transforms *cis* into *trans*, but the details of this process are not yet very clear. Many authors assume that already very small amounts of AsF_5 or iodine are sufficient to induce a complete transformation and that consequently all doped samples would be *trans*-polyacetylene. References to the *cis*-to-*trans* transformation are listed in Appendix 7.

The structural changes due to doping are not only the *cis*-to-*trans* conversion and the change of the chain packing mentioned above, but also an increase in the concentration of point defects and, associated with that, an apparent decrease of the effective conjugation length of the π -electron system. The effective conjugation length can be inferred from the profile of the Raman lines [19]. Figure 14 [22] shows the change of the Raman spectrum of *trans*-polyacetylene during doping with AsF_5 (for these investigations the samples were thermally converted into the *trans* form before doping). The Raman line at 1500 cm^{-1} is mainly determined by the stretching vibration of the double bond; that at 900 cm^{-1} corresponds to the stretching of the single bond. Both lines are resonance enhanced. The resonance enhancement and the position of

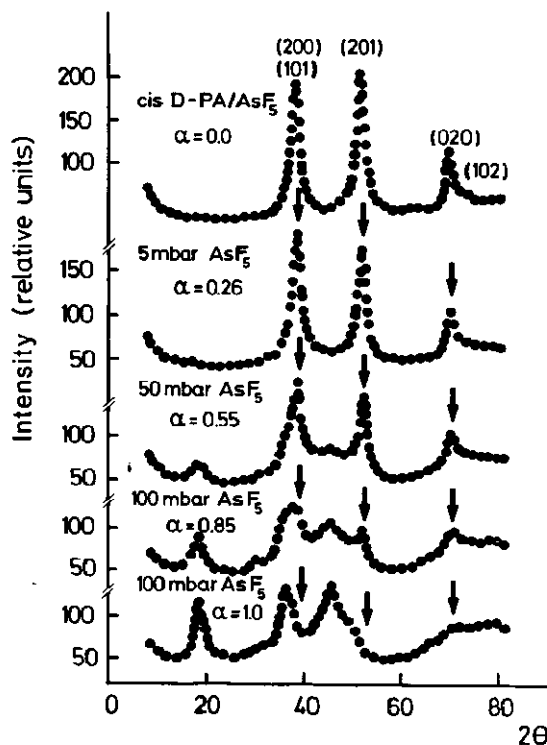


Figure 13. Structural change of *cis*-polyacetylene upon doping with AsF_5 . Neutron diffraction data from [12].

the lines depend separately on the effective conjugation length. The resonance enhancement occurs when the exciting laser line does not lead to a virtual state (as in the ordinary Raman effect) but is in resonance with a real excitation of the sample. In the case of conjugated polymers the laser line resonates with excitations across the Peierls gap. Because this gap depends on the effective conjugation length from the unfolding of the line profile, the distribution of the effective conjugation length can be determined. A large number of short chains would lead to a pronounced shoulder at the high-wavenumber side of the peaks in figure 14; long chains contribute to the low-wavenumber side. Therefore figure 14 tells us that doping reduces the effective conjugation length [22].

However, even for pristine polyacetylene the effective conjugation length is fairly small. In most samples this is not longer than 10 to 20 double bonds. In addition to these chains of only modest length, there might also be a small number of very long chains. However, their existence will be very difficult to prove. The apparent predominance of short conjugation lengths is a severe obstacle to the observation of physical phenomena that are specific to mobile solitons (see the next section). Appendix 8 presents a compilation of literature on the Raman effect in polyacetylene.

2.5. Stability

It is apparent that a necessary condition for high electrical conductivity in polymers is the existence of extended systems of conjugated double bonds (it is this

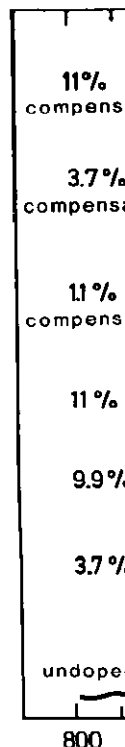


Figure 14. Doping-induced changes in Raman spectra. Shoulders on the high-energy side of the peaks indicate short chains (low values of the effective conjugation length).

conjugation that leads to high conductivity (see the next section for the behaviour). Unfortunately, the conductivity of doped polyacetylene is very low. An example of the poor conductivity of doped polyacetylene is shown in the long-time experiment of Figure 15. The conductivity is plotted for various inert gas, laboratory conditions. The conductivity has not yet been reported a new form of polyacetylene. This new form seems to be more stable than polythiophene. Although the conductivity is considerably lower than in polyacetylene, it is a substance very promising. Polyacetylene is soluble and hence polythiophene might be best suited for applications.

Figures 16 and 17 show the use of doped polyacetylene in solar cells and electrochromic devices, which has been doped into

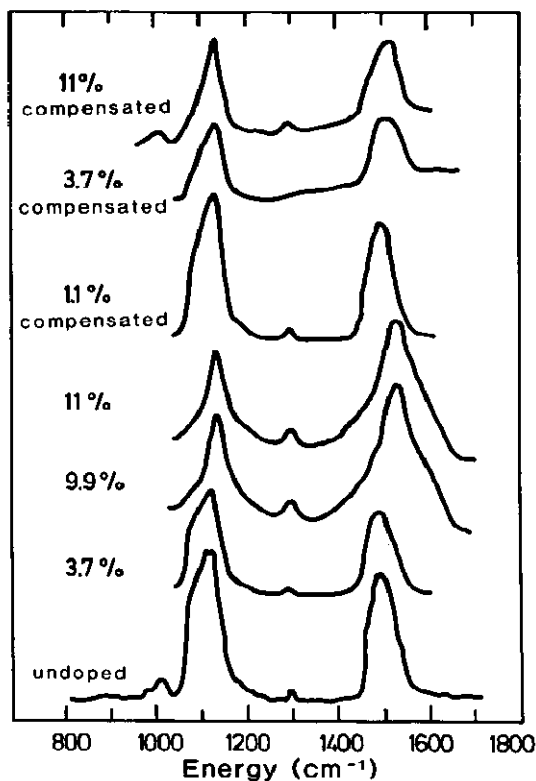


Figure 14. Doping-induced change of the profile of Raman lines in *trans*-polyacetylene [22]. Shoulders on the high-energy side of the lines are interpreted as contributions of short chains (low values of the effective conjugation length).

conjugation that leads to the delocalization of the π -electrons and to metallic behaviour). Unfortunately, however, unsaturated hydrocarbons are very unstable. An example of the poor chemical stability of standard Shirakawa polyacetylene is shown in the long-time experiment of figure 15. Here the decay of the electrical conductivity is plotted for various conditions of sample storage (inert gas in a freezer, inert gas, laboratory conditions) [23]. Very recently Naarmann and Theophilou [24] have reported a new form of polyacetylene having very high conductivity without any significant drop in the conductivity during 30 days in laboratory air. Polypyrrole seems to be more stable than conventional polyacetylene and even more stable is polythiophene. Although in polythiophene up to now, the initial conductivity is considerable lower than in polyacetylene, the apparent stability does make this substance very promising. Moreover, the addition of alkyl side groups makes polythiophene soluble and hence processable [25–27], so that some experts believe that this substance might be best suited for technical applications.

2.6. Applications

Figures 16 and 17 show schematically two examples of technical applications: solar cells and electrochemical batteries. The solar cell consists of a polyacetylene film which has been doped into the semiconducting state. This film is covered with a very

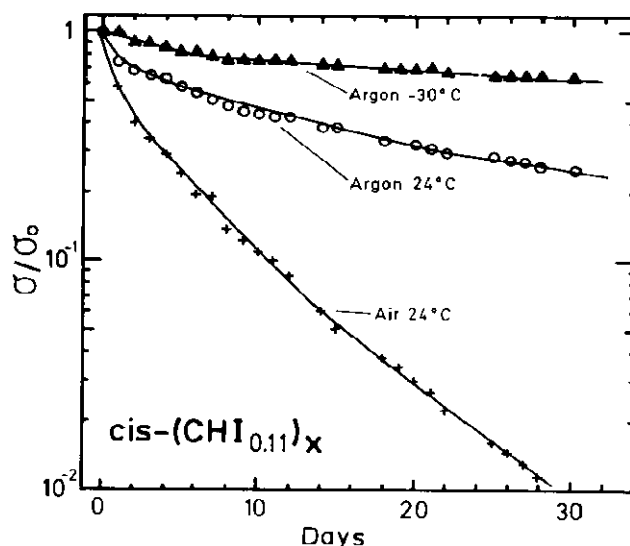


Figure 15. Ageing of iodine-doped polyacetylene samples under different storage conditions. The normalized room-temperature conductivity is plotted against the storage time [23].

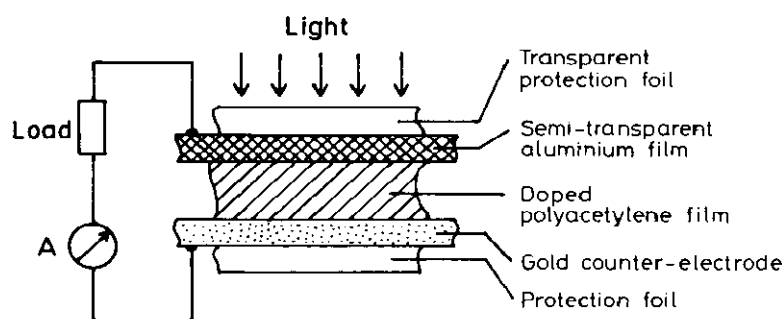


Figure 16. Schematic view of polyacetylene solar cell.

thin transparent aluminium layer, which forms a Schottky barrier with the doped polyacetylene (as it does with silicon). If light is absorbed, electrons and holes are created, as in ordinary semiconductors. In polyacetylene the electrons and holes can quickly convert into solitons and antisolitons or into polarons, but this is not essential for the functioning of the cell. The photo-generated carriers are separated by the intrinsic field of the Schottky barrier and electric current flows through the outer circuit. Solar cells of this type have already reached an efficiency of about 1% [28]. This value is considerably lower than that for silicon solar cells, but the 'energy harvest factor' of polyacetylene cells is already higher than for silicon cells (polyacetylene is synthesized and doped at room temperature, whereas in silicon these processes have to be carried out at high temperatures, so that a silicon cell has to run for several years until it has produced as much energy as was needed for its fabrication).

The polyacetylene battery [29] makes use of the reversibility of electrochemical doping. Two differently doped polyacetylene films are two different synthetic metals. If they are dipped into an electrolyte a voltage will build up and electric current can

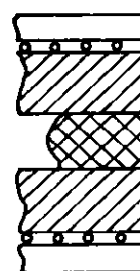


Figure 17.

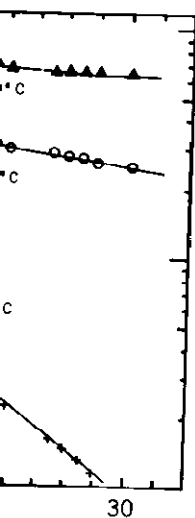
be taken out until the cell is recharged. The advantage of a polyacetylene battery (which is compensated by the loss of about 10%) but that the polyacetylene battery is associated with the open circuit voltage to be quickly recharged for applications of conductive

The properties of polyacetylene are determined by its chemical preparation. For example, polyacetylene prepared by the Shirakawa group and characterized in

Table 1. Parameters

Synthesis

Thickness
Diameter
Density
Dark conductivity
Spin concentration (ESR)
ESR linewidth at RT
Crystallinity (X-ray)
Elemental analysis:
Effective conjugation length
Morphology



under different storage conditions.
ed against the storage time [23].

Transparent
protection foil
Semi-transparent
aluminium film
Doped
polyacetylene film
Gold counter-electrode
Protection foil
ylene solar cell.

notky barrier with the doped
orbed, electrons and holes are
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alarons, but this is not essential
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n efficiency of about 1% [28].
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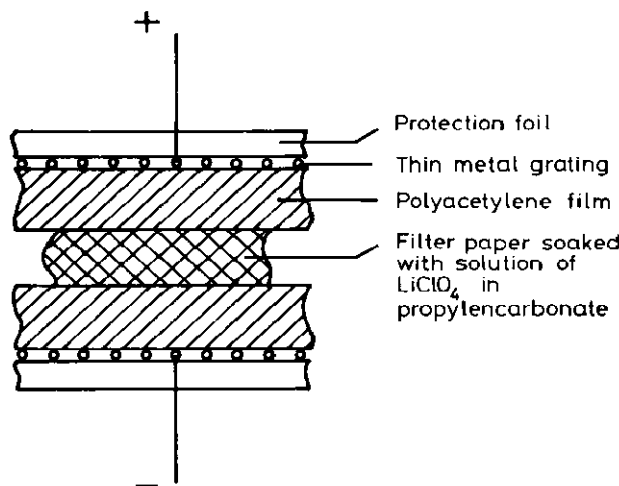


Figure 17. Schematic view of polyacetylene battery.

be taken out until the corresponding electrochemical reaction has equalized the different doping levels of the films. By loading the battery, the difference is restored. The advantage of a polymer battery is apparently not so much that it is light-weight (which is compensated by the heavy dopants and upper limits in the dopant level of about 10%) but that the polymer offers a versatile morphology. The large inner surface associated with the open fibrillar structure of polyacetylene, for example, allows the battery to be quickly loaded and unloaded. Further examples of technical applications of conductive polymers are given in the references of Appendix 1.

2.7. Sample characterization

The properties of polyacetylene samples depend very much on the details of their chemical preparation. For our own work on unoriented samples we used films prepared by the Shirakawa method, characterized by the parameters given in table 1. The work on oriented samples was carried out on material obtained from the Graz group and characterized in table 2.

Table 1. Parameters of the Stuttgart standard polyacetylene samples.

Synthesis	Shirakawa method [4] at -80°C , film floating on catalyst solution
Thickness	5–200 μm
Diameter	5 cm
Density	0.3–0.4 g cm^{-3}
Dark conductivity	$2 \times 10^{-6} \text{ S cm}^{-1}$ (<i>trans</i> , pristine, d.c., RT)
Spin concentration (ESR)	400 p.p.m. (<i>trans</i> , undoped)
ESR linewidth at RT	1 G (<i>trans</i> , undoped)
Crystallinity (X-ray)	80%
Elemental analysis:	99.3% CH
Effective conjugation length (Kuzmany)	20% chains with more than 20 CH units
Morphology	See electron micrographs (figures 5(a) and (b))

Table 2. Parameters of the Graz standard polyacetylene samples.

Synthesis	Durham [7]–Graz [8] method
Thickness	0.2–5 μm
Density	1.15 g cm^{-3}
Dark conductivity	$\sigma_{\parallel} = 3 \times 10^{-5} \text{ S cm}^{-1}$; $\sigma_{\perp} = 3 \times 10^{-7} \text{ S cm}^{-1}$ (<i>trans</i> , pristine, d.c., RT)
Spin concentration (ESR)	250 p.p.m. (<i>trans</i> undoped) = 10^{19} g^{-1}
ESR linewidth at RT	1.8 G ($\mathbf{H} \perp c$); 2.75 G ($\mathbf{H} \parallel c$)
Crystallinity (X-ray)	> 95%
Effective conjugation length	Comparable to the Shirakawa material
Morphology	See electron micrograph (figure 7)

3. Solitons in conjugated polymers

3.1. Significance of soliton concept

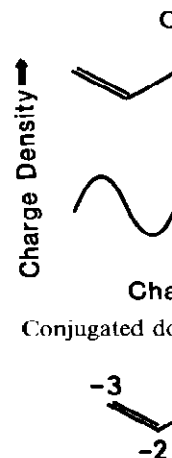
In recent decades the thinking of physicists has largely been dominated by attempts to describe systems in terms of linear differential equations and their solutions. Deviations from their harmonic behaviour, which lead to nonlinear terms in the differential equations, have been treated as perturbations by introducing interactions between the quasi-particles corresponding to the harmonic solutions (electron–electron and electron–phonon collisions, etc.). The idea of the soliton concept is to solve the nonlinear differential equations not by numerical approximations but analytically and to associate new quasi-particles with the exact solutions, the solitons.

An important characteristic of solitons is their non-dispersive (shape conserving) motion. Conventional wave packets will lose their shape because the Fourier components of the packet propagate at different velocities. In a nonlinear medium the velocity not only depends on the frequency of a wave but also on its amplitude. In favourable circumstances the effect of the amplitude dependence can compensate that of the frequency dependence, resulting in a stable solitary wave. A technical application of this idea is the propagation of soliton-like pulses in fibre optics, which considerably increases the bit rate in data transmission.

For one-dimensional systems interactions between electrons and phonons are very important because the low-dimensionality increases the probability of collisions. This leads to the nonlinear behaviour of linear chains. The simple structure of polymers, especially, with conjugated double bonds and particularly the high symmetry of *trans*-polyacetylene confer on these substances much importance in discussions on the utility of the soliton concept. Even if it turns out that solitons are not needed to explain the experimental observations in *real* polyacetylene the theoretical investigation of *ideal* polyacetylene has high didactic value. Basic literature on solitons in solid-state physics is listed in Appendix 9.

3.2. Conjugated chains, charge-density waves, the alternation parameter and the Peierls transition

Figure 18 shows the conjugated chain of *trans*-polyacetylene. The essential feature of a conjugated system is that a double bond 'knows' that the next but one is again a double bond: double bonds should not be considered individually but as part of a collective system. If the system is disturbed at one site, the whole system will be affected (cf. the Chinese proverb: If you pull one little hair the whole body is changed!). Theoretical investigations have shown that perturbations of the conjugation propagate like solitary waves in water. In addition the conjugation leads to interesting symmetry

Figure 18. Conjugated chain of *trans*-polyacetylene.Figure 19. Definition of the alternation parameter p .

properties, which bear some resemblance to those of solitons. Therefore, it is quite plausible to consider the conjugated chain as a one-dimensional system.

There is a strong intellectual incentive to consider the conjugated chain as a one-dimensional system illuminated both from the classical and quantum mechanical points of view and one is then encouraged to use both wave mechanics and quantum mechanics consequently to use both wave mechanics and quantum mechanics in a double bond there are two electrons, the electron density oscillates precisely in polyacetylene the electron density is not modulated at the double bond sites.)

The charge-density wave (CDW) concept (see also the discussion of CDW groups). In order to establish a higher electron density, i.e. a shorter bond length, a distortion occurs (this distortion is so called Peierls distortion). The Peierls parameter, which is given by the ratio of the bond lengths are denoted as in figure 19.

Here a and b symbolize the bond lengths of the conjugated structure. In figure 19 $p = \frac{a-b}{a+b}$. If the values from the NMR measurements are used $p \sim 6\%$. The sign of p is arbitrary, but in this step it is important to show the sign of p (see figure 22). By marking one

acetylene samples.

[8] method

 cm^{-1} ; $\sigma_1 = 3 \times 10^{-7} \text{ S cm}^{-1}$

c., RT)

undoped) = 10^{19} g^{-1} 5 G ($\mathbf{H} \parallel c$)

the Shirakawa material

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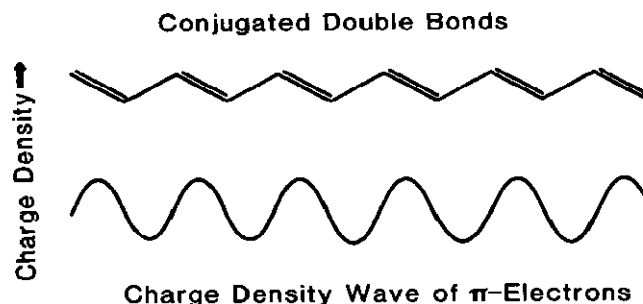
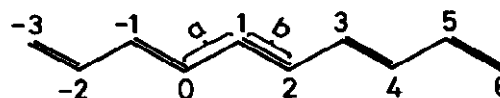
Figure 18. Conjugated double bonds as charge-density wave in a π -electron system.

Figure 19. Definition of the bond-alternation parameter in Equation (3). Odd and even lattice sites after marking a zero.

properties, which bear some analogy to the behaviour of elementary particles. Therefore, it is quite plausible to relate conjugational defects to solitons.

There is a strong intellectual appeal in treating a system of conjugated double bonds as a one-dimensional metal. In this way, one and the same phenomenon is illuminated both from the chemical side and from the viewpoint of solid-state physics, and one is then encouraged to hop frequently between their respective languages and consequently to use both ways of thinking. While a chemist looks at a conjugated system as alternating single and double bonds a physicist sees a charge-density wave: in a double bond there are more electrons than in a single bond. Therefore, the electron density oscillates periodically if one moves along the chain (figure 18). (More precisely in polyacetylene this phenomenon is termed a bond-order wave, because the electron density is not modulated at the lattice sites but rather between the lattice sites.)

The charge-density wave of the electrons modifies the lattice of 'positive ions' (CH groups). In order to establish local charge neutrality the ions move to regions of higher electron density, i.e. into the double bonds. This makes the double bond shorter than the single bond. As far as the lattice is concerned a Peierls distortion occurs (this distortion is sometimes called dimerization, because the ions group in a pairwise fashion). The Peierls distortion can be characterized by the bond alternation parameter, which is given by the relative difference of the bond lengths. If the bond lengths are denoted as in figure 19 we have

$$p = \frac{a - b}{(a + b)/2} \quad (3)$$

Here a and b symbolize respectively the 'left' and the 'right' slope of the zig-zag structure. In figure 19 $p > 0$, because a double bond is shorter than a single bond. If the values from the NMR nutation spectroscopy [16] are put into (3) we obtain $p \sim 6\%$. The sign of p is arbitrary as long as there is no 'mark' on the chain. In a first step it is important to show only that at a conjugational defect p changes sign (see figure 22). By marking one site on the chain, the zero of a numeration is defined and

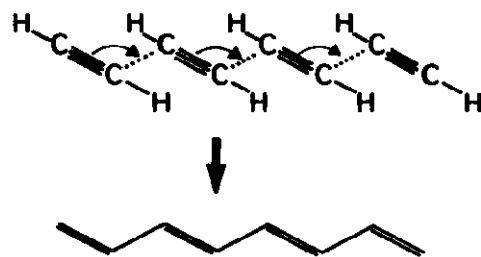


Figure 20. Polymerization of acetylene. The carbon pairs of the monomer are preserved in the polymer.

one can distinguish between odd and even sites. Then one can agree that the distance a should be between an even and the next higher odd site.

From the chemical point of view, conjugation comes about from taking not individual sites but pairs (C_2H_2 groups) as the building blocks. This is the way in which polyacetylene is synthesized in practice (one bond of an acetylene molecule snaps over to the neighbouring molecule, figure 20). For the physicist, the conjugation arises from symmetry breaking. She starts from an infinitely long chain of CH units, where the sp^2 -orbitals have already established σ -bonds to the neighbours, but where the remaining p-electron has not yet decided whether it should bind to the left or to the right. This hypothetical state would be stable in polyacetylene at temperatures above about 10 000 K. It would be a one-dimensional metal with a half-filled energy band: the p-electrons are completely delocalized, metallic, and are now called π -electrons. If the metal is cooled down, a charge-density wave and a corresponding deformation of the lattice of the CH group will form, as required by Peierls' theorem [30]. In the energy band of the π -electrons a gap will form at the Fermi level (i.e. in the middle of the band in the case of half-filling). The formation of the gap allows the system to lower its electronic energy. Part of the energy gained is used as elastic energy in the Peierls distortion of the lattice, but it can be shown that at low temperatures the energy balance is positive. The opening of the gap transforms the metal into a semiconductor. Such metal-to-semiconductor transitions are well known in other one-dimensional systems. A relevant review article is [31].

The change in the band structure arising from the Peierls transition is shown schematically in figure 21. According to a convention in semiconductor physics, the lower (and filled) sub-band is called the 'valence' band; the upper (empty) sub-band, the 'conduction' band. In chemistry the terms π and π^* band are common: the former contains the bonding; the latter the antibonding states. the HOMO (highest occupied molecular orbital) is at the edge of the valence band, at the edge of the conduction band is the LUMO (lowest unoccupied molecular orbital). Strictly speaking the zig-zag structure of *trans*-polyacetylene is biatomic already, without a Peierls distortion, because of the alternation of the bond angles ('zig' and 'zag'). Owing to the existence of mirror planes at each site, however, this biatomicity does not yet have an influence upon the physical properties of polyacetylene. Nevertheless, a completely straight chain, like in polycarbene (figure 3) would be more satisfactory from the point of view of aesthetics.

3.3. Conjugational defects as solitons

In figure 22 a conjugational defect in a polyene chain is shown schematically. One could imagine that dimerization of the chain has started at two different places,



Figure 21. Peierls distortion. A half-filled energy band turns into a semiconductor.

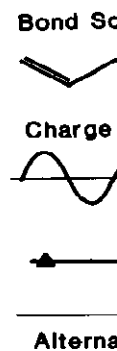


Figure 22.

dimerized domains have grown, leaving some CH units left over. In the language of chemists might call it a *soliton*. In general terms, it is a domain wall in the scheme of chemical bonds. It represents a phase jump of 180° at the defect site, indicated by the broken line. The bond length parameter changes sign at the defect (from right-hand slopes to left-hand slopes).

If the unbonded electron is trapped at the defect, the conjugational defect is stabilized by a positive hole (an unpaired electron) or a negative charge (a lone pair) jump in the charge-density wave.

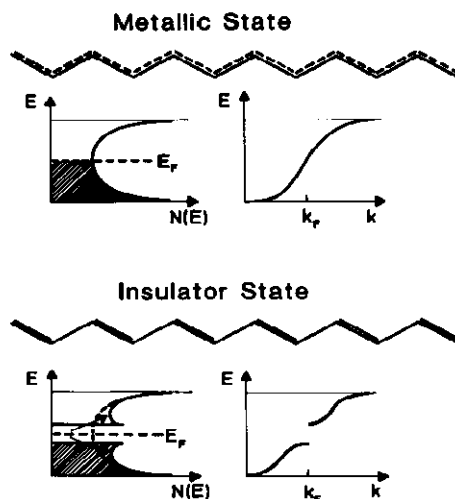


Figure 21. Peierls distortion. Upon cooling the atoms of a monomolecular metal (with half-filled energy band) approach pairwise, a gap opens at the Fermi level and the metal turns into a semiconductor.

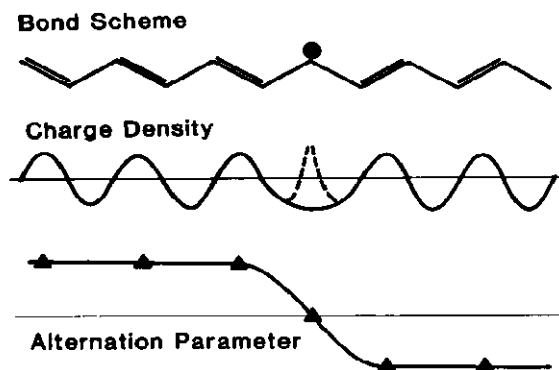


Figure 22. Conjugational defect on a polyene chain.

dimerized domains have grown and when they finally touch an unbonded electron is left over. In the language of semiconductor physicists this is a dangling bond. Polymer chemists might call it a misfit, alternation defect or Pople-Walmsley defect [32]. In general terms, it is a domain wall. The figure shows this defect not only in the scheme of chemical bonds but also as a charge-density wave. As can be seen, there is a phase jump of 180° at the defect (the charge density of the unbonded electron is indicated by the broken line). As one can also see from the figure, the alternation parameter changes sign at the defect (the double bonds switching from right-hand slopes to left-hand slopes).

If the unbonded electron of figure 22 is removed, for example by oxidizing the chain, the conjugational defect does not vanish. The dangling bond has been replaced by a positive hole (an uncompensated nuclear charge in the CH group) but the phase jump in the charge-density wave and the sign inversion of the alternation parameter

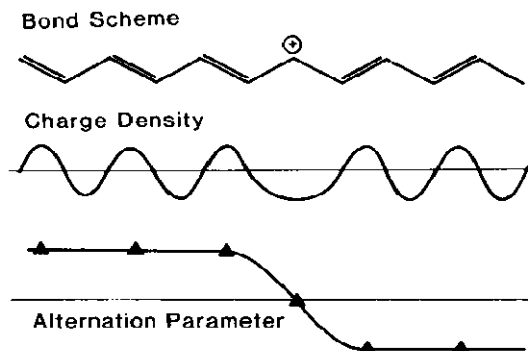


Figure 23. Positively charged conjugational defect.

remain (figure 23). Alternatively a conjugational defect can also catch a second electron and acquire a negative charge (when the chain is reduced, i.e. n-doped).

In solid-state physics there are many examples of domain walls which can move: Bloch walls in ferromagnets, dislocations in crystals, etc. Phase-slip centres in charge-density waves can also move. We can conjecture that the conjugational defects of figures 22 and 23 are also mobile and perhaps move as solitary waves (the step in the alternation parameter very much resembles a flood wave). To 'prove' solitary wave motion one would have to show that this step does not change shape during motion, that it does not disperse, and that it cannot be constructed as a superposition of harmonic waves (see § 1). Experimentally such a proof will be difficult, but Rice [33], Su, Schrieffer and Heeger [34], and Brazowski [35] have formulated nonlinear differential equations, which describe a conjugated polymeric chain to within a certain approximation and which, in the continuum limit, have solitary-wave solutions.

The essential features can be seen by looking at the differential equation for coupled double-well potentials:

$$c^2 \phi_{xx} - \phi_{tt} = 2\omega^2(\phi^3 - \phi). \quad (4)$$

This model does not take into account the long range of the electron-phonon interaction. Therefore, it does not correctly reproduce the dynamics of a conjugated chain, but it nevertheless illustrates the topological aspects of the problem.

Setting the right-hand side zero, equation (4) turns into the classical wave equation, the prototype linear differential equation with harmonic waves as solutions. The full equation (4) is known to have solitary solutions $\phi(x, t) = \phi(x - vt)$, where v is the velocity of the solitary wave and

$$\phi(x) = \tanh(x/\xi), \quad (5)$$

with $\xi^2 = (c^2 - v^2)/\omega^2$.

The application of (4) to polyacetylene is illustrated in figure 24.



Figure 24. Coupled double-well potentials to illustrate conjugational defects in polyacetylene.

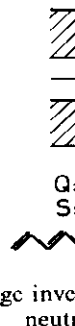


Figure 25. Spin-charge inversion.

Figure 22 suggests that the Peierls transition. When Consequently a conjugation midgap. This midgap state ing on the charge at the de the electrons on the chain inversion for the conjugat electron and consequently a but there is an uncompens is overcompensated (nega inversion can be regarded a of a half-filled band (see b dangling bonds in silicon, relationship to fractional c

If one wants to termina chains appear to be termin on chains with odd number the ground state. One can usually the bond-alternati figure 22 and the defect w spread over about 15 CH g simulations on a chain of 6

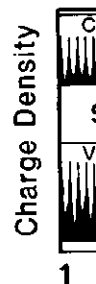


Figure 26. Charge distribution.

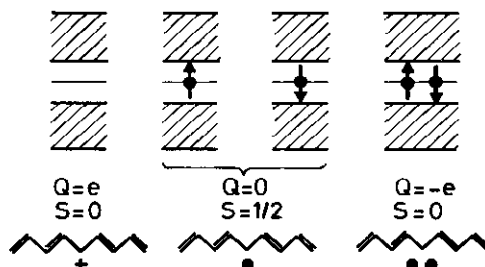


Figure 25. Spin-charge inversion of a conjugational defect. Charged solitons are spinless; neutral solitons carry a magnetic moment.

3.4. The midgap state

Figure 22 suggests that we regard a conjugational defect as a local suppression of the Peierls transition. Where there is no Peierls transition there is no energy gap either. Consequently a conjugational defect is associated with an electronic state exactly at midgap. This midgap state can be unoccupied or carry one or two electrons, depending on the charge at the defect: positive, neutral or negative (figure 25). By counting the electrons on the chain one finds the surprising result that there is a spin-charge inversion for the conjugational defect: if the defect is neutral there is an unpaired electron and consequently a magnetic moment. If there is no electron, there is no spin, but there is an uncompensated nuclear charge. If there are two electrons, the charge is overcompensated (negative), but the spins are compensated. This spin-charge inversion can be regarded as a manifestation of fractional charges for the special case of a half-filled band (see below; of course, spin-charge inversion will also exist for dangling bonds in silicon, but in three-dimensional semiconductors there is no close relationship to fractional charges).

If one wants to terminate polyene chains on both sides with double bonds (all real chains appear to be terminated like that) then there must be a conjugational defect on chains with odd numbers of sites. In such chains a soliton is already a property of the ground state. One can ask the question about the spatial extension of a soliton: usually the bond-alternation parameter will not change as abruptly as is shown in figure 22 and the defect will affect several lattice sites. Most calculations indicate a spread over about 15 CH groups. Stafström and Chao [36] have carried out computer simulations on a chain of 61 carbon atoms. The result is reproduced in figure 26. The

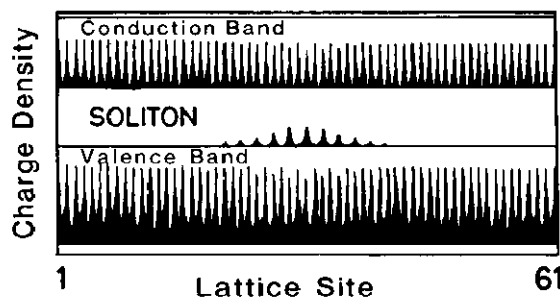


Figure 26. Charge distribution of a conjugational defect on a *trans*-polyacetylene chain of 61 carbon atoms [36].

diagram shows the electron density at each lattice site. It is clearly seen that the midgap state is built up at the expense of the valence and conduction band and that it extends over more than 10 sites. It also should be noted that odd lattice sites only are affected by the defect.

3.5. Fractional charges

In figure 26 we considered a chain of 61 CH groups. Each group contributes one p molecular orbital to the π -electron system. There are 61 states per spin quantum number: 1 at midgap, 30 in the valence and 30 in the conduction band. All valence states are occupied, all conduction states are empty, the midgap state is occupied with one electron. Consequently, it is electrically neutral and carries a magnetic moment.

Let us now look at a chain with 60 sites. This is even-numbered and there is no soliton in the ground state. There are 30 states per spin in the valence band and 30 in the conduction band. We assume that we create a single soliton (we can create solitons only in pairwise fashion, so we start out with a chain of 120 sites, create two solitons, separate them and look only at the left half of the chain). Now there is one state per spin at midgap and $29\frac{1}{2}$ states per spin are left in the valence and $29\frac{1}{2}$ in the conduction band. Since there are two spin orientations, the half-state is of no peculiar consequences. But if we were to live in a world with only one possible spin orientation (!) we could either put 29 electrons on the chain and leave half a nuclear charge uncompensated or we could occupy the midgap state by putting 30 electrons on the chain. Then we would overcompensate the nuclear charge by half an electronic charge. In this hypothetical world there would be fractional charges with $q = \pm e/2$. In the real world with two spin orientations there are only integer charges but there is spin-charge inversion.

If we had a one-dimensional metal with the energy band one-third filled (at high temperatures), the Peierls transition would lead to three sub-bands separated by two gaps. Whereas, in the half-filled case, four states (two for each spin orientation) are spread over two solitons, upon filling to one-third there are four states shared by three solitons. For each soliton there are $2/3$ states per spin orientation, located in two gaps. This situation is shown in figure 27. If the soliton states are now filled with electrons, the first electron goes to $1/3$ per soliton into the spin-up state of the lower gap, the second to $1/3$ into the spin-down state. Each soliton is spin-compensated but there is only a charge of $q = 2e/3$.

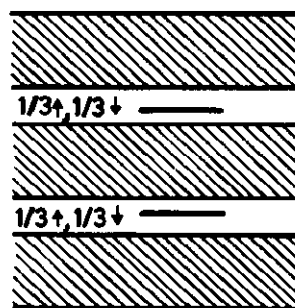


Figure 27. One-dimensional metal with band filling to one-third with two Peierls gaps and solitonic states in the gaps.

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Figure 28. Electron counting

The relevant electron-counting situation for polyacetylene is, for simplicity the zig-zag chain. In polyacetylene by sliding the centres to infinity, the chain becomes a one-dimensional metal. In comparison to the undistorted soliton-carrying chain segment, As expected this leads to one of the figure shows the hybridization of bonds is such that corresponds to a band filled with ends are again unaffected. Counting the double bonds and bond. The two uncompensated defects, so that the effective

It is not quite clear whether solitons created simultaneously just a book-keeper's trick. Comparison to fractionally charged a similarity to quark confinement cannot be 'removed'. Further, in one-dimensional metals and related [37]. The similarity between the Hall effect has been pointed

Polyfractiolenes cannot be only be stabilized properly. The experiment would already break down in one-dimensional metals with band filling. Fractional charges might cause their existence [39]: via the measurement of charges is measured, the nuclear spectrum of the current. It so on.

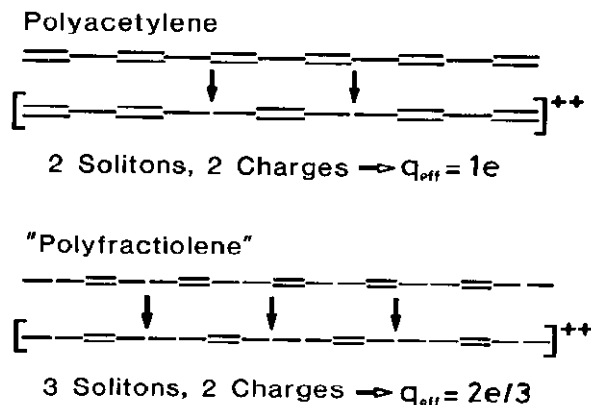


Figure 28. Electron counting to demonstrate fractional charges on one-dimensional chains.

The relevant electron-counting is demonstrated in figure 28. In the upper part, the situation for polyacetylene is shown for the sake of comparison (for the sake of simplicity the zig-zag chain is rendered straight). If two solitons are created in polyacetylene by sliding the charge-density wave along the chain from two phase-slip centres to infinity, the chain only changes between the solitons; the ends are unaffected. In comparison to the undisturbed chain there is one double bond missing on the soliton-carrying chain segment. Hence the chain segment is doubly positively charged. As expected this leads to one electronic charge per soliton ($q = 1e$). The lower part of the figure shows the hypothetical substance 'poly-fractiolene'. Here the arrangement of bonds is such that there are two single bonds between a double bond. This corresponds to a band filled to one-third. If now three solitons are created, the chain ends are again unaffected (a soliton corresponds here to a phase jump of 120°). Counting the double bonds in the central part, again shows the lack of one double bond. The two uncompensated nuclear charges have now to be spread over three defects, so that the effective charge per defect is $q = 2e/3$.

It is not quite clear whether one is allowed to look at individual solitons. If all solitons created simultaneously have to be viewed together, then fractional charges are just a book-keeper's trick. On the other hand, fractional charges on solitons are a nice analogy to fractionally charged quarks in elementary-particle physics. There is also a similarity to quark confinement: solitons are only defined on conjugated chains and cannot be 'removed'. Further relationships between charge fractionization in one-dimensional metals and relativistic field theory are discussed by Jackino and Schrieffer [37]. The similarity between fractionally charged solitons and the fractional quantum Hall effect has been pointed out by Schrieffer [38].

Polyfractiolene cannot be synthesized. The bond sequence of figure 28 can only be stabilized properly by putting protons onto the chain, but the proton arrangement would already break the symmetry on the chain. But there are inorganic one-dimensional metals with bands filled to $1/3$ or $1/4$, like NbSe_3 , and in these systems fractional charges might occur. One could even imagine an experiment to show their existence [39]: via the current flowing through a conductor the number of charges is measured, the number of carriers is inferred from an analysis of the noise spectrum of the current. Divide number of charges by number of carriers, and so on.

3.6. Symmetry properties and conservation of particle number

The word 'soliton' implies non-dispersive shape-conserving motion, on the one hand, and on the other hand, the ending 'on' suggests particle-like properties. One aspect of these particle-like properties is the conservation of the particle number. Chains with an even number of sites carry no soliton in the ground state; those with an odd number exactly one (see above). Further, solitons can only be generated in pairs: soliton and antisoliton. In the discussion of figure 26 we noted that only the *odd* lattice sites are affected by the soliton. One can also create conjugational defects, which affect the *even* sites only. In this way one can distinguish between solitons and antisolitons. One is free to call a conjugational defect on an infinite chain either soliton or antisoliton. But between two defects on the same chain there is either a soliton-soliton or a soliton-antisoliton relationship. By inversion of pair generation, soliton and antisoliton can also annihilate, but a single soliton can never vanish; it can only get trapped, for example at the ends of a chain.

From the chemical point of view pair generation in conjugated chains is trivial: breaking a double bond always leads to *two* dangling bonds. Equally trivial, but nevertheless surprising, is the classification into solitons and antisolitons. This is seen in figure 29. When solitons move they stay in the upper, odd sites. The even sites are reserved for antisolitons. A soliton can only jump to the next site but one, never to the site immediately adjacent. These double steps are easily understood from the last two traces of figure 29: the unpaired electron at site 5 decides to form a bond with the electron at site 4; the electron at site 3 then remains unpaired and the conjugational defect has migrated by *two* steps from 5 to 3. In addition to the generation of pairs of neutral particles and antiparticles, pairs of charged particles can also be created. This is shown in figure 30. In this case not only has the conservation of the particle number to be obeyed, but also charge conservation.

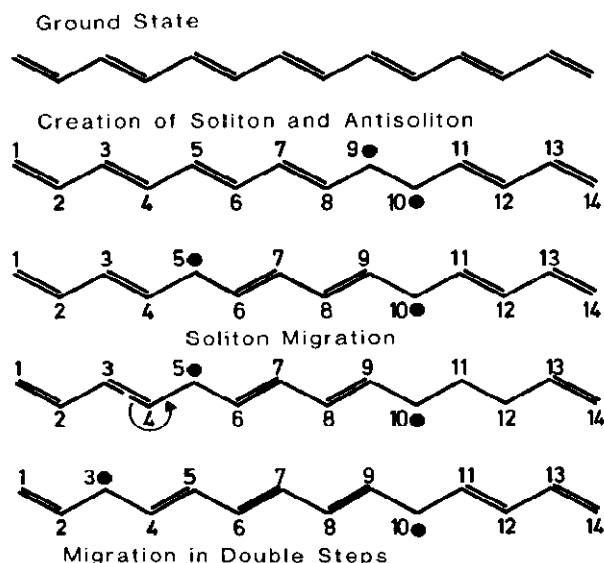


Figure 29. Solitons and antisolitons. The presence of a soliton on a polyene chain allows a classification of the lattice sites as even and odd, and of all further conjugational defects as solitons or antisolitons.

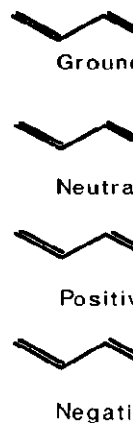


Figure 30. Pair creation of solitons.

One can also inject solitons of functional groups. But after the other: a soliton has no conservation of particle number. The 'soliton bifurcation' (figure 31) shows that once a soliton has gone, only the third particle is left. Only the third particle is the 'inverter' (figure 32) a soliton back along the chain. The inverter can transform a soliton into an antisoliton and the inverter have been used in electronics. Of course, their feasibility is not yet proven or theoretically. (It is not clear if they do move quite freely over several lattice sites.)

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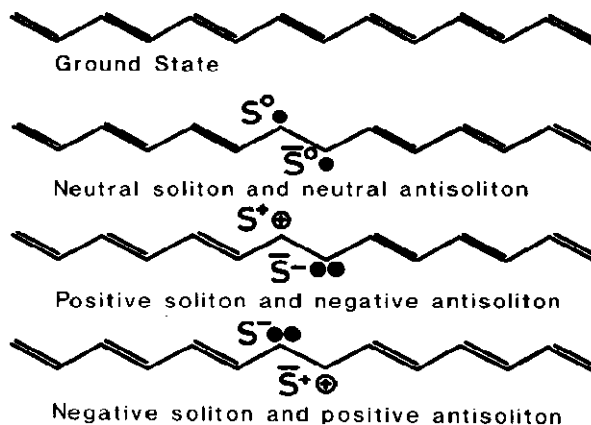


Figure 30. Pair creation of solitons and antisolitons conserving particle number and charge.

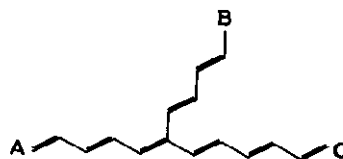


Figure 31. Soliton bifurcation [40].

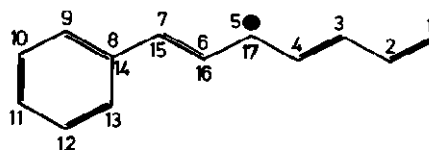


Figure 32. Soliton inverter [40].

One can also inject solitons from chain ends, for example by optical excitation of functional groups. But one cannot inject two particles of the same kind one after the other: a soliton has always to be followed by an antisoliton. The conservation of particle number is also obeyed in all complicated conjugated systems. In the 'soliton bifurcation' (figure 31) a particle injected at A can go either to B or to C. But once a soliton has gone to B, the next one (an antisoliton) also has to go to B. Only the third particle is again free to choose between B and C. In the 'soliton inverter' (figure 32) a soliton runs into an aromatic ring, is inverted there, and runs back along the chain. The inverter changes the direction of motion of the soliton but no inverter can transform a soliton into an antisoliton. Structures like the bifurcation and the inverter have been proposed by Carter [40] as components of molecular electronics. Of course, their feasibility has not yet been investigated, either experimentally or theoretically. (It is not yet clear how easily solitons can move, but even if they do move quite freely, they might get trapped at the linkages. Moreover solitons extend over several lattice sites, as indicated in figure 26. The main purpose of diagrams like figures 31 and 32 is to demonstrate the symmetry properties of solitons.)

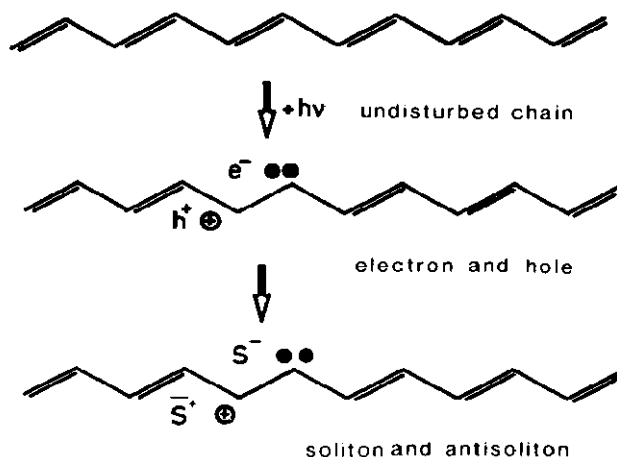


Figure 33. Photogeneration of solitons.

3.7. Creation of solitons: photogeneration and doping

Single solitons can only be created by the chemist when he synthesizes polyene chains with an odd number of carbon atoms (such chains carry a soliton in the ground state, see above). But it is likely that most chains are even-numbered, because the chemist starts from acetylene, C_2H_2 , where the carbon atoms are paired already (cf. figure 20). The physicist creates soliton-antisoliton pairs by breaking double bonds. Heating the sample is not very likely to break bonds: an energy of 1 or 2 eV would be needed, corresponding to a temperature of more than 10 000 K. Visible light, however, can break double bonds. This is shown schematically in figure 33. According to theoretical predictions [41] the bonds are not only broken, but, as in conventional semiconductors, electron-hole pairs are created. Owing to the strong electron-phonon coupling in polyacetylene the electrons and holes relax into charged solitons and antisolitons (S^- and S^+). The photogeneration of spinless and consequently charged particles, rather than magnetic but neutral entities, has been experimentally demonstrated by the Santa Barbara group [42]. Photo-generated charged solitons should move in an applied electric field and lead to photoconductivity (see § 7).

Very efficient tools to create solitons are chemical and electrochemical reactions (doping). The ionization potentials of the dopants are of the order of eV. Therefore they can break the double bonds and take electrons out of the polymer chain (oxidative or acceptor doping, p-doping) or push additional electrons in (reductive or donor doping, n-doping). This process is illustrated in figure 34.

It appears that the stoichiometry of most doping reactions is such that two electrons are transferred (see figure 11 and equations (1) and (2)), but as a *gedanken* experiment figure 34 is quite instructive. It demonstrates nicely that not single solitons but soliton-antisoliton pairs are generated. The charged soliton or antisoliton is likely to be electrostatically bound to the dopant ion, but a neutral soliton could diffuse freely—at least towards the left. If the chain is long enough it could meet an antisoliton, originating from another doping event, and recombine. But soliton-soliton collisions are impossible, because the solitons are always on the left-hand side of the antisolitons and these block the way. As will be shown later, however, there can be an attractive interaction between soliton and antisoliton, which leads to the formation of polarons.

①
②
③

Figure 34. Chemical creation of solitons.

Figure 35. Light-doping charged solitons.

Light doping is expected to be stronger than chemical doping. Stronger doping breaks double bonds more easily, thus increasing the number of solitons. Because a soliton is a local disturbance, it leads to a global suppression of the conductivity. Any deviation from the half-filled state leads to a global suppression of the conductivity. So does the electrostatic potential of the dopant ion.

At this point it should be noted that, even if one is speaking of isolated chains, the introduction of solitons is not a simple process. There are phase transitions [43], and of phase transitions in packed chains and interchain interactions, which are doped regions.

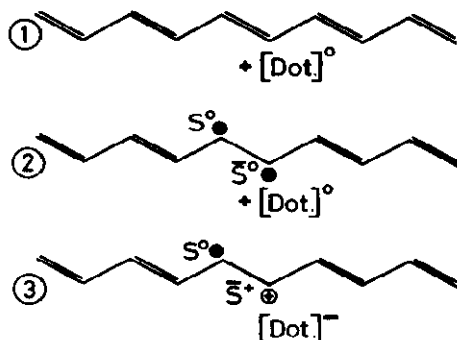


Figure 34. Chemical creation of solitons by doping (oxidation) of a polyene chain.

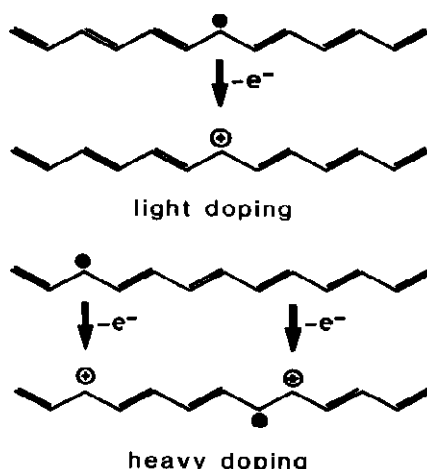
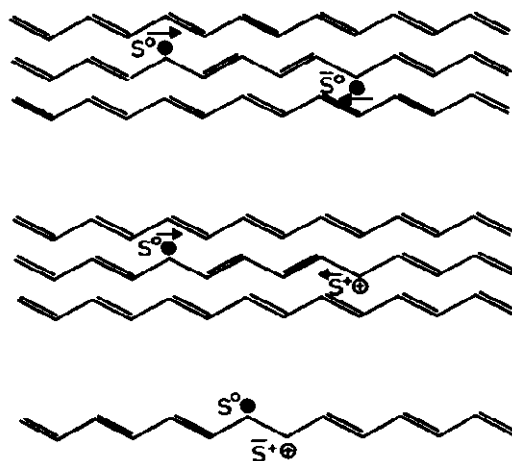


Figure 35. Light-doping charges already existing neutral solitons; heavy-doping creates new solitons by breaking double bonds.

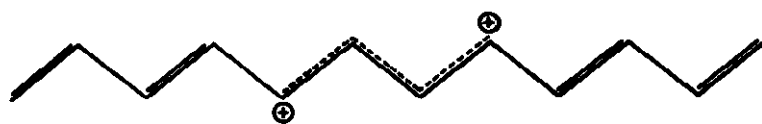
Light doping is expected to charge the already existing neutral solitons, whereas stronger doping breaks double bonds and creates new solitons (figure 35). At high doping levels the number of solitons increases so much that finally the solitons overlap. Because a soliton is a local suppression of the Peierls transition, the overlap of solitons leads to a global suppression: the metal-insulator transition is removed and the polyene chain becomes metallically conducting. But the suppression of the Peierls transition is not specific to solitons: the midgap state need not be caused by solitons. Any deviation from the half-filled band places the Peierls transition at a disadvantage. So does the electrostatic potential of the randomly distributed doping ions (I_3^- , AsF_6^-).

At this point it should be noted that 'continuous doping' is a useful concept when speaking of isolated chains and non-interacting defects. If an interaction between solitons is introduced, there is the possibility of forming a soliton lattice, of phase transitions [43], and of phase separation. Especially in real polyacetylene with closely packed chains and interchain interactions there will be a tendency to separate into domains, which are doped to saturation and separated by undoped or only slightly doped regions.



Polaron

Figure 36. Attractive interaction between solitons sitting on the same chain arising from interactions between neighbouring chains.

Figure 37. Bi-polaron in *trans*-polyacetylene.

3.8. Soliton complexes and polarons

Two solitons on an infinitely long perfect chain of *trans*-polyacetylene suspended in vacuum will not interact. But if the polyene chains are embedded in a crystal the interactions between the chains will lead to an attractive interaction between the solitons. The charge-density waves on neighbouring chains tend to establish a fixed phase relation. Between two solitons, however, the phase is inverted. Therefore, the solitons will move together (figure 36). If the solitons are neutral they will annihilate (there are always solitons *and* antisolitons). If one of the solitons is charged, however, they cannot annihilate, because there is no way to get rid of the electric charge. They approach each other as closely as possible and finally form one common defect, which has both spin *and* charge, and which distorts the lattice. In analogy to classical semiconductor physics this type of defect is called a polaron. A polaron can be considered a bound state of two solitons (a molecule made of soliton atoms). Two solitons with opposite charge will also annihilate, of course. However, equally charged solitons will be stabilized by the Coulomb repulsion: the interchain interaction pushes them together; the electrostatic force keeps them apart. This entity is called a 'bisoliton' or a 'bipolaron' (figure 37) (When two polarons approach each other the neutral solitons annihilate and the charged ones remain.) For a polaron there are *two* states in the gap, because it comprises two solitons. As a result of the interaction of the components, these levels are pushed out of midgap and approach the edges of the valence and the conduction band. An important reaction between quasi-particles on a chain is the collision between polarons and neutral solitons. As shown in figure 38

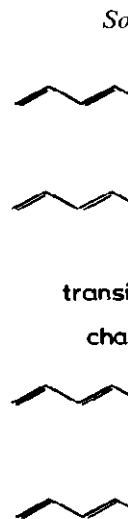


Figure 38. Collision between polaron and neutral soliton.

Vacuum state
Neutral solution
Positive soliton
Negative soliton
Positive polaron
Negative polaron
Positive bisoliton (bipolaron)
Negative bisoliton (bipolaron)

Figure 39. Complex conjugation of solitons.

the neutral components annihilate. The mechanism will be made when a

Figure 39 brings together the solitons that can be constructed in *trans*-polyacetylene. Not only neutral solitons but also polarons can be combined to form the other elementary excitations. In general, for reasons of symmetry, the elementary excitations are: the neutral soliton, the neutral antisoliton, the charged soliton, the charged antisoliton. In general: they can also move in *cis*-polyacetylene. The excitation is actually just a molecule.

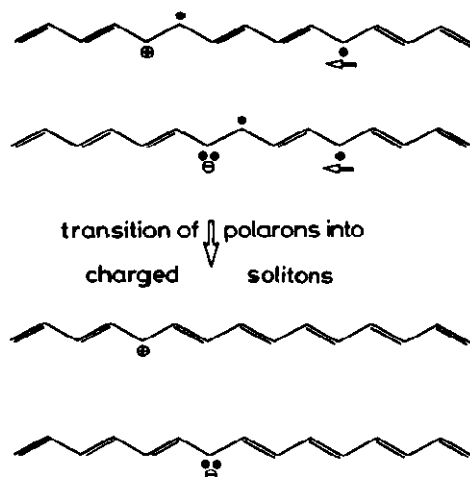


Figure 38. Collision between polarons and neutral solitons leading to charged solitons.

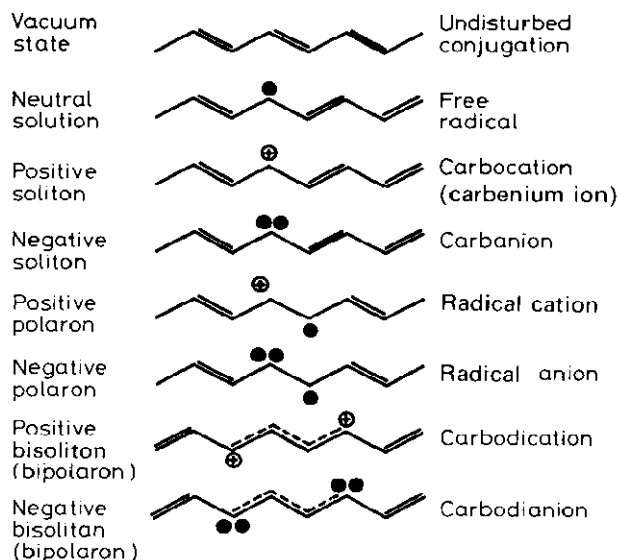


Figure 39. Complex conjugational defects constructed from solitons: a 'physical chemical dictionary'.

the neutral components annihilate and charged solitons are left over. Use of this mechanism will be made when discussing photoexcitations in § 7.

Figure 39 brings together the various simple and complex conjugational defects that can be constructed in *trans*-polyacetylene following the above ideas. Not only solitons but also polarons can be regarded as the 'elementary' particles which are combined to form the other entities. Usually solitons are regarded as the more elemental, for reasons of symmetry, but polarons have the advantage of being more general: they can also move in *cis*-conjugated systems. The choice of the 'elementary' excitation is actually just a matter of taste. Figure 39 can be used as a kind of

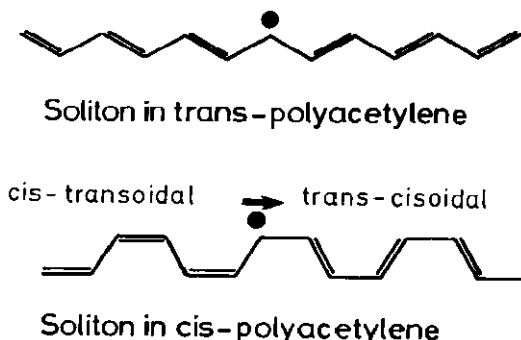


Figure 40. Different symmetry properties of *cis*- and *trans*-polyacetylene. Only in *trans*-polyacetylene there is a mirror plane through the conjugational defect. In *cis*-polyacetylene, the defect separates two different structures with different lattice energies.

physical-chemical dictionary because it contains the names of the defects in both languages—*cum grano salis*, of course. (The physicist starts from an infinite solid and wants to explain why the extent of a soliton is finite and not infinite. The chemist thinks atomistically and wants to explain why the soliton extent is finite and not zero.)

3.9. Solitons in *cis*-polyacetylene

Cis-polyacetylene is very different from *trans*-polyacetylene, as far as solitons are concerned. Certainly the band structure is more complicated because there are four atoms in an elementary cell along the chain instead of two. But the crucial difference is related to symmetry. In figure 40 a soliton in *trans*-polyacetylene is set in contrast to one in *cis*-polyacetylene. In *trans*-polyacetylene there is a mirror plane at the soliton, but not in *cis*! In *cis*-polyacetylene a soliton separates a *cis*-transoidal domain from a *trans*-cisoidal. The latter is richer in energy and the soliton is pushed through the chain so that it destroys the energy-rich part. Therefore, single solitons will always move the chain ends. This forced motion of the solitons corresponds to the motion of Bloch walls if a magnetic field is applied to a ferromagnet or to the migration of dislocations in a strain field. Therefore, solitons in *cis*-polyacetylene are 'principally immobile'.

There could also be polarons in *cis*-polyacetylene, and these could be mobile. Even without interchain interaction there is a soliton-antisoliton attraction in *cis*-polyacetylene because of the energy difference between the *cis*-transoid and the *trans*-cisoid structure. Figure 41 shows polarons and bipolarons in *cis*-polyacetylene. In

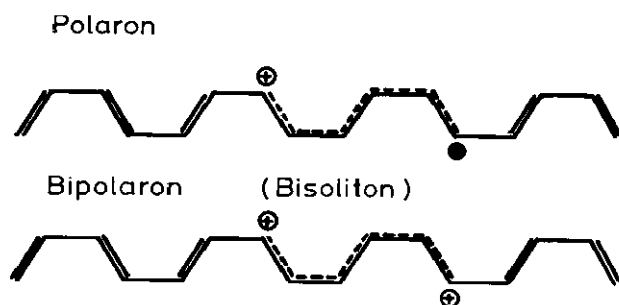


Figure 41. Polaron and bipolaron in *cis*-polyacetylene.

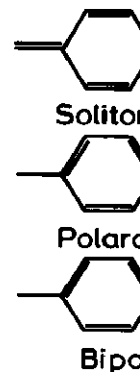


Figure 42. Soliton structures in polyacetylene.



Figure 43. Demonstration of parison with the lower polymers. (After [44].)

polyparaphenylene the situation of *cis*-polyacetylene can be respectively conjugational defect polyacetylene, with its degenerate case. It is the only conjugated on both sides of a conjugation respect like *cis*-polyacetylene.

The discussion in this section, which leads to the complete consideration, is not complete. In fact, both interactions cannot be treated just as a

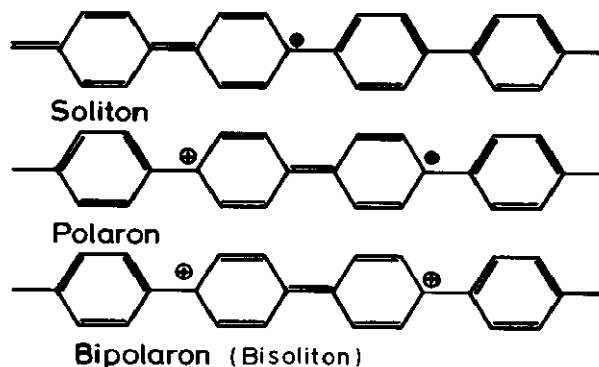
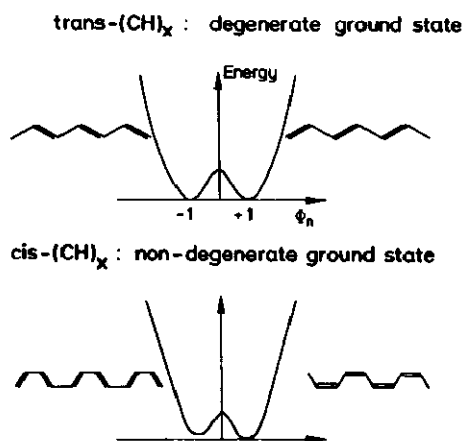


Figure 42. Soliton, polaron and bipolaron in polyparaphenylene.

Figure 43. Demonstration of the high symmetry of a *trans*-polyacetylene chain (a) in comparison with the lower symmetry in *cis*-polyacetylene and (b) all other conjugated polymers. (After [44].)

polyparaphenylene the situation is very similar to that in *cis*-polyacetylene (the meander of *cis*-polyacetylene can be envisaged as the upper part of the phenylene rings). The respective conjugational defects of polyparaphenylene are shown in figure 42. *Trans*-polyacetylene, with its degenerate ground state (and polycarbyne), is indeed a unique case. It is the only conjugated polymer in which symmetry ensures equal lattice energy on both sides of a conjugational defect. All other conjugated polymers behave in this respect like *cis*-polyacetylene (figure 43).

3.10. Electron correlation

The discussion in this section has so far been based on electron-phonon interaction, which leads to the Peierls transition, as demonstrated in figure 21. For a more complete consideration, electron-electron interaction also has to be taken into account. In fact, both interactions are of about equal importance in polyacetylene: one cannot be treated just as a small perturbation of the other. The Hamiltonian of the

system with both interactions will look like

$$H = \frac{M}{2} \sum_n \dot{u}_n^2 + \frac{K}{2} \sum_n (u_n - u_{n+1})^2 - \sum_{n,s} [t_0 + \alpha(u_n - u_{n+1})] \times (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}) + U \sum_n (c_{n\uparrow}^+ c_{n\uparrow} - \frac{1}{2})(c_{n\downarrow}^+ c_{n\downarrow} - \frac{1}{2}), \quad (6)$$

where M is the mass of the CH group, K the elastic constant of the σ -bond, $W = 4t_0$ the width of the π -band, α the electron-phonon coupling constant, and U the Hubbard parameter for the on-site electron-electron interaction. The creation and annihilation operators for a π -electron on site n with spin s are $c_{n,s}^+$ and $c_{n,s}^-$, respectively. The variable u_n is the displacement of the lattice site from the hypothetical position in the undimerized case.

The first two terms in equation (6) are the kinetic and the elastic energy of the system, the third is the electron hopping term, and the fourth corresponds to the correlation energy. If $U = 0$, equation (6) reduces to the Su-Schrieffer-Heeger Hamiltonian [34] with a Peierls gap of

$$2\Delta = 16t_0 \exp \left[- \left(1 + \frac{1}{2\lambda} \right) \right], \quad (7)$$

where $\lambda = 2\alpha^2/(\pi t_0 K)$ and with midgap solitons having a tanh-wavefunction as drawn in figure 26. If, on the other hand, the electron-phonon interaction is switched off, i.e. if $\alpha = 0$, equation (6) reduces to the 'pure Hubbard case'. Here once again an energy gap at the Fermi level is found, but instead of the Peierls distortion a spin-density wave is formed. Ukrainskii [45] and Horsch [18] have shown that the combination of electron-phonon and electron-electron interaction can lead to increased dimerization (spin Peierls state). Following Baeriswyl and Maki [46] and Baeriswyl [47], for small values of U , the gap energy can still be described by equation (7) if λ is replaced by $\tilde{\lambda} = \lambda + 0.133(U/4t_0)^2$. For very large values of U , the Peierls case has to be treated as a perturbation of the Hubbard case and a smooth transition between both cases is expected [47].

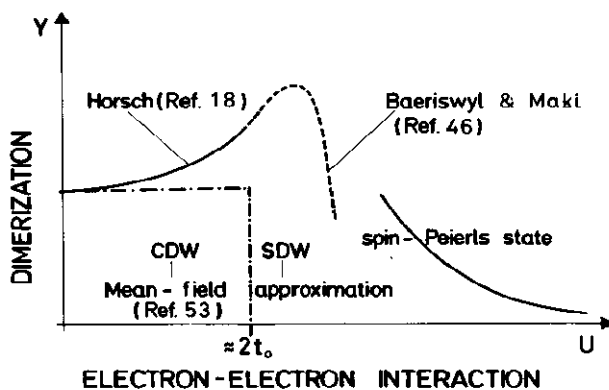


Figure 44. Dimerization of a polyene chain as a function of the Hubbard parameter U . The dot-dashed line shows the phase boundary in the mean-field approximation according to calculations by Kivelson and Heim [53]. The solid lines show the qualitative behaviour for small and large U s, respectively; the dashed line corresponds to the extended theory of Baeriswyl and Maki. (After [54].)

According to theoretical obtained from electron energy induced absorption measurements double resonance (ENDOR) experiments to be between 7 and 9 eV in polyene. This is very difficult to treat theoretically by Hirsch [51] and early analytical calculations are available. As a summary of the effects of correlation, the dimerization (bond alternation) is a function of the Hubbard parameter U , however, that within the scientific community the effects of electron correlation are

4.1. Remarks

If there are mobile charged species, they can contribute to the conductivity. In perfect chains of *trans*-polyacetylene, the transport is very low. If, however, the undimerized chains are short, say some 100 Å, the solitons move with a velocity of sound has been found. The long-wavelength sound ($\lambda = 100$ Å) has a velocity of sound v_s . The sound velocity along a chain is the upper limit for the velocity of the lattice distortion. An electric field can reach the velocity of sound. A distance in the order of 100 Å only become important at a.c.

In the d.c., conventional acoustics contribute indirectly to the conductivity. In this case electrons would hop between segments, but on the chains the hopping is to the strong electron-phonon interaction. It depends very much on the shape of the hopping process and therefore the principle, furnish evidence of the effect of the simple semiconductors, like polyacetylene, in qualitative agreement with the measurements of the hopping conductivity in

4.2. Conclusions

The electron micrographs of polyacetylene are uniform solids but rather heterogeneous. The dimerization of this structure is shown in figure 44, which, in a *gedanken* experiment, is related to the electrical conductivity. In the measurement of charge transport

According to theoretical considerations [18, 46] and experimental evidence obtained from electron energy-loss spectroscopy by Fink *et al.* [48], from photo-induced absorption measurements by Vardeny *et al.* [49] and from electron-nuclear double resonance (ENDOR) experiments by Grupp *et al.* [50], the value of U seems to be between 7 and 9 eV in polyacetylene. This case where neither λ nor U dominates is very difficult to treat theoretically. Today only preliminary numerical calculations by Hirsch [51] and early analytical results by Krivnov and Ovchinnikov [52] are yet available. As a summary of this discussion on the importance of electron-electron correlation, the dimerization (bond-alternation parameter) is drawn schematically as a function of the Hubbard parameter U in figure 44. It should be pointed out, however, that within the scientific community there is no agreement as yet on the effects of electron correlation in polyacetylene [55, 56].

4. Electrical conductivity

4.1. Remarks concerning soliton conductivity

If there are mobile charged solitons in polyacetylene (figure 23) one could expect them to be responsible for the electrical conductivity. If we had samples with very long perfect chains of *trans*-polyacetylene, we would probably observe this solitonic charge transport. If, however, the undisturbed conjugated segments in polyacetylene are very short, say some 100 Å, the soliton current will stop very quickly—after only a few picoseconds if the solitons move at the velocity of sound. (In polyacetylene films the velocity of sound has been found to be $v = 2 \times 10^5 \text{ cm s}^{-1}$ [59]. However, this is for long-wavelength sound ($\lambda = 1.4 \times 10^{-2} \text{ cm}$) propagating in the fibrillar network. The sound velocity along a chain is probably $v \sim 10^6 \text{ cm s}^{-1}$.) The sound velocity is the upper limit for the velocity of the solitons, because solitons carry with them a lattice distortion. An electric field would accelerate charged solitons until they have reached the velocity of sound. But, alas, in real polyacetylene they would stop after a distance in the order of 100 Å. According to this estimate soliton conductivity would only become important at a.c. frequencies in the terahertz regime.

In the d.c., conventional a.c. and even in the microwave regime, solitons can only contribute indirectly to the conductivity, for example by acting as hopping centres. In this case electrons would hop or tunnel from chain to chain or from segment to segment, but on the chains themselves they would form solitons or polarons (owing to the strong electron-phonon interaction in polyacetylene). The hopping probability depends very much on the shape of the wavefunction of the states participating in the hopping process and therefore the investigation of the conductivity should, in principle, furnish evidence of the existence or non-existence of solitons. But since even in the simple semiconductors, like amorphous silicon, hopping theories are only in qualitative agreement with the experimental data, we cannot expect that an analysis of the hopping conductivity in polyacetylene will tell us very much about solitons.

4.2. Conductivity in heterogeneous media

The electron micrographs of figure 5 tell us that polyacetylene films are not at all uniform solids but rather heterogeneous structures of fibres and grains. An idealization of this structure is shown in figure 6. The points 1 to 4 indicate microprobes which, in a *gedanken* experiment, would allow one to separate various contributions to the electrical conductivity. Probes 1 and 2 sit on the same chain and would permit the measurement of charge transport along a polymer chain (perhaps direct soliton

conductivity). From probe 2 to probe 3 a hopping or tunnelling process is necessary and the charge carrier has to change the chain. From 3 to 4 even the fibre has to be changed. In a real experiment we can only measure the transport from 1 to 4, i.e. a complicated superposition of various transport processes. In a simplified way this superposition can be expressed as a series of resistances

$$R_{1,4} = R_{1,2} + R_{2,3} + R_{3,4}. \quad (8)$$

The total behaviour of the sample is determined by the largest resistance. In highly doped samples this will be the resistance from fibre to fibre ($R_{3,4}$) or across grain boundaries in the non-fibrillar Durham Graz material. This type of internal contact resistance is well known from metal powders, sputtered metal layers, and polymers compounded with carbon black or metal flakes. Theories of fluctuation-induced tunnelling have been developed to describe this case [58–60]. They show that at finite temperatures the barriers between the individual particles are modulated by statistically fluctuating potential differences.

In lightly doped samples, the resistance $R_{2,3}$ will dominate. For this case Kivelson [61] has developed the elegant theory of inter-soliton hopping: charged solitons are assumed to be electrostatically trapped by the ions of the dopant. Neutral solitons are mobile and diffuse. When a neutral soliton comes close to a charged soliton on a neighbouring chain they can exchange their charge. This idea has been extended to polarons by Bredas [62] in order to find a mechanism that can work in all polymers (as noted above, solitons are only mobile in *trans*-polyacetylene, see figure 39; polarons could be mobile in any conjugated system). Inter-soliton hopping and inter-polaron hopping are just two special cases of hopping conductivity in general and hardly so specific that they can be distinguished experimentally.

Hopping mechanisms are of general importance for charge transport in amorphous or heavily disordered semiconductors. Some relevant articles are listed in Appendix 10. Some authors stress that conductivity in polyacetylene is a percolation problem [63] and point to unavoidable inhomogeneities in the dopant concentration. But hopping is also a percolation phenomenon [64], so that from the functional dependence of the conductivity on the doping level alone not much information on the type of the inhomogeneities can be obtained. The resistance $R_{1,2}$, which might perhaps be dominated by direct soliton conductivity, does not seem to be accessible to measurement. In §7 the question of how much one can learn about soliton transport from pulsed photoconductivity experiments will be discussed. A collection of literature on transport phenomena in conductive polymers is given in Appendix II.

4.3. D.c. conductivity of polyacetylene

The temperature dependence of the d.c. conductivity of polyacetylene is shown in figures 45 (a) and (b) for various doping levels [60, 65, 66]. We immediately see that the conductivity seems to be similar in *cis*- and in *trans*-polyacetylene, conforming quite well to our expectation that direct soliton conductivity does not play an important role (solitons are only mobile in *trans*-polyacetylene. But doping might transform *cis* into *trans*, see §2). In highly doped samples there is only a weak temperature dependence of the conductivity, but the conductivity still decreases upon cooling. The term 'metallic conductivity' has not been chosen with respect to the temperature coefficient but in view of the room-temperature value of the conductivity (the present world record of $1.5 \times 10^5 \text{ S cm}^{-1}$ [3] is, indeed, in the metallic regime;

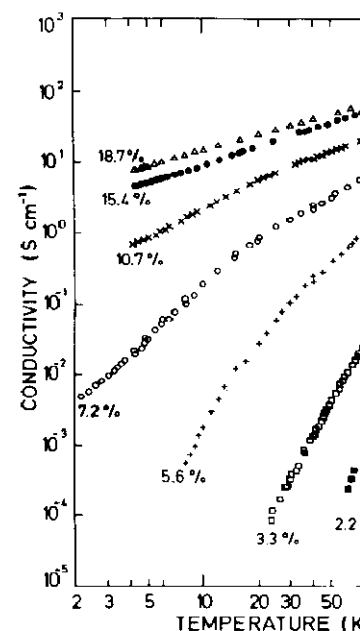


Figure 45. (a) Temperature dependence of the d.c. conductivity for various levels of iodine doping.

see §2) and because of the small thermopower.

The lower the doping level, the more pronounced is the temperature dependence. Not only iodine-doped samples show this behavior. The conductivity of pristine polyacetylene also follows a law $\sigma \propto T^n$ can be fitted to the data in *trans*-polyacetylene by equation (9).

There is no simple analytical expression for the temperature dependence of the conductivity in (a) and (b) and, in view of the different transport mechanisms, one would not expect a simple law. It turns out that

works remarkably well. The value of γ to be chosen is $\gamma = 1/2$ in (a) and (b) and (c), where plots of $\ln \sigma$ versus $1/T$ are shown.

In equation (9) there are several parameters: σ_0 is the pre-exponential factor, σ_{∞} is the limiting value of the conductivity at high temperatures, σ_{∞} is the limiting value of the conductivity at high temperatures, and σ_{∞} is the limiting value of the conductivity at high temperatures.

annealing process is necessary to 4 even the fibre has to be transport from 1 to 4, i.e. a es. In a simplified way this

(8)

largest resistance. In highly fibre ($R_{3,4}$) or across grain This type of internal contact metal layers, and polymers ries of fluctuation-induced [60]. They show that at finite re modulated by statistically

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large transport in amorph- rant articles are listed in yacetylene is a percolation the dopant concentration. that from the functional not much information on istance $R_{1,2}$, which might not seem to be accessible can learn about soliton ll be discussed. A collec- ve polymers is given in

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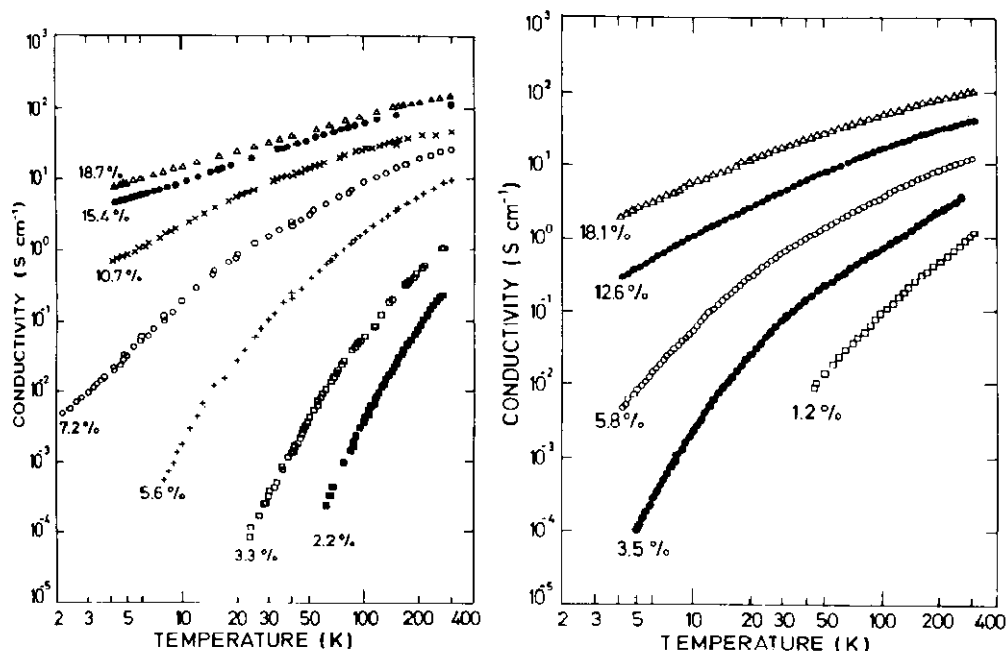


Figure 45. (a) Temperature dependence of the d.c. conductivity of *cis*-polyacetylene for various levels of iodine doping [60]. (b) Same in *trans*-polyacetylene [60].

see § 2) and because of the suppression of the Peierls gap. In addition it is in accord with the small thermopower and its temperature dependence [67].

The lower the doping concentration, the stronger the temperature dependence. Not only iodine-doped samples behave this way but all samples investigated so far. The conductivity of pristine polyacetylene drops so rapidly on cooling that a power law $\sigma \propto T^n$ can be fitted to the data with $n \gtrsim 10$. Figure 46 shows data measured in *trans*-polyacetylene by Epstein [68]. The solid line corresponds to $\sigma \propto T^{14}$.

There is no simple analytic form to describe the family of curves in figure 45 (a) and (b) and, in view of the complicated superposition of various charge-transport mechanisms, one would not expect one. But if one wants a quick parametrization it turns out that

$$\sigma = \sigma_0 \exp [-(T_0/T)^\gamma] \quad (9)$$

works remarkably well. The value of γ would depend on the doping level but if a fixed value is to be chosen $\gamma = 1/3$ is the best compromise. This is seen from figure 47 (a), (b) and (c), where plots of $\ln \sigma$ against various powers of T are tried [69].

In equation (9) there are only two parameters, σ_0 and T_0 . Inspection of the ensemble of all our conductivity data suggests that there is a correlation between these parameters [70]. This is implied by figure 48, where T_0 is plotted as a function of the conductivity at room temperature. The universal correlation between the absolute value of the conductivity and its temperature coefficient seems to hold not only for

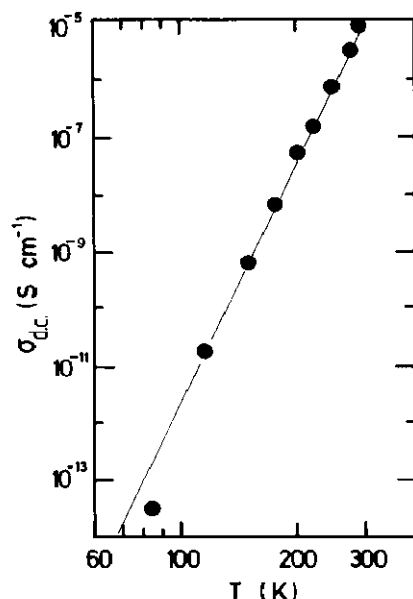


Figure 46. Temperature dependence of the d.c. conductivity of undoped polyacetylene. (After [68].)

polyacetylene doped with various agents, but also for all other conductive polymers investigated so far.

We believe that equation (9) and the universality in figure 48 comes about from complicated averaging over the heterogeneities of the sample and that only in the limiting cases of fairly high and fairly low doping concentrations would further analysis be useful and instructive. At high doping concentrations (above 10% in the case of iodine) the resistance between fibres, $R_{3,4}$, should dominate and the model of fluctuation-induced tunnelling [59] should be applicable. This model assumes elastic tunnelling at low temperatures, which is independent of temperature. At higher temperatures thermally activated tunnelling processes are added. Figure 49 shows that this model can, indeed, describe the experimental data very well [60, 73].

At low doping concentrations the electrical conductivity should be mainly due to hopping processes. For the d.c. conductivity this should be variable-range hopping, i.e. hopping between localized electronic states which are distributed at random in space and energy [74, 75]. In the low-temperature limit the theory predicts

$$\ln \sigma \propto T^{-1/(1+d)}, \quad (10)$$

where d is the dimensionality of the hopping process (in three dimensions this leads to Mott's famous $T^{-1/4}$ law). We do not claim that our compromise value $\gamma = \frac{1}{3}$ in equation (9) and figure 47 implies two-dimensional hopping. The data do not really permit one to distinguish between $\gamma = \frac{1}{3}$ and $\gamma = \frac{1}{4}$. Furthermore, most of the data were not taken in the low-temperature limit. A critical discussion of the validity range of the low-temperature approximation (10) to variable-range hopping is given in [65] and [66].

At very low doping concentrations, equation (10) fits the data just as well as a power law $\sigma \propto T^n$, $n \gtrsim 10$ (figure 46). Such a power law is predicted for inter-soliton

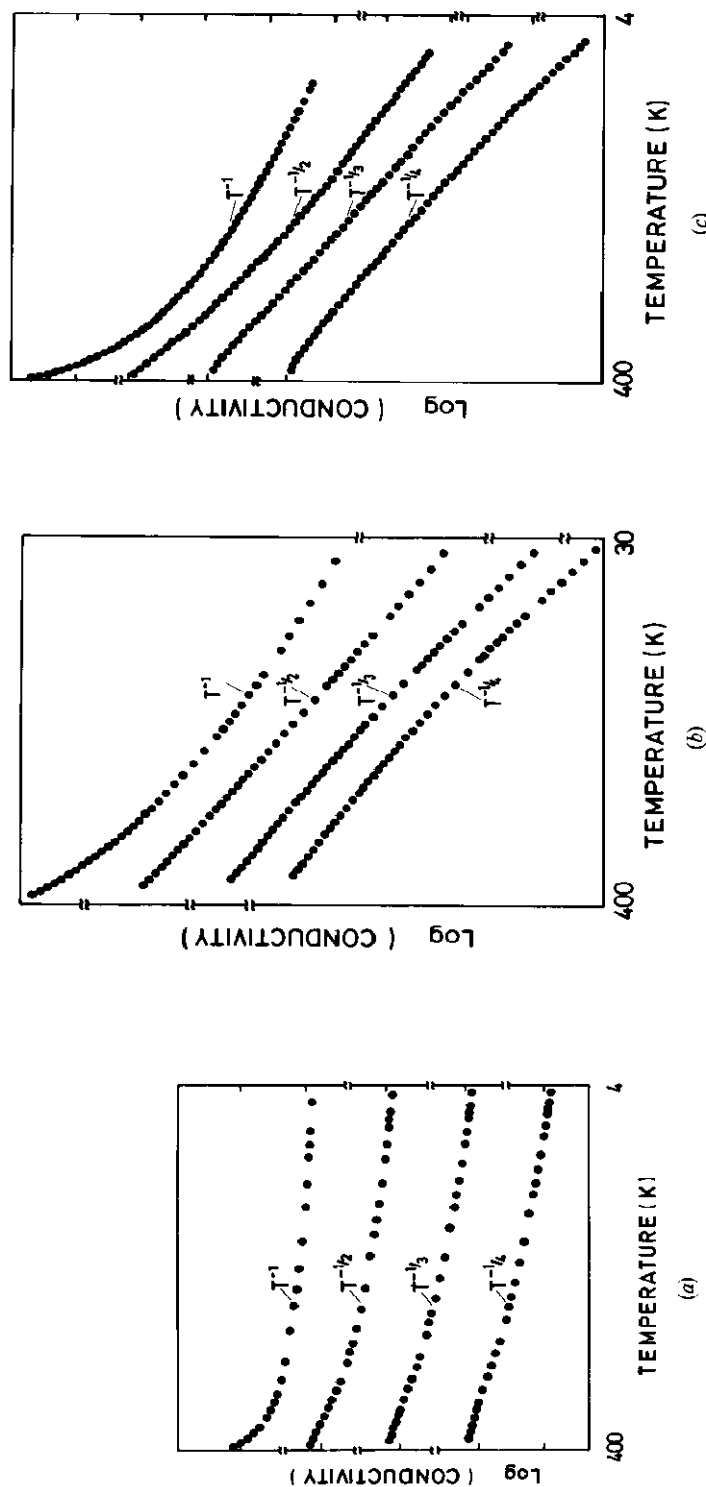


Figure 47. Simple parametrization of the temperature-dependent conductivity. In σ is plotted against various powers of T . The abscissa scale is chosen in such a way that straight lines were to be obtained for the respective value of γ indicated and that the abscissas coincide at 4 K and room temperature [69]: (a) 19% I; (b) 1.26% FeCl₃; (c) 1.7% InI₃.

ity of undoped polyacetylene.

other conductive polymers

Figure 48 comes about from simple and that only in the concentrations would further dominate and the model of This model assumes elastic of temperature. At higher e added. Figure 49 shows ata very well [60, 73].

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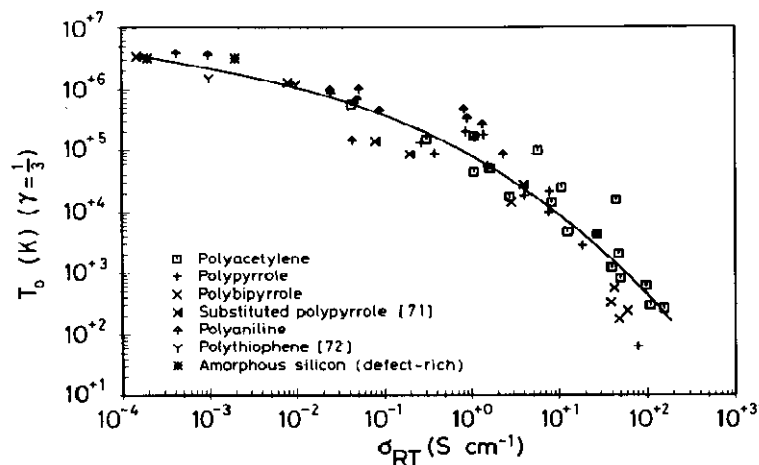


Figure 48. Universal correlation between room-temperature conductivity and T_0 (equation (9)) [70].

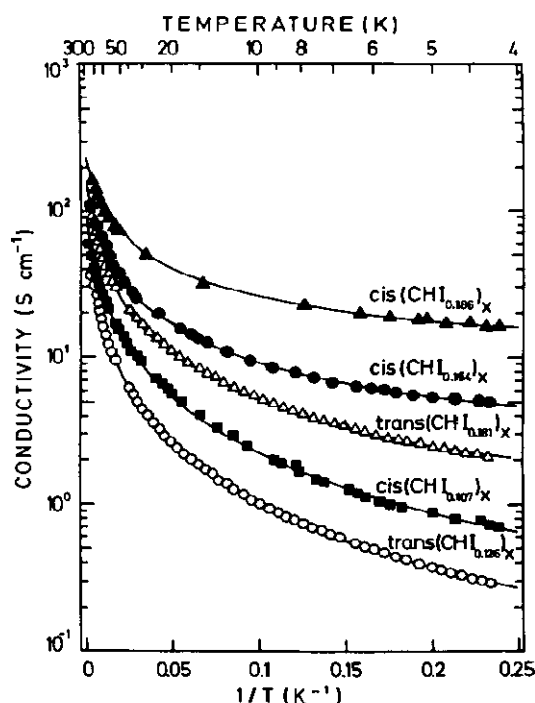


Figure 49. Temperature dependence of the d.c. conductivity of heavily (iodine) doped polyacetylene and fit of the model of fluctuation-induced tunnelling [60]. Solid curve: theoretical fit.

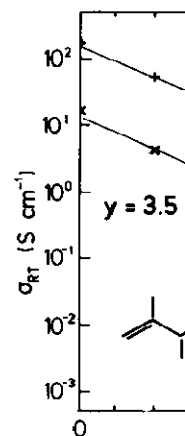


Figure 50. Dependence of the room-temperature conductivity on the concentration of defects, which interrupt the conjugated chain [79].

hopping [61]. Apparently the results do not yet reveal very much about the details of the mechanism, the question as to whether or not it is a hopping process.

Moses *et al.* [76] have measured the temperature dependence of the conductivity of polyacetylene under various pressures. In Kivelson's model the temperature dependence should change with pressure if the level changes [75]. The experimental results are in good agreement with the Kivelson mechanism. But in order to confirm this one would have to know more about the details of its behaviour under pressure.

Several experiments have shown that the conductivity of polyacetylene is very sensitive to structural defects. Artificial defects have been introduced into the chain, for example, by interrupting the conjugated chain with a nonconjugated group, for example, CH_2 [78], as indicated in the inset of Figure 50. The conductivity after doping to the same level has dropped by about four orders of magnitude. Phenomenologically the relationship between the conductivity and the defect concentration. It is interesting to note that in polyacetylene, the temperature dependence of the conductivity is the same as the behaviour of figure 48. This is also the case for segmented polyacetylene, where the segment length by resonance Raman spectroscopy is about 100 Å.

4.4. Hopping

It is well known that the conductivity of a material depends on the frequency. In the hopping mechanism the conductivity is

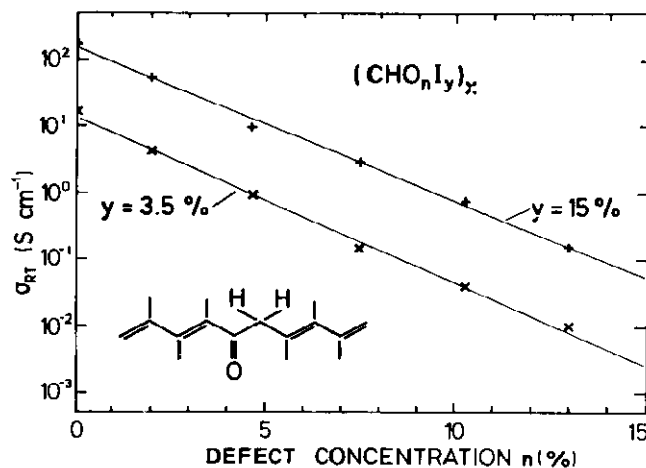


Figure 50. Dependence of the conductivity of doped polyacetylene on the concentration of defects, which interrupt the conjugation of double bonds ('segmented polyacetylene') [79].

hopping [61]. Apparently the temperature dependence of the conductivity cannot reveal very much about the details of the hopping process. In particular, it leaves open the question as to whether or not solitons are involved.

Moses *et al.* [76] have measured the conductivity of *trans*-polyacetylene at various pressures. In Kivelson's model [61] at all pressures there should be the same temperature dependence. In the case of variable-range hopping, however, the temperature dependence should change with pressure, because the density of states at the Fermi level changes [75]. The experiment shows no difference in the temperature dependence between ambient pressure and 8.74 kbar. Moses *et al.* take this as an evidence for the Kivelson mechanism. But in order definitely to exclude variable-range hopping we would have to know more about the electronic band structure of polyacetylene and its behaviour under pressure.

Several experiments have been carried out to investigate the dependence of the conductivity of polyacetylene on the conjugation length [77]. For this purpose artificial defects have been introduced into the polyene chains, so that the conjugation is interrupted, for example, CH_2 groups or a combination of carbonyl and CH_2 groups [78], as indicated in the inset of figure 50 [79]. In figure 50 the room-temperature conductivity after doping to 3.5 and 10% iodine, respectively, is plotted as a function of the defect concentration. In a sample with 12% defects the conductivity has dropped by about four orders of magnitude for both doping concentrations. Phenomenologically the relation $\sigma(n) = \sigma(0) \exp(-55n)$ is found, where n is the defect concentration. It is interesting to note, that in these samples of 'segmented' polyacetylene, the temperature dependence of the conductivity also follows the universal behaviour of figure 48. This is shown in figure 51. In addition to conductivity studies, segmented polyacetylene also permits the determination of the effective conjugation length by resonance Raman scattering [70, 79].

4.4. A.c. conductivity of polyacetylene

It is well known that the conductivity of disordered materials increases with frequency. In the hopping model this is easy to understand: for d.c. conduction the

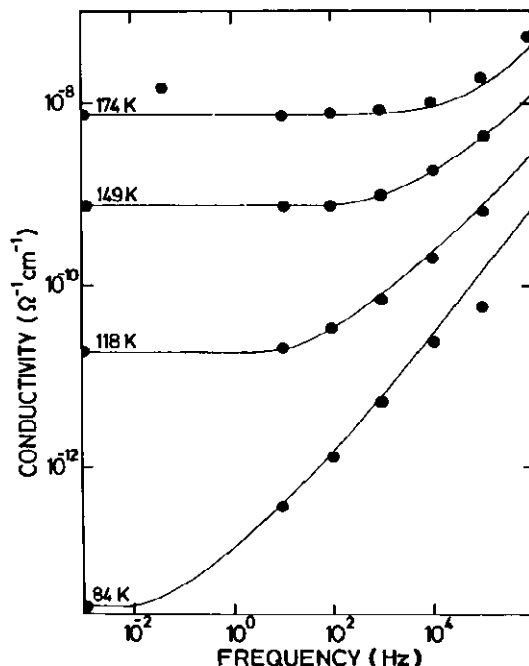


Figure 52. A.c. conductivity of undoped *trans*-polyacetylene: after [68] (full dots) and fit of Summerfield's hopping model [66, 81].

dip or pseudo-gap has to be sunk at the Fermi level, as shown schematically in figure 54. Looking at figure 54 we soon realize that the density of states has become quite complicated. The originally antagonistic positions—soliton and amorphous semiconductors—are now thoroughly blurred. The soliton model will start from a δ -function in the density of state (midgap state!); the amorphous semiconductor from a constant density of states. The δ -function could be broadened by soliton-soliton interactions. The pseudo-gap could be caused by Coulomb interactions, in both models (see figure 55).

Can we learn more when we go to higher frequencies than those of microwaves? Figure 56 shows the frequency dependence of the conductivity of a polyacetylene sample doped with AsF_5 , measured in the entire frequency regime from d.c. up to terahertz (submillimetre waves; at room temperature) [83]. To cover such a wide frequency range, five different experimental methods had to be applied: four-probe measurements at d.c., microwave cavity (10 GHz), oversized multimode resonator (5–150 GHz), transmission and reflection of a laser beam (300 GHz), and far-infrared Fourier spectroscopy (> 300 GHz). The experimental data show a surprising minimum between 50 and 100 GHz. If this is not an artefact caused by the shift between various experimental techniques nor an effect of (perhaps) impurity-induced infrared-active low-frequency lattice vibrations, one would have to assume a superposition of two different mechanisms of conductivity. Perhaps there are some highly doped regions where the conductivity is really metallic and where the Drude formula holds:

$$\sigma_D = \sigma_0 / (1 + \omega^2 \tau^2), \quad (11)$$

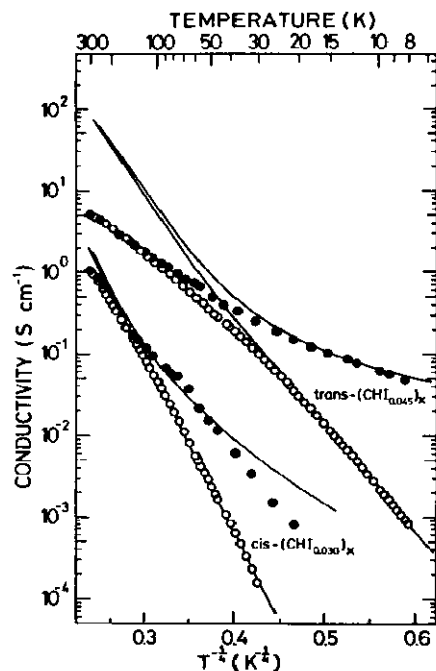


Figure 53. D.c. and microwave conductivity of iodine-doped polyacetylene and fit of extended-pair approximation [66]: ○ 30 Hz; ● 9.9 GHz.

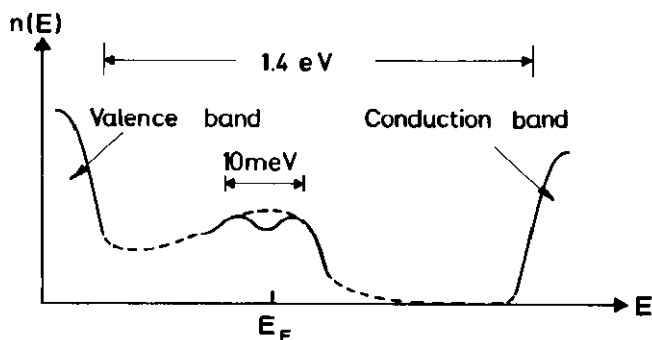


Figure 54. Schematic view of the density of states to fit the experimental data of figure 53.

with

$$\sigma_0 = Ne\mu \quad \text{and} \quad \mu = e\tau/m^*. \quad (12)$$

Here N is the carrier concentration, μ the mobility, m^* the effective mass and τ the collision time. Then we could determine N and τ . From measurements in the low-frequency regime only, the $\mu\tau$ -product can be determined: $\sigma_D = Ne\tau/m^*$ for $\omega\tau \ll 1$. Since at high frequencies $\sigma_D \propto N/\tau$, N and τ can be determined separately if data over the whole frequency regime are available. Under these assumptions the analysis of figure 56 yields $N \sim 10^{15} \text{ cm}^{-3}$ and $\tau \sim 10^{-11} \text{ s}$, which would lead to the surprisingly

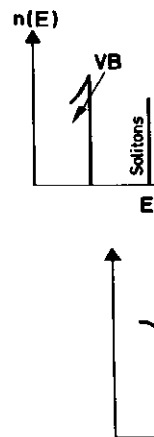


Figure 55. The density of states of a narrow soliton line or band in a semiconductor.

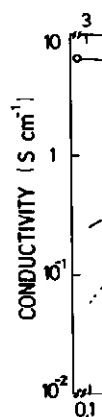


Figure 56. Frequency dependence of conductivity at 300 K in the film.

high mobility of $\mu \sim 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (figure 57). As mentioned above, a particle moving with the velocity v over a distance of 100 Å with the characteristic time τ would travel a distance of 100 Å with the characteristic time τ .

If one subtracts the 'Drude' curve (dotted curve) results. Phonon scattering, e.g., by using equation (5.47),

$$\sigma_b(\omega)$$

where $N(E_F)$ is the density of states at the Fermi level and ψ the wavefunction of a hopping site.

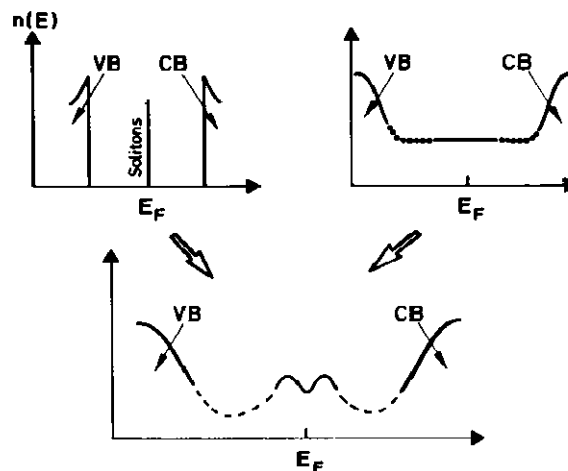


Figure 55. The density of states function of figure 54 can either be obtained by broadening a narrow soliton line or by structuring the smooth density of states of an amorphous semiconductor.

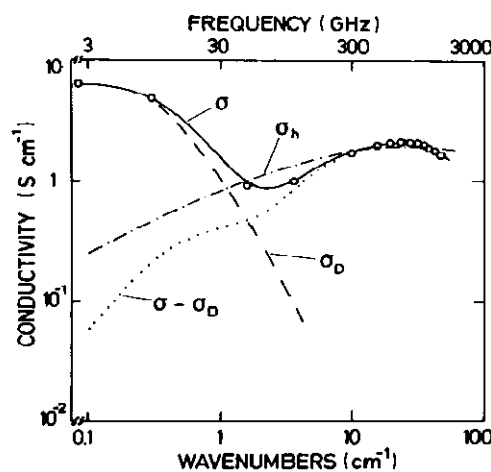


Figure 56. Frequency dependence of the conductivity of 0.7% AsF_5 -doped *cis*-polyacetylene at 300 K in the frequency range from d.c. to far-infrared [83].

high mobility of $\mu \sim 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (see also the discussion of the magnetoresistance; figure 57). As mentioned above, a τ of some picoseconds would correspond to a particle moving with the velocity of sound along a polyene chain and colliding after a distance of 100 \AA with the chain end. But this agreement is probably just fortuitous.

If one subtracts the 'Drude term' from the total conductivity in figure 56, the dotted curve results. Phonon-assisted hopping can be fitted successfully to this curve, e.g., by using equation (5.47) in Nagels' paper [84]:

$$\sigma_h(\omega) = e^2 k T N^2(E_F) \beta^3 \omega [\ln(\omega_{ph}/\omega)]^4, \quad (13)$$

where $N(E_F)$ is the density of states at the Fermi level, β the spatial extension of the wavefunction of a hopping site and ω_{ph} the frequency of the phonons assisting in the

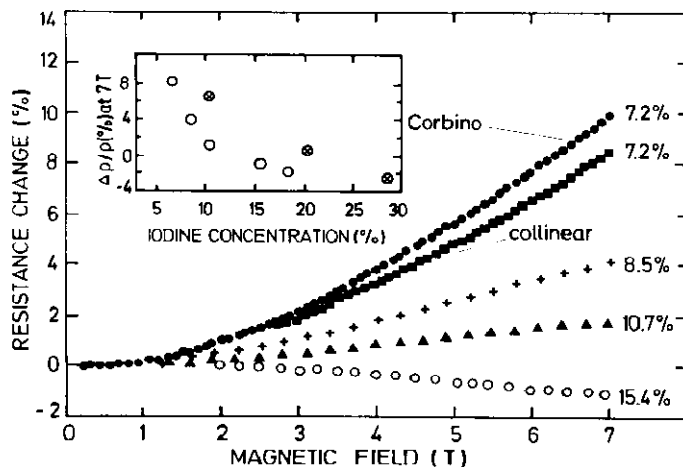


Figure 57. Magnetoresistance of iodine-doped polyacetylene at liquid-helium temperature [87].

hopping process. The frequency ω_{ph} can be estimated from the maximum conductivity in figure 56. By assuming 'reasonable' values for β , $N(E_F)$ can be calculated. For β between 20 and 50 Å we obtain values for $N(E_F)$ between 4×10^{19} and $4 \times 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$.

4.5. Missing spins

If all charge carriers have a well defined magnetic moment the carrier concentration can be determined from the magnetic susceptibility. Measurements of this kind will be discussed in § 5. In the case of localized carriers, which are assumed in hopping conductivity, the carrier concentration can be calculated from the Curie constant. From the susceptibility data in figure 58 we get for a polyacetylene sample doped with 0.7% of AsF_5 , an upper limit for the spin concentration of $N_s < 10^{18} \text{ cm}^{-3}$. If all states were equally distributed over the energy gap we would obtain $N_s(E_F) < 7 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$. This limit is by an order of magnitude lower than the carrier concentration we would need in equation (13) to reproduce the hopping conductivity of figure 56, even under the most favourable assumptions for β . Consequently there must be spinless charge carriers which are not seen magnetically. At least in *trans*-polyacetylene, these spinless carriers could be solitons (in § 3 we have seen that charged solitons have no spin). Epstein *et al.* [75] arrive at the same conclusion when interpreting their investigations of the conductivity in iodine-doped polyacetylene, as do Chung *et al.* [85] in view of their results on polyacetylene doped with sodium.

This phenomenon of missing spins, however, is not very new. It has already been observed in inorganic semiconductors. If two electrons sit in the same trap they will arrange their spins to be antiparallel and they will be magnetically invisible. Such blind traps are formally described by a negative correlation energy U and have been reported in chalcogenide glasses and even in silicon [86]. In polyacetylene, however, U is known to be positive. But interchain coupling can lead to the formation of bipolarons which are also spin-compensated, as discussed in § 3 (figures 37 and 41). Therefore, missing spins, taken alone, are not yet evidence of solitons.

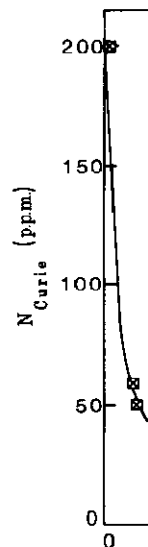


Figure 58. Decrease of spin concentration has been calculated.

4.6. Magn

As an attempt to obtain further information on the magnetic properties of conducting polymers, the magnetoresistance of samples at liquid-helium temperature was measured. The magnetoresistance in highly doped samples contributed to a better understanding of the hopping process. We have attempted an explanation of the observed magnetoresistance which could be related to the pseudogap model. Another possibility is localization of carriers [91]. Finally there are theories which relate the magnetoresistance to the formation of bipolarons [92]. Further measurements are being carried out by Ettlinger *et al.* [93] and by others.

If polyacetylene were a bulk material, the positive part of the magnetoresistance would be expected. The morphology shown in figures 5 and 6 is not representative. The value is two orders of magnitude lower than the hopping conductivity $\sigma = N\mu e$ by estimating N from the macroscopic magnetoresistance $R_{3,4}$ in equation (8), whereas magnetoresistance would lead to the optimistic opinion that the conductivity is only the macroscopic magnetoresistance $R_{3,4}$. (The recent values of the magnetoresistance reported at the Kirchberg Winter School are in good agreement with the extent this has already happened in the case of a Hall mobility in doped polyacetylene.)

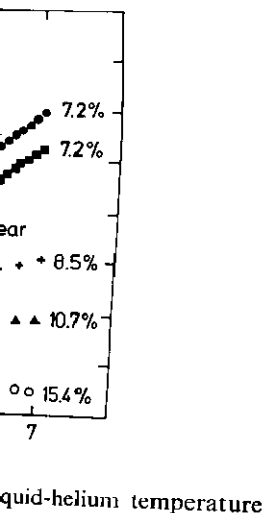


Figure 58. Decrease of spin concentration of polyacetylene upon doping. The spin concentration has been calculated from the intensity of the ESR signal [98].

4.6. Magnetoresistance and the Hall effect

As an attempt to obtain further information on the mechanism of conductivity in conducting polymers, the magnetoresistance of polyacetylene has been investigated. In figure 57 the resistance change in fields up to 7 T is shown for various iodine-doped samples at liquid-helium temperature [87]. The most remarkable result is the negative magnetoresistance in highly doped samples, but up to now this effect has not yet contributed to a better understanding of charge transport in polymers. Röss *et al.* [88] have attempted an explanation using a two-band model (perhaps these two bands could be related to the pseudogap structure in the density of states in figure 54). Another possibility is localization [89, 90] and its suppression by the magnetic field [91]. Finally there are theories which predict a negative magnetoresistance in hopping models [92]. Further measurements of a negative magnetoresistance have been reported by Ettlinger *et al.* [93] and by Gould *et al.* [94].

If polyacetylene were a bulk isotropic solid one could calculate the mobility from the positive part of the magnetoresistance. If one tries this, in spite of the fibrillar morphology shown in figures 5, a value of $\mu \approx 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is obtained [87]. This value is two orders of magnitude higher than the one we would obtain from the conductivity $\sigma = Nue$ by estimating N from the doping concentration. Therefore one could argue that the macroscopic conductivity is limited by inter-fibrillar resistance $R_{3,4}$ in equation (8), whereas magnetoresistance measures the 'intrinsic' mobility. This would lead to the optimistic opinion that one could win two orders in magnitude in the conductivity if only the morphology of polyacetylene could be improved to reduce $R_{3,4}$. (The recent values of the very high conductivity in a new type of polyacetylene, reported at the Kirchberg Winter School [3] may be taken as evidence that to a certain extent this has already happened.) On the other hand, Seeger *et al.* [95] have measured a Hall mobility in doped polyacetylene of $\mu_H = 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Such inconsistencies

in the mobility are quite common in disordered materials [96] and some authors doubt whether the mobility is a useful parameter in these solids.

5. Magnetic properties

In § 3 we saw that spin-charge inversion is one of the remarkable features of a conjugational defect in polyacetylene: charged defects are spinless; neutral defects carry a magnetic moment. This inversion is related to fractionized charges, which also occur in elementary-particle physics and in the fractionized quantum Hall effect [38]. Spin-charge inversion is a symmetry property of the system, it makes use of the quasi-particle concept, but non-dispersive motion is not essential in this respect.

The magnetic moment of a neutral soliton can be seen in the ESR signal and in the static susceptibility as a paramagnetic contribution (unpaired electrons!). In the metallic state, when the Peierls transition is suppressed and there is a finite density of states at the Fermi level (no gap), the delocalized electrons will lead to a Pauli paramagnetism, which contributes to the static susceptibility and produces a Knight shift in NMR experiments. Evidence for the motion of solitons can be obtained from NMR-relaxation experiments and from the lineshape of the ESR signal (motional narrowing).

5.1. Magnetic susceptibility

A very nice manifestation of the spin-charge inversion is seen when polyacetylene is doped (figure 58). One might expect that the introduction of electrons or holes will increase the paramagnetic susceptibility, as it does in conventional semiconductors. But, in fact, the susceptibility *decreases* upon doping. In undoped polyacetylene there are usually some 10^{19} neutral solitons per cm^3 (because there are short polymer chains or short chain segments, some of which have an odd number of carbon atoms, and in an odd-numbered chain there is a soliton in the ground state). When the sample is doped (oxidized with AsF_5) the solitons get charged and lose their spin. This experiment was first carried out by Goldberg *et al.* [97] and was subsequently repeated by several other groups, e.g. Davidov *et al.* [98].

In figure 35 we saw that light doping changes the charge of already existing solitons, and heavy doping creates new solitons by breaking double bonds. Single solitons are only stable in the highly symmetric chains of *trans*-polyacetylene. In *cis*-polyacetylene and all other conjugated polymers the stable defect is the polaron, an entity having charge *and* spin (figures 41 and 42). If polypyrrole is doped electrochemically, initially individual polarons are created and the paramagnetic susceptibility increases. When the polaron concentration has reached a certain level, bipolarons, which are spinless, will form and the susceptibility will decrease. This has been demonstrated by Nechtschein *et al.* in an *in-situ* ESR chemical-doping experiment and is shown in figure 59 [99].

When the static magnetic susceptibility is measured, there are usually three contributions

$$\chi_{\text{total}} = C/T + \chi_{\text{Pauli}} + \chi_{\text{core}} \quad (14)$$

The first term can be identified by its temperature dependence, and from the Curie constant C the spin concentration can be calculated (as it can from the intensity of the ESR signal). The contribution of the closed electron shells χ_{core} is without interest in our context. It can be estimated from chemical tables like those given in Haberditzl

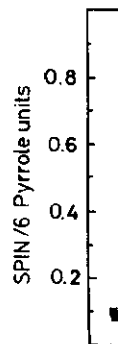


Figure 59. Creation of polarons.

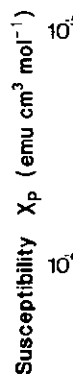


Figure 60. Pauli susceptibility as a function of the doping level [101]; ESR data (●) of

[100]. The term χ_{Pauli} is proportional to the density of states at the Fermi level. A finite value

In figure 60 [101], the concentration for polyacetylene is no Pauli susceptibility (the Fermi level is in the Peierls gap) but these states are localized. Curie term of the susceptibility. If doubly occupied they do not contribute. The value of the Pauli susceptibility is suppressed globally, there is no Pauli susceptibility, however, is the pronounced

[6] and some authors doubt

remarkable features of a spinless; neutral defects ionized charges, which also quantum Hall effect [38]. In this system, it makes use of the essential in this respect.

in the ESR signal and in unpaired electrons!). In the there is a finite density of ions will lead to a Pauli susceptibility and produces a Knight shift. These can be obtained from the ESR signal (motional

seen when polyacetylene of electrons or holes will conventional semiconductors. In doped polyacetylene there are short polymer chains (number of carbon atoms, and state). When the sample and loose their spin. This was subsequently repeated

large of already existing double bonds. Single of *trans*-polyacetylene. In the defect is the polaron, polyacetylene is doped electrochemically. At a certain level, bipolarons, decrease. This has been in a doping experiment and

there are usually three

(14)

ance, and from the Curie law can from the intensity of χ_{core} is without interest those given in Haberditzl

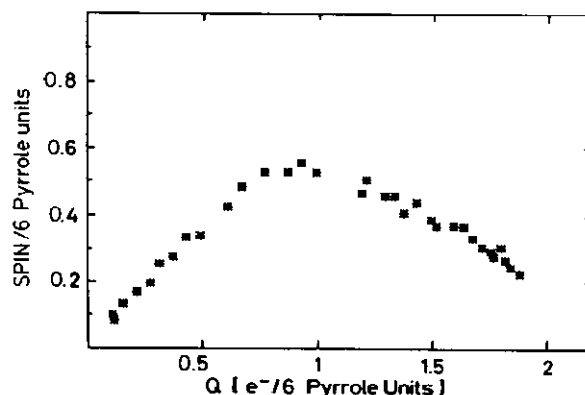


Figure 59. Creation of polarons and bipolarons in electrochemical doping of polypyrrole [99].

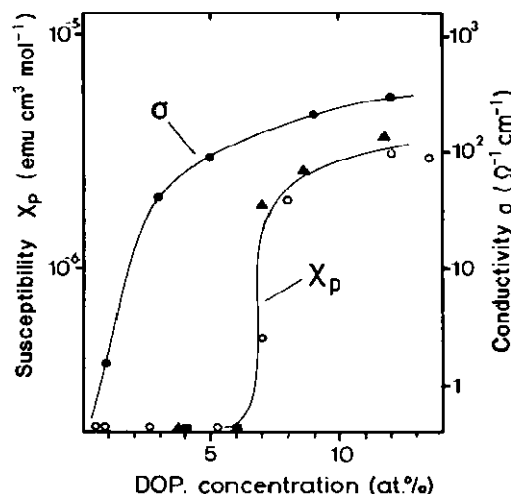


Figure 60. Pauli susceptibility χ_p and conductivity σ in a sample of (originally) *cis*-polyacetylene as a function of the doping concentration (Faraday balance AsF_6^- (▲) and I_3^- (■); M. Peo [101]; ESR data (●) of [102])

[100]. The term χ_{Pauli} is proportional to the density of extended electronic states at the Fermi level. A finite value of χ_{Pauli} is therefore a typical metallic property.

In figure 60 [101], the value of χ_{Pauli} is plotted as a function of the doping concentration for polyacetylene doped with AsF_5 . At low doping concentrations there is no Pauli susceptibility (within experimental limits). This is not surprising, because the Fermi level is in the Peierls gap. There are electronic states in the gap (see figure 54), but these states are localized, and if they are singly occupied they contribute to the Curie term of the susceptibility, not to the Pauli term (if they are unoccupied or doubly occupied they do not contribute at all). Not surprising, either, is the finite value of the Pauli susceptibility at high doping levels. Now the Peierls transition is suppressed globally, there is no gap, and we have a 'true' metal. Very surprising, however, is the pronounced step in χ_{Pauli} at a critical doping concentration. This is

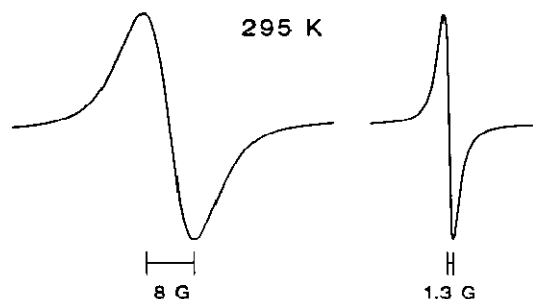


Figure 61. ESR signal for undoped *cis*- and *trans*-polyacetylene at room temperature [108].

quite reminiscent of a phase transition, and Kivelson and Heeger [43] have formulated a theory for a first-order phase transition from a soliton lattice into a polaron lattice. For the sake of comparison, the conductivity σ is also plotted in figure 60. It shows no anomaly at the critical concentration but tends to saturate at considerably lower doping levels. There is the remarkable regime between 2 and 6% doping, where there is high conductivity but no magnetic susceptibility, either Curie or Pauli. (Similar behaviour has also been observed in polyparaphenylene [103].) These results seem to be supported by Knight-shift measurements in NMR investigations [101, 104].

The results of figure 60 have been obtained by several groups [101, 102, 105]. Very often, however, the step in χ_{Pauli} is smeared out, as noted by Tomkiewicz *et al.* [106], probably as a result of inhomogeneous distribution of the dopant. Sharp steps at about the same critical dopant concentration have also been seen in n-type (sodium) doping [85]. Their interpretation of this step as a phase transition is very likely to be accepted [107], but it remains unclear whether or not this transition is really driven by effects on the polymer chains. It is known that the chain-packing changes with doping (see e.g. figure 13) and the arrangement of the dopant ions might contribute more to the total free energy than soliton or polaron formation. It will be very important to find out whether the critical concentration depends on the dopant species used or not, but different crystallinities of the samples and different *cis/trans* ratios will make a reliable determination difficult.

5.2. Magnetic resonance

Neutral solitons carry a magnetic moment and can be seen in ESR experiments. The linewidth is mainly determined by the hyperfine interaction with the hydrogen atoms on the polymer chain or by the lifetime of the spin state. Figure 61 shows the ESR signal of an undoped *cis*- and an undoped *trans*-polyacetylene sample at room temperature. As usual in this type of experiment, the derivative of the resonance line is plotted. The distance between the two extrema is the peak-to-peak linewidth ΔH_{pp} . For a well localized and immobile electron, the hyperfine interaction would lead to a linewidth of about 30 G [109]. As seen in figure 61, however, ΔH_{pp} is only 8 G in *cis*- and only about 1 G in *trans*-polyacetylene. This narrowing is partially due to the non-zero extension of the soliton wavefunction (figure 26), which averages over the various fields produced by the individual hydrogen atoms. Because this averaging goes with the square root of the number of sites averaged, 8 G will correspond to an extension of the soliton wavefunction over $(30/8)^2 \approx 15$ lattice sites, in fair agreement with figure 26. In *trans*-polyacetylene the line is even narrower. If the soliton moves over many lattice sites during one period of the microwave field (some 0.1 ns)

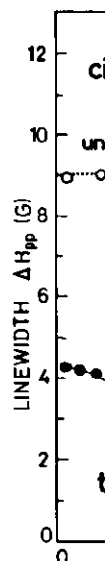


Figure 62. Temperature dependence of the ESR linewidth [108].

there will be further averaging and the soliton would have to visit all sites from the resonance Raman effect. As an entity, the essential requirements for narrowing). When the sample is cooled, the linewidth can become quite narrow, as seen in figure 62 [108]. In doped polyacetylene, the linewidth can become quite narrow, as seen in figure 62 [108]. In doped polyacetylene, the linewidth can become quite narrow, as seen in figure 62 [108]. In doped polyacetylene, the linewidth can become quite narrow, as seen in figure 62 [108].

Nechtschein *et al.* [110] have observed the proton NMR signal of the soliton. The spin is relaxed by collisions with other solitons. The observed $\omega^{1/2}$ dependence of the linewidth is one-dimensional with an average lifetime of about 10 ns.

There have been several attempts to measure the spatial extension of the soliton wavefunction [111]. But this essentially amounts to a deconvolution of the ESR signal. Deconvolutions are to a great extent arbitrary. Kahol [112] has shown that different soliton wavefunctions lead to different ESR line shapes.

Pulsed ENDOR (electron nuclear double resonance) experiments can resolve this ambiguity. The data to the following spin density

$$\rho_j = \frac{1}{l} \text{ se}$$

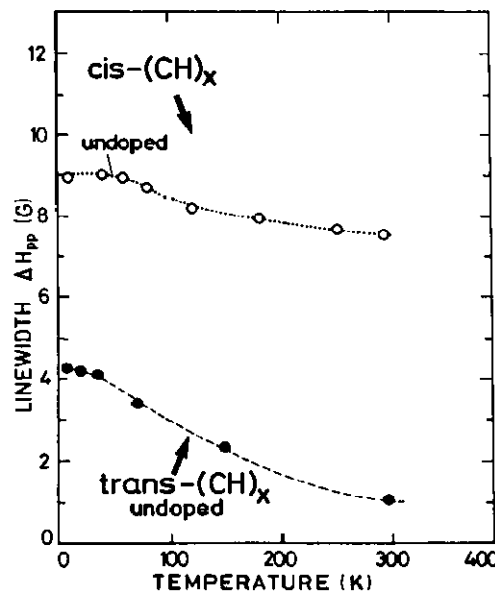


Figure 62. Temperature dependence of ESR linewidth in undoped *cis*- and *trans*-polyacetylene [108].

there will be further averaging (motional narrowing). To obtain a linewidth of 1 G, the soliton would have to visit 900 sites, much more than the chain length expected from the resonance Raman effect (Figure 14). But the soliton does not have to move as an entity, the essential requirement is only that the spin state is conserved (exchange narrowing). When the samples are cooled, the motional narrowing freezes out, as can be seen in figure 62 [108]. In doped polyacetylene the temperature dependence of the linewidth can become quite complicated. An example is given in figure 63 [108]; the minimum observed in doped *trans*-polyacetylene is explained by a superposition of motional narrowing and lifetime broadening due to relaxation with electrons in extended states.

Nechtschein *et al.* [110] have investigated the frequency dependence of the relaxation of the proton NMR signal in *trans*-polyacetylene. They assume that the proton spin is relaxed by collisions with solitons moving along the polymer chain. From the observed $\omega^{1/2}$ dependence of the relaxation time they conclude that the soliton motion is one-dimensional with an anisotropy of at least $\sigma_{\parallel}/\sigma_{\perp} \geq 4 \times 10^5$.

There have been several attempts to obtain more precise information on the shape and spatial extension of the soliton wavefunction from the lineshape of the ESR signal [111]. But this essentially amounts to a deconvolution of the ESR line, and such deconvolutions are to a great extent not possible in an unambiguous way. Mehring and Kahol [112] have shown that the observed ESR line is compatible with a variety of different soliton wavefunctions.

Pulsed ENDOR (electron nuclear double resonance) and pulsed triple resonance experiments can resolve this ambiguity. Grupp *et al.* [50] have fitted their experimental data to the following spin distribution function:

$$\rho_j = \frac{1}{l} \operatorname{sech}^2\left(\frac{j}{l}\right) [g \cos^2(j\pi/2) - u \sin^2(j\pi/2)]. \quad (15)$$

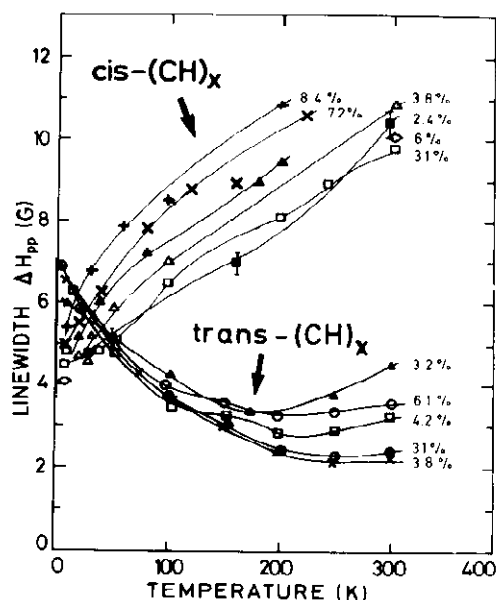


Figure 63. ESR linewidth of iodine-doped *cis*- and *trans*-polyacetylene as a function of temperature [108].

where j is the lattice site index, $2l$ the full width at half-maximum of the soliton wavefunction, and g and u represent the population of even- and odd-numbered lattice sites, respectively. The fit yields $l = 11$ and $u/g = 0.43$. In the pure Peierls case (Su-Schrieffer-Heeger model, last term equal to zero in equation (6)) there would be $l = 7$ and $u/g = 0$. A finite value of u/g indicates that the soliton wavefunction is non-zero also at the sites reserved for antisolitons. Assuming that this antisolitonic admixture is caused by electron-electron correlation, Grupp *et al.* obtain $U \approx 8$ eV for the Hubbard U . The soliton wavefunction of Grupp *et al.* is shown in figure 64. A compilation of literature on magnetic resonance experiments in polyacetylene is given in Appendix 12.

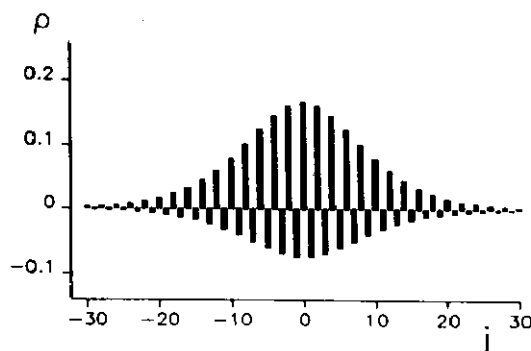


Figure 64. Distribution of the spin density of a soliton defect on a polyene chain with $l = 11$ and $u/g = 0.43$ used for simulations of double- and triple-ENDOR spectra [50].

6. Optical spectra

The midgap state is used in polyacetylene. Typical absorption levels with AsF_5 are shown in figure 65. The edge corresponding to a gap peak grows in the gap. This is not only in *trans*-polyacetylene, but also in *cis*-polyacetylene. Inspection of figure 65 shows that this is explained by soliton-impurity states. The morphology of the same is a result of real absorption spectra supported by Markowitz *et al.* [114]. The spectra can be considered as typical for polyacetylene samples.

A careful investigation of polyacetylene has been carried out by photothermal deflection spectroscopy. The samples are treated with ammonia. The solitons should remain and not move to midgap and from midgap to the gap. The authors of [115] suggest that the far away from the midgap

Mele and Rice [117] suggest that *trans*-polyacetylene would be caused by the π -electrons of the soliton. The new model of induced solitons [118] and

Optical Density
2.0
1.5
1.0
0.5
0.0

Figure 65. Absorption spectra of polyacetylene samples.

6. Optical spectroscopy and electron energy-loss investigations

6.1. Midgap state

The midgap state is usually considered as one of the optical signatures of solitons in polyacetylene. Typical absorption spectra of *trans*-polyacetylene doped to various levels with AsF_5 are shown in figure 65 [113]. In undoped polyacetylene the absorption edge corresponding to a gap of 1.7 eV is clearly seen. Upon doping a (fairly broad) peak grows in the gap. This midgap absorption has been observed by many authors, not only in *trans*-polyacetylene but also in iodinated β -carotene [114]. A closer inspection of figure 65 shows that the peak is not exactly at midgap. This could be explained by soliton-impurity interactions or by correlation effects. In addition, the morphology of the sample might produce some structure which is not completely a result of real absorption but caused by light scattering [115]. This view is also supported by Markowitsch *et al.* [116] who show that the structure of reflectivity spectra can be considerably changed by pressure compaction of the fibrillar polyacetylene samples.

A careful investigation of the absorption edge of undoped *cis*- and *trans*-polyacetylene has been carried out by Weinberger *et al.* [115] using the technique of photothermal deflection spectroscopy. The result is shown in figure 66. If the samples are treated with ammonia, nearly all states in the gap are removed. But the neutral solitons should remain and lead to absorption by excitations from the valence band to midgap and from midgap to the conduction band. This is not observed. The authors of [115] suggest that the Coulomb interaction might shift the soliton state very far away from the midgap position.

6.2. Infrared soliton modes

Mele and Rice [117] have predicted that the presence of charged solitons in *trans*-polyacetylene would lead to new infrared-active modes. These new modes are caused by the π -electrons of the conjugated system oscillating through the charge of the soliton. The new modes have, indeed, been observed both in the case of doping-induced solitons [118] and of photoexcitation [119, 120]. Compared with other

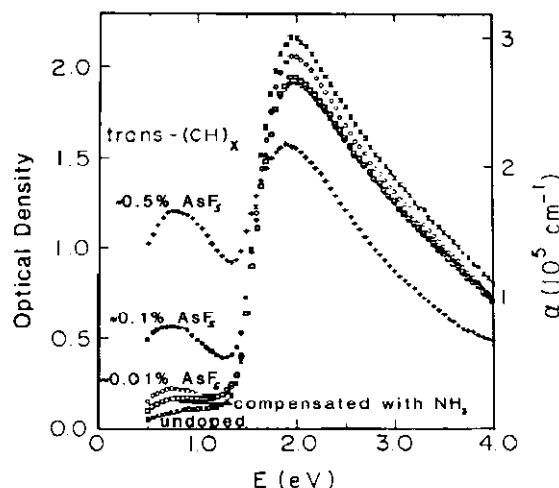


Figure 65. Absorption spectra of *trans*-polyacetylene doped to various levels of AsF_5 [113].

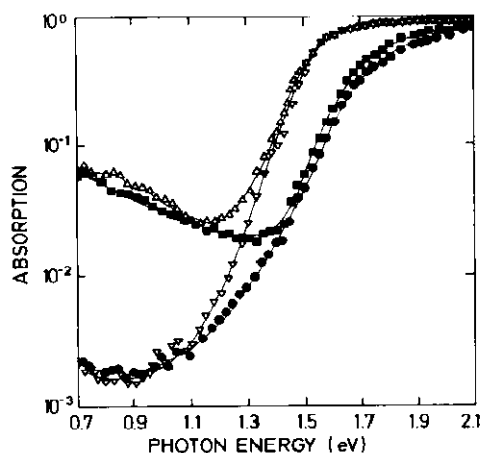


Figure 66. Absorption edge of undoped *cis*- and *trans*-polyacetylene measured by photo-thermal deflection spectroscopy: ■ *cis*, as-grown; ● *cis*, ammonia treated; △ *trans*, as-grown; ▽ *trans*, ammonia treated. (After [115].)

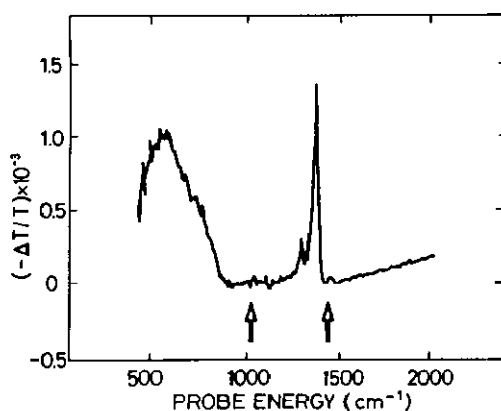


Figure 67. Light-induced infrared-active modes in *trans*-polyacetylene at $T = 77$ K. [125]. The arrows mark the position of the additional modes, which have been seen experimentally very recently.

features, however, they are less closely related to the solitonic properties of the defects. They neither make use of solitary-wave motion nor of pronounced quasi-particle properties. A localized charge on a conjugated chain is all that is needed to produce these modes [121]. In addition to these so-called translational modes some less intense i.r. lines associated with solitons have been proposed theoretically [122, 123] and, more recently, supported by experimental evidence [124, 125]. Figure 67 shows these infrared-active modes in *trans*-polyacetylene after optical excitation [125].

6.3. Electron energy-loss spectroscopy

A very powerful method to study the electronic structure of solids is electron energy-loss spectroscopy (EELS). Because electrons not only transfer energy to the solid (as do photons) but also momentum, in addition to the energetic position of the

Figure 68. Electron energy-loss spectrum of $\text{H}-(\text{CH}_2)_4-\text{SO}_3^-$ for

electronic states, the dispersion of the energy-loss spectrum of polyacetylene [126]. The various curves were obtained by different authors. The dashed lines connect corresponding transitions into narrow bands from the broad bands. The maxima in the curves are related to the maximum of the dispersion curve. An exact evaluation, a Kramers-Kronig transformation, is very strongly inclined against the interpretation of two transitions are not dispersion bands or localized states. The results of these investigations have been presented in [127].

In figure 69 electron energy-loss spectra are presented [48]. The direct excitation of the polymer chains (0) to the conduction band is observed for the low energy loss. The Peierls gap and it is not possible to transfer momentum along the chain. This also allows one to determine the energy of the results of these investigations of 12.8 ± 0.5 eV and the energy of the references on EELS literature.

Photoexcitation is one of the most important aspects of the nature of defects like solitons.

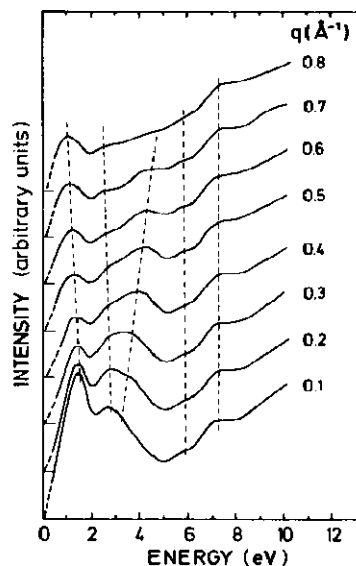


Figure 68. Electron energy-loss spectra of polypyrrole doped with the sulphonic acid $\text{H}-(\text{CH}_2)_4-\text{SO}_3^-$ for various values of the momentum transfer [126].

electronic states, the dispersion of the bands can also be studied. Figure 68 shows the energy-loss spectrum of polypyrrole doped with the sulphonic acid $\text{H}-(\text{CH}_2)_4-\text{SO}_3^-$ [126]. The various curves were recorded at different values of momentum transfer q . The dashed lines connect corresponding peaks. Vertical lines are characteristic of transitions into narrow bands (without dispersion), whereas inclined lines indicate broad bands. The maxima in the spectrum with low momentum transfer (bottom curve) are related to the maxima in the electronic joint density of states, but for an exact evaluation, a Kramers-Kronig analysis has to be carried out. The third dashed line is very strongly inclined and marks transitions into the conduction band. The first two transitions are not dispersive. Consequently they correspond to very narrow bands or localized states. These states have been identified as bipolaron states. Similar investigations have been performed in polyparaphenylene [127].

In figure 69 electron energy-loss spectra of oriented Durham-Graz polyacetylene are presented [48]. The direction of momentum transfer has been varied from parallel to the polymer chains (0) to perpendicular (90). A pronounced orientation dependence is observed for the low-energy feature. This corresponds to transitions across the Peierls gap and it is not surprising that they are most easily excited when the momentum transfer is along the conjugated chains. This orientational dependence also allows one to determine the anisotropy of the optical constants. Very important results of these investigations are the first experimental value for the total π -bandwidth of $12.8 \pm 0.5 \text{ eV}$ and the estimate of the on-site Hubbard U of about 7 to 8 eV. For references on EELS literature see Appendix 13.

6.4. Photoexcitation

Photoexcitation is one of the most powerful methods for the investigations of the nature of defects like solitons and polarons in polyacetylene. For a consistent

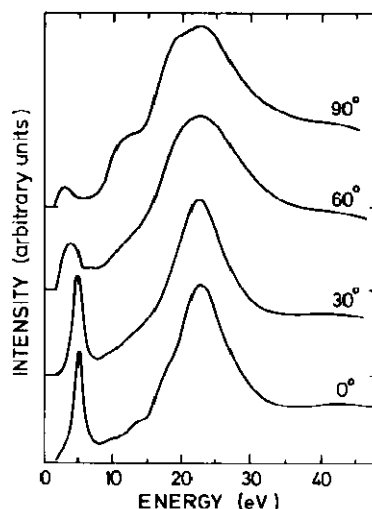


Figure 69. Electron energy-loss spectra of oriented polyacetylene for various angles between momentum transfer and chain direction [48].

discussion of the various results of photoexcitation, several aspects have to be considered:

- (a) photo-induced absorption (PA) spectra from the i.r. (500 cm^{-1}) up to 2.5 eV ; and
- (b) photoconductivity (PC).

C.W. experiments as well as time-resolved measurements down to picosecond resolution have been carried out for both PA and PC. Photo-induced absorption measurements yield information on the number of photo-excited particles (charged and neutral), while the photocurrent is due to the product of number of carriers and their mobility, and is only sensitive to charged excitations. Therefore comparison of the results of both types of experiment gives maximum information on photoexcitations in polyacetylene.

6.5. Photo-induced absorption

In photo-induced absorption experiments the change in transmission of a sample, $\Delta T/T$ due to a photoexcitation (usually across the band gap) is measured. The exciting, so-called 'pump beam', produces in a first step electron-hole pairs in polyacetylene. According to the theoretical predictions of Su and Schrieffer [41] these pairs should rapidly (on a time scale of 10^{-13} s) generate lattice deformations and relax into solitons with electronic states at meV . These states can be detected, provided their lifetime is sufficiently long, by looking for additional absorption peaks inside the band gap. This detecting 'probe beam' has sufficiently low intensity so as to keep the excitation in itself as low as possible. More generally speaking there are two kinds of signal, photo-induced absorption ($\Delta T/T < 0$) and photo-induced bleaching ($\Delta T/T > 0$). The former are associated with transitions where the population of the initial state is increased by illumination or the final state is depleted, the latter *vice versa*.

The PA-spectrum of *trans*-polyacetylene measured at 10 K is shown in figure 70 [128]. Essentially there are three different features: the first absorption peak at 0.45 eV

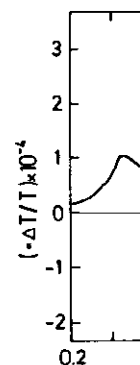


Figure 70. Photo-induced absorption spectrum of *trans*-polyacetylene at 10 K [128].

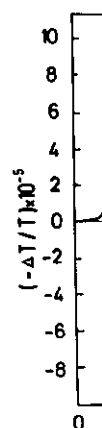


Figure 71. Photo-induced absorption spectrum of *trans*-polyacetylene at 10 K [128].

(LE, low-energy peak), the high-energy peak (HE, high-energy peak), and the interband transition (IBT, interband transition) at higher than 200 K (figure 71). The LE peak remains at 0.45 eV and the HE peak vanishes. The interband transition bleaching at 1.5 eV with temperature.

In figure 71 the photo-induced charge [119] is determined. From temperature dependence has been shown [119] that the HE peak, however, is frequently one can conclude that the photo-induced charge is therefore comparable to neutral.

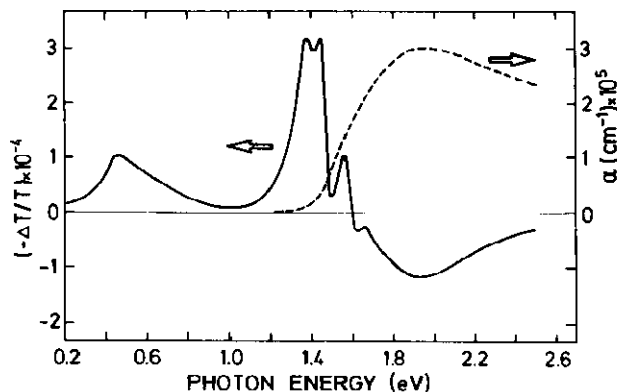


Figure 70. Photo-induced absorption spectrum of *trans*-polyacetylene after illumination with 2.4 eV (at 10 K) [128].

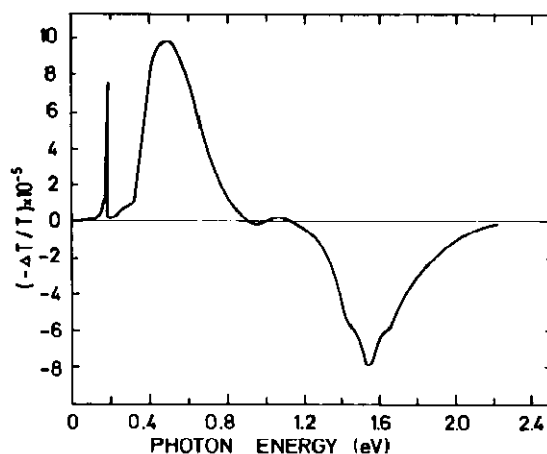


Figure 71. Photo-induced absorption spectrum of *trans*-polyacetylene at 210 K showing in addition the infrared soliton modes [128].

(LE, low-energy peak), the second absorption peak at about 1.4 eV (HE, high-energy peak), and the interband transition bleaching between 1.9 and 2.0 eV. At temperatures higher than 200 K (figure 71) [128] the HE peak and the interband transition bleaching vanish. The LE peak remains and a new bleaching band at about 1.5 eV shows up. The interband transition bleaching is therefore correlated with the HE peak and the bleaching at 1.5 eV with the LE peak.

In figure 71 the photo-induced i.r.-active modes are shown in addition at the left-hand side of the figure. Since these i.r. modes are without doubt due to photo-induced charge [117] the origin of the photo-induced features can be determined. From temperature-, intensity- and frequency-dependent measurements it has been shown [119] that the i.r. modes behave in the same manner as the LE peak. The HE peak, however, is not at all correlated to any such i.r. modes [44]. Consequently one can conclude that the LE peak is due to charged excitations (and therefore comparable to results of PC experiments), whereas the HE peak is overall neutral.

Therefore transient measurements in the spectral range from 1.3 to 2.5 eV [129, 130], which are mostly determined by the features of the neutral excitations, cannot be compared with the decay behaviour of the photocurrent. Nevertheless the creation and decay times of the neutral excitation itself can be studied. Shank *et al.* [130] have observed a rise time for the appearance of the HE peak of less than 0.15 ps and a fast decay which can be fitted by $A(t) = \text{erf}(\sqrt{\tau_D}/t)$ with $\tau_D = 0.1$ ps at 300 K and $\tau_D = 1.0$ ps at 20 K. From these data it is obvious that the disappearance of the HE peak with increasing temperature (figures 70 and 71) can be explained by a decrease in the lifetime of this neutral excitation.

At present, three different concepts have been discussed in the literature to explain the origin of the HE peak. Bishop *et al.* [131] attribute this feature to a so-called breather mode, a neutral dynamically changing but localized excitation remaining when the photo-generated soliton and antisoliton separate. Another possibility to explain the HE peak is an even state ($2A_g$) as the lowest lying excited state, investigated both theoretically and experimentally by Hudson and Kohler [132, 133] on polyenes with well-defined chain lengths up to seven double bonds. Kivelson and Wu [134] have recently shown that even a very weak interaction, which breaks the charge-conjugation symmetry, will lead to a rapid conversion of photo-generated charged solitons into bound neutral soliton pairs. Such a defect species should then be responsible for the HE peak. Finally it should be noted that there is a close relationship between the A_g -state and the neutral soliton pairs, as pointed out by Hudson and Kohler [133] and by Orenstein [44]. Both models seem to describe the same property in two different languages.

In summary, the LE peak is apparently due to charged solitons, and the HE peak to neutral soliton pairs. In the framework of the SSH model [34] the levels of both excitations should be at midgap, at about 0.8 eV. The shift of these levels out of the centre of the gap can be attributed to electron-electron interaction, as already discussed in §3 [49].

The transient behaviour of the LE peak at 0.45 eV is, for experimental reasons, much more difficult to investigate than that of the HE peak. Recently, however, Rothberg *et al.* [135] succeeded in measuring the time behaviour in this spectral region to picosecond resolution. As shown in figure 72, the photo-induced signal at 0.45 eV

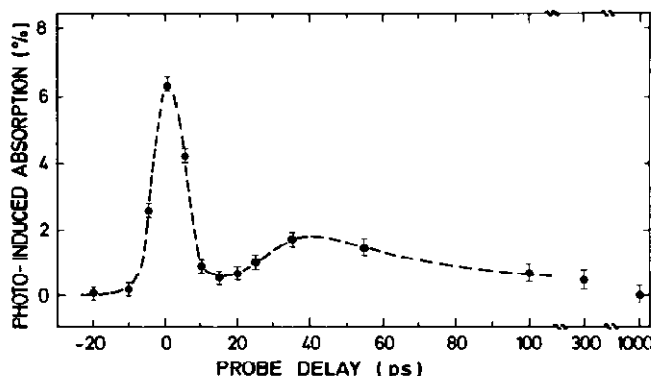


Figure 72. Time behaviour of the LE-peak in the picosecond regime [135] at $T = 25$ K. The early feature (before 10 ps) is attributed to instantaneously created charged solitons, the second maximum is explained by the retarded-creation charged solitons, produced in a collision mechanism like that of figure 38.

first decays very rapidly (resolved with the experiment), the distribution shows up, reaching a maximum. The decay of this peak on a logarithmic scale (tenths of a second) can be explained by the initial excitation of charge carriers, which decays extremely quickly, and of a slower component, which lasts for several seconds. These properties of the photoconductivity, which are observed in PA experiments is summarized in figure 73.

Photoconductivity experiments show a fast recombination but also on a long time scale. This is given in Appendix 15. Under the influence of the excitation profile of photo-generated energy was needed to create a soliton-antisoliton pair is lower ($2A_g$) than the energy of the neutral excitations. Investigations of the optical properties show a close relationship between the excitation profile and the photoconductivity.

From time-resolved PA experiments it is known that photo-generated carriers, a soliton-antisoliton pair, are created. Several time-resolved PC experiments in *trans*-polyacetylene consist of a sub-nanosecond time-scale (from picoseconds to seconds [54, 137]. The time scale of the decay of the photoconductivity is [140]. The sample was illuminated by a YAG laser. From these data it is concluded that the component to be $\tau_{1/2} \approx 100$ ps. This is shown in figure 73 but at an intensity below the threshold for the photoconductivity more clearly in figure 74 where the photoconductivity is shown as a function of the probe delay.

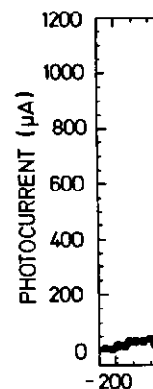
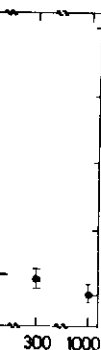


Figure 73. Decay of the fast component of the photoconductivity [135] at $T = 25$ K.

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first decays very rapidly (probably on a subpicosecond time-scale that cannot be resolved with the experimental set-up employed). After about 20 ps a retarded contribution shows up, reaching its maximum 40 ps after excitation. When studying the decay of this peak on a long time-scale ($t > 10^{-6}$ s) a power-law decay up to some tenths of a second can be observed [44, 136]. Therefore the LE peak consists of an initial excitation of charged solitons, which is built up instantaneously and decays extremely quickly, and of a subsequent long-lived part, having lifetimes up to several seconds. These properties of the LE absorption have to be compared with results of the photoconductivity, which is also a manifestation of *charged* excitations. Literature on PA experiments is summarized in Appendix 14.

6.6. Photoconductivity

Photoconductivity experiments give information not only on the mechanism of recombination but also on transport of carriers. A compilation of relevant references is given in Appendix 15. Until fairly recently there was controversy over the form of the excitation profile of photoconductivity because it seems as if less than the bandgap energy was needed to create photocarriers [137]. This was taken as evidence for *direct* photogeneration of solitons because the energy for the creation of a soliton-antisoliton pair is lower ($2(2\Delta_0/\pi)$) than that of an electron-hole pair ($2\Delta_0$). Careful investigations of the optical absorption edge [115], however, show no disagreement between the excitation profile for photoconductivity and the absorption edge.

From time-resolved PA measurements we get information on the lifetime of photo-generated carriers, and transient PC tells for how long these particles move. Several time-resolved PC experiments have been carried out. It turns out that the PC in *trans*-polyacetylene consists of two components: a fast component decaying on a sub-nanosecond time-scale [138–140]; and a slow component with carrier lifetimes up to seconds [54, 137]. The time behaviour of the fast component is shown in figure 73 [140]. The sample was illuminated by 25-ps pulses from a frequency-doubled Nd-YAG laser. From these data we determine a relaxation time of the fast PC component to be $\tau_{1/2} \approx 100$ ps. The slow PC component would be a very long tail in figure 73 but at an intensity below the experimental detection limit. This can be seen much more clearly in figure 74 where the decay of the PC (after excitation with 500-ps pulses)

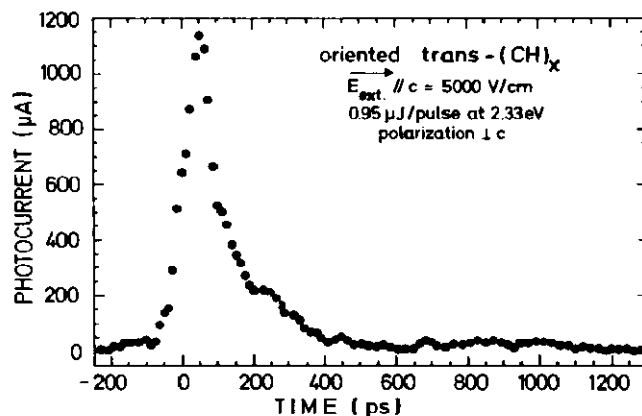


Figure 73. Decay of the fast component of the photoconductivity in *trans*-polyacetylene after illumination with 25-ps pulses [140].

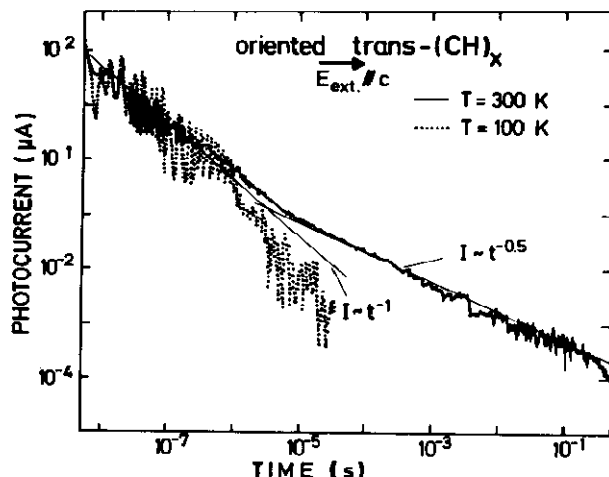


Figure 74. Decay of the photocurrent after 500 ps excitation from nanoseconds to seconds at two different temperatures [140].

is followed over eight orders of magnitude in time and plotted on a log-log scale [140]. The two components can easily be distinguished, the fast one decaying nearly linearly in time and the slow one as $t^{-1/2}$. At room temperature the fast component is observable up to 1 μ s, from then on the slow component dominates. Extrapolating the slow component to 10^{-10} s the initial values of both components differ by two orders of magnitude. Upon cooling, the slow component decreases and at 100 K we cannot observe it anymore, within experimental sensitivity. This becomes obvious when looking at the temperature dependence of both PC components. Figure 75 [141] shows

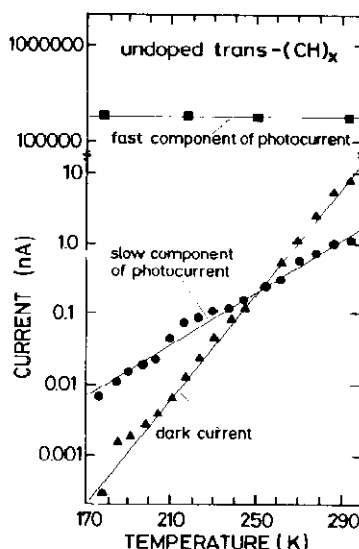


Figure 75. Temperature dependence of fast and slow photoconductivity component and of dark conductivity in *trans*-polyacetylene [141].

the temperature-dependent (circles), and the temperature-independent (triangles) component. The remarkable lack of temperature dependence of the slow component over the temperature range 100–300 K.

From the absence of a fast PC component [44] it is inferred that the high mobility of photo-generated carriers is not hindered by defects. The observed decay of the fast component is a mobility relaxation time. This, as will be discussed later in connection with the decay of the fast component, is not the dark conductivity (see §4). In stretch-oriented *trans*-polyacetylene an oriented material permits, as will be shown, the properties of polyacetylene. The electric field (parallel or perpendicular to the chain) for the dark conductivity as well as the fast PC component also shows this anisotropy. We infer from the anisotropy that the fast PC component is due to the motion of carriers is primarily along the chain. 'hot' carriers during their motion up to 400 Å at an applied electric field. $\mu_{\parallel} \approx 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are found.

In stretch-oriented *trans*-polyacetylene, the fast PC component is found for the LE peak in EPR. The signals vary significantly with polarization relative to the chain direction. This behaviour was reported for the measured peak photocurrent as a function of polarization angles after an

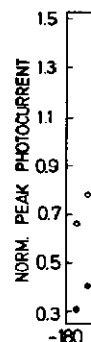


Figure 76. Anisotropy of the photocurrent with respect to the polarization and the chain direction. Data; \circ data normalized.

the temperature-dependent dark conductivity (triangles), the flatter slow component (circles), and the temperature-independent fast PC component (squares). This remarkable lack of temperature dependence in the fast component is not only measured over the temperature range shown in figure 75 but also down to 10 K [139].

From the absence of a PA component (at 0.45 eV) decaying in correlation to the fast PC component [44] it is concluded that the main part of the fast PC is due to the high mobility of photo-generated carriers before they become trapped at various defects. The observed decay time $\tau_{1/2} \approx 100$ ps is therefore not a carrier lifetime but a mobility relaxation time. The fast PC is not identical with the initial peak in figure 72 as will be discussed later in more detail. The motion of the trapped carriers (after the decay of the fast component) can be described by hopping, just as in the case of the dark conductivity (see §4). All the results discussed so far are valid in standard Shirakawa polyacetylene and also in stretch-oriented Durham-Graz material. The oriented material permits, additionally, the study of the anisotropic (one-dimensional) properties of polyacetylene. The anisotropy of the current with respect to the applied electric field (parallel or perpendicular to the chain direction) has a value of about 50 for the dark conductivity as well as for the two PC components. The fact that the fast component also shows this anisotropy, especially can be taken as clear evidence that the motion of carriers is primarily along the polymer chains and not perpendicular to them. We infer from the unusual temperature independence and from this field anisotropy that the fast PC is due to 'hot' photocarriers moving with high kinetic energy relatively freely along the polymer chains. The average drift distance of these 'hot' carriers during their relaxation time of $\tau_{1/2} \approx 100$ ps can be estimated. Values up to 400 Å at an applied electric field of $1.5 \times 10^4 \text{ V cm}^{-1}$ and a mobility of $\mu_0 \approx 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are found [140].

In stretch-oriented *trans*-polyacetylene an additional type of anisotropy has been found for the LE peak in PA measurements and for PC. The measured PA and PC signals vary significantly when the polarization angle of the incident light is turned relative to the chain direction. For the slow PC components and for PA, such behaviour was reported for the first time by Townsend *et al.* [142]. Figure 76 shows the measured peak photocurrent of the fast component (solid circles) at different polarization angles after an excitation with 500-ps pulses at 2.6 eV. These data have

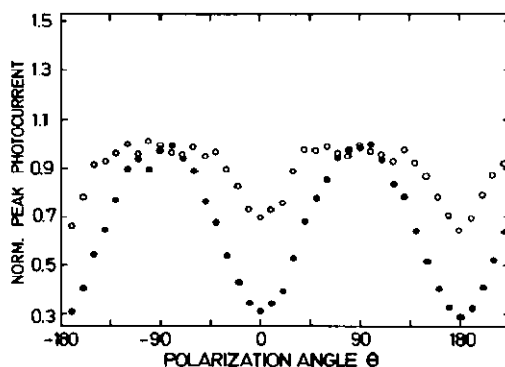


Figure 76. Anisotropy of the fast component of the photocurrent in oriented *trans*-polyacetylene with respect to the polarization of the incident light (θ is the angle between the polarization and the chain direction): $T = 300 \text{ K}$; $E_{\text{ext}} \parallel c$; excitation energy 2.6 eV; ● measured data; ○ data normalized to a constant number of absorbed photons. (After [145].)

to be corrected for the total number of absorbed photons since the optical properties (absorption and reflection coefficients) are strongly anisotropic ([143, 144], and G. Leising, private communication). After this correction, a real anisotropy of about 1.7 between parallel and perpendicular polarization remains (open circles). For the slow component [143, 145] and the PA data [143] this anisotropy is larger and has a value of about 4. A consistent explanation of this anisotropy is the higher probability for the direct creation of charge carriers on different chains in the case of perpendicular polarization. Carriers on different chains escape geminate recombination more easily. Therefore the photocurrent has to be higher if the exciting light is polarized perpendicular to the chain direction. From symmetry arguments the inter-chain carriers must be polarons rather than solitons. Consequently, they do not contribute to the LE peak in PA measurements, but they are seen in the fast PC component. By collision with neutral solitons these polarons are converted into charged solitons (figure 38) and can then give rise to the retarded contribution to the LE peak in the PA experiment shown in figure 72 [135].

From all these data we conclude that the photocurrent is mainly due to interchain carriers. In addition to direct interchain carrier creation as discussed before (and recently calculated by Danielsen [146]), some intrachain carriers should be able to hop to a neighbouring chain before they can relax into charged solitons on a sub-picosecond time-scale (early feature in figure 72). All other carriers remaining on the same chain recombine or may convert into the neutral excitations, responsible for the HE peak in PA. The fast PC component should therefore be mainly due to polarons before they collide with neutral solitons to form charged solitons. These charged solitons can then be observed in the slow PC component and in the LE peak of PA (for $t > 30$ ps).

On the basis of experimental data available today, it cannot be decided whether these solitons have not only the topological but also the dynamical properties of solitons (non-dispersive motion). It is not easy to imagine how their shape can be probed since even in the case of 'hot' carriers their mean free path is only of the order of some hundred ångström.

6.7. Photoexcitations in *cis*-polyacetylene

The optical bandgap of *cis*-polyacetylene is about 0.5 eV larger than that of *trans*-polyacetylene. The main difference in the optical properties between *cis* and *trans* is not the corresponding shift in excitation energy but the absence of the LE peak and the i.r.-active modes in the PA spectrum [147]. This result is consistent with the absence of photoconductivity in *cis*-polyacetylene reported by Etemad *et al.* [137]. Our experiments have shown that the photocurrent in *cis*-polyacetylene is more than two orders of magnitude lower than in the *trans* material. The small photocurrent which we have observed can be attributed to some *trans* content in nominally *cis* samples. These results have been taken as evidence for soliton conduction in polyacetylene. On the other hand, photoconductivity has been observed in other poly- and hetero-aromatics like polythiophene or polyphenylenevinylene, which also have a non-degenerate ground state like *cis*-polyacetylene. At the moment it is not clear why the generation and/or recombination of charged excitations in *cis*-polyacetylene behave completely differently from those in *trans*-polyacetylene.

7. Conclusion

Polymers with conjugated double bonds show many physical properties which make them interesting both for technical applications and for basic research. The soliton concept, an extremely useful tool of modern physics, can be very impressively demonstrated

in idealized polyacetylene. Polyacetylene and other conjugated polymers are consistent with the soliton model. Solitons for their explanation that can be transformed into electrical conductivity in high resistance between grains are a main contribution to charge transport. The mechanism of hopping can be worked out. In particular, the solitonic character.

The magnetic and optical properties of solitons (spin-charge susceptibility on the doping-induced absorption) infrared-active modes, spatially sampled by ENDOR experiments for the discussion of conjugated polymers, a strong experimental data, a strong picture is based. The question or in a non-dispersive way can be worked out. It is even

This work originated from Karlsruhe and was supported by Stuttgart. It cannot be a conductive polymers: to the have to be considered. The as a critical evaluation of own work or that in which support the argument in the of M. Peo (Konstanz 1984) and D. Se

We thank our colleagues for co-operation; D. Baeriswyl for valuable discussions; our colleagues of our group for all Xander and Günther Wilk for critical reading of the text; gratefully acknowledged.

Appendix 1. List of

Antistatics
Batteries
Electrochromic
Electromagnetic
Molecular electronics
Semiconductors
Solar cells

the optical properties isotropic ([143, 144], and real anisotropy of about (open circles). For the property is larger and has a is the higher probability s in the case of perpen- seminate recombination if the exciting light is try arguments the inter- sequently, they do not are seen in the fast PC ons are converted into ded contribution to the

mainly due to interchain discussed before (and rs should be able to hop ons on a sub-picosecond ing on the same chain nsible for the HE peak to polarons before they arged solitons can then of PA (for $t > 30$ ps). ot be decided whether namical properties of ow their shape can be ath is only of the order

larger than that of rties between *cis* and bsence of the LE peak is consistent with the v Etemad *et al.* [137]. cetylene is more than e small photocurrent tent in nominally *cis* a conduction in poly- ved in other poly- and e, which also have a ent it is not clear why in *cis*-polyacetylene e.

properties which make arch. The soliton con- cessively demonstrated

in idealized polyacetylene chains. Most phenomena that can be measured in real polyacetylene are consistent with the existence of solitons, but they do not demand solitons for their explanation. On a microscopic scale polyacetylene is a semiconductor that can be transformed into a metal by heavily p- or n-type doping. The macroscopic electrical conductivity in highly doped samples is dominated by the inner contact resistance between grains and fibres. In lightly doped polyacetylene, hopping is the main contribution to charge transport. But there are so many parameters involved in the mechanism of hopping conductivity, that details on the hopping sites cannot easily be worked out. In particular, it is especially difficult to prove that these sites have solitonic character.

The magnetic and optical behaviour of polyacetylene reflects the symmetry properties of solitons (spin-charge inversion as seen by the dependence of the magnetic susceptibility on the doping level, electronic states within the energy-gap (photo- and doping-induced absorption) time dependence of photoexcitations, soliton-induced infrared-active modes, spatial distribution of the spin associated with a soliton, as sampled by ENDOR experiments). In this respect the soliton concept is very instructive for the discussion of conjugational defects. To obtain a consistent description of the experimental data, a strong electron-electron interaction has to be taken into account, which is as important as the electron-phonon interaction on which the original soliton picture is based. The question as to whether conjugational defects move in a dispersive or in a non-dispersive way cannot yet be decided on the evidence presented by existing experimental data. It is even likely that this question will remain open forever.

Acknowledgment

This work originated from a Habilitationsschrift (S.R.) at the University of Karlsruhe and was supplemented by a Ph.D. thesis (H.B.) at the University of Stuttgart. It cannot be a comprehensive review of all the literature published on conductive polymers: to that end, up to 2000 papers on polyacetylene alone would have to be considered. The literature cited should be taken as examples rather than as a critical evaluation of priority or importance. Quite naturally we have quoted our own work or that in which we have participated, whenever it seemed appropriate to support the argument in this article. We have largely benefited from the Ph.D. theses of M. Peo (Konstanz 1982), R.J.K. Schweizer (Konstanz 1984), K. Ehinger (Konstanz 1984) and D. Schäfer-Siebert.

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Appendix 1. Literature on applications of conductive polymers

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Semiconducting devices	iii-v, vii, viii, xvi, xxiii
Solar cells	i-v, vii, viii, xii, xiii, xviii

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Appendix 2. Topical conferences on one-dimensional metals and conductive polymers

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