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Semiconducting Polymers

by

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Semiconducting Polymers

To

***Professor D. D. Eley, the founder
of modern research in the field of
electrical properties of organic
solids, and***

to

***Professor A. A. Berlin, who has
initiated the studies of synthesis
and properties of semiconducting
polymers.***

Preface to the Polish Edition

The physical chemistry of semiconductors is a typical representative of the currently "fashionable" borderline disciplines. It benefits equally from both, not much older branches of knowledge: namely, solid state physics and the chemistry of high-molecular weight compounds. This field, of interest not only to physical chemists, but also to research workers in electronics, and even to biologists, has been developing rapidly in the last several years. Every year hundreds of new publications appear discussing the results of both experimental and theoretical investigations.

Despite this, or perhaps because of that there have been few monographs in the world literature which present a review of researches in the field of the physical chemistry of semiconducting polymers. This book is precisely an attempt at such a monographic approach. In writing it I have tried to give a wider consideration to all the more important lines of research in the field. Readers who are interested in specific problems may refer to the extensive bibliography at the end of this book.

It remains for me to acknowledge my indebtedness to those who have assisted me most directly in the writing of this book, especially my colleagues engaged in the study of semiconducting polymers and dielectrics. It is in the course of our work and discussions that the idea of writing this monograph took shape. In particular I would like to express my appreciation of the valuable assistance of Dr Aleksander Szymański, who read a good deal of the book, Dr Józef Świątek, who has helped me with the correction of proofs and preparation of the bibliography and Mrs. Zofia Kalinowska, who prepared the manuscript. I am particularly indebted to Professor Krzysztof Pigoń, who kindly read the full text and made numerous valuable suggestions.

Finally, I must acknowledge here the patience and understanding shown by my family while this book was being written.

Łódź, 1968

M. KRYSZEWSKI

Preface to the English Edition

Work on the English edition of this book, which was first published in Polish in 1968, was initiated in the early 1970's. The process of enlarging the book by including in it all the latest developments in the rapidly expanding field of polymeric semiconductors was completed in 1973. Hence, the literature references in the main body of the book cover the publications that appeared up to that time. Translation of the book and verification of the English version also took some time during which significant progress was made in the studies on the electrical properties of organic semiconducting systems, especially with regard to preparation of highly conducting organic systems whose conductivity may have a metallic character. Also prepared were the first macromolecular systems exhibiting superconductivity and macroscopic polymeric monocrystals which might have semiconducting properties. The spatial ordering of these systems is similar to that of molecular organic crystals. This, in addition to many other interesting developments, such as synthesis of new or modified semiconducting polymers, studies of their electrical and magnetic properties and, especially, studies of the photoconductivity of systems doped with compounds capable of forming charge transfer complexes constitutes a significant step forward in the theory of charge carrier generation and transport in organic semiconductors and makes for a better understanding of some general principles.

Being aware of this, and having obtained the publishers' permission I undertook further modification and updating of the book, particularly of its last Chapter (Recent Progress and Trends in the Research on Semiconducting Polymers) which has been considerably enlarged to include the above mentioned developments and pertinent findings, and to indicate future trends both in the theory and experiment. This seemed to be the most reasonable way of bringing the book up to date, but it has resulted in disproportionate increase in the length of Chapter 9. The literature references in that Chapter are of three kinds: those in ordinary type refer to the main body of references arranged in the alphabetical order and collected at the end of the book; those in italics are listed in the literature supplement to

Chapter 9 also in alphabetical order; those in bold italics refer to references "Added in proof" on p. 685. No claim is made that these lists are complete, especially as the number of publications that have recently appeared is enormous, but it is hoped that the books and articles cited present a fair and representative picture of the state of the art in the field under discussion.

I would like to acknowledge my indebtedness to my colleagues whose comments and suggestions have helped me in the work on the new version of Chapter 9. I am particularly grateful to Mr. Jerzy Tomaszczyk who verified the English translation of the whole book and translated the enlarged version of Chapter 9. I would also like to thank the Publishers who allowed me to make innumerable changes in the content of the book until the very last moment before the book went to the press.

It is not impossible that some findings as well as some aspects of the theory of macromolecular organic semiconductors have been left out; also literature references do not, as a rule, include patent reports. It seemed, however, that presentation of major achievements and general trends, as well as some personal views would be of more importance and use to the reader than exhaustiveness, especially in a field that has been developing so rapidly in recent years.

Łódź, 1979

M. KRYSZEWSKI

Introduction

The great significance of high-molecular weight organic materials—polymers—in the life of contemporary man and the very wide application of these materials in technology, is connected with their good mechanical and dielectric properties, resistance to chemical agents, relatively easy processing, and usually low cost. Thus organic polymers have created enormous interest during the past 25 years. From the standpoint of their electrical properties polymers are good insulators, characterized by low values of dielectric permittivity and dielectric loss, and high resistivity. The electrical properties of polymers depend on their physical and chemical structure, on the conditions of previous thermal treatment, the presence of plasticizers, filling agents, etc., and hence they can be modified within wide limits.

A second group of substances with very interesting electrical properties are semiconducting materials.

In the course of systematic investigations a sufficient understanding of the electrical properties and structure of semiconducting materials has been obtained to allow for work on the preparation of high-molecular weight substances combining the valuable properties of polymers and semiconductors to be undertaken.

The basic role in these investigations is played by solid state physics, and especially by the physics of organic solids. Experimental work has provided much valuable information on the mechanism of electric conduction in crystalline low-molecular weight organic compounds and on the interdependence of molecular parameters and the electronic properties of these compounds. Valuable data have been obtained concerning the techniques of synthesizing polymers, the kinds of monomers required and the methods of modifying the properties of the polymers already known so as to obtain products with semiconducting properties. In this way a new branch of science has been founded: the physics and chemistry of semiconducting polymers, which, although it has emerged only in the last 10 years, has made considerable progress thanks to the concerted and cooperative efforts of physicists and chemists.

Owing to the fact that intensive studies in this field are of very recent

origin our understanding of the properties and techniques of preparation of semiconducting polymers is still far below that obtained in the research on inorganic semiconductors. Another reason is the obvious fact that these two groups of semiconducting substances are different in many respects— suffice it to say, by way of example, that the chemical and physical structure of semiconducting polymers is considerably less defined (in most cases they are amorphous or partially crystalline materials), they are also more difficult to obtain in the pure state; these facts call for the necessity of using other measuring techniques. However, the results obtained thus far are fairly encouraging from both the theoretical and practical point of view and warrant further intensive investigations in this field. An attempt might also be made to establish some general rules.

Theories accounting for the properties of inorganic semiconductors do not always give good results in the case of high-molecular weight organic semiconductors. Therefore, interpretation of the phenomena observed is often rendered much more difficult. Some models used in the theory of inorganic semiconductors cannot be applied; they are only guidelines which determine the proper course of investigations. The limited applicability of these models results from the differences between organic and inorganic semiconductors, and concerns both low molecular weight organic compounds and polymers.

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General Characteristics of the Properties of Semiconducting Polymers

High-molecular weight compounds (polymers) usually exhibit low electrical conductivity generally not exceeding $10^{-15} \text{ ohm}^{-1}\text{cm}^{-1}$ and therefore can be classified as good insulators.

In the main chain of the molecule of a typical polymer the valence electrons are tightly bound to their parent atoms, creating covalent bonds. This applies first of all to the molecules whose main chains have no $-(\text{C}=\text{C})-$ conjugated bonds, conjugated aromatic systems, or heteroatoms. In connection with this, these electrons do not, in the main, take part in charge transfer, even within one molecule. It is also difficult, in this case, to explain the mechanism of charge transfer between the molecules in a macroscopic sample of synthetic material. It was therefore easy to foresee the experimentally established good insulating properties of polymers. Thus, the electrical conductivity of typical polymers is first of all connected with the presence of charge carriers (electrons or holes) injected into the dielectric, and with the presence of impurity ions, or ions formed by the ionization of polymer molecules under the influence of external factors.

Similarly, as it has been found in the case of numerous inorganic dielectrics, the electrical conductivity or resistivity of high-molecular weight substances depends on the time of their exposure to an external electric field and on temperature. The dependence of the logarithm of resistivity on the reciprocal of the temperature for various times of exposure to the electric field is of a complicated nature. The corresponding minima of resistivity are related to the occurrence of dielectric loss of a dipole-elastic character and to a number of polarization processes, the mechanism of which is not yet fully known. However, it can be said that dipole-elastic phenomena play a smaller role in the polarization processes than has hitherto been assumed. Organic

substances belonging to dielectrics, both of low molecular weight as well as polymers, show a different dependence of resistivity (and conductivity) on the temperature than metals. In the case of metals within a rather small range of temperature changes, a linear fall of resistivity is observed with increasing temperature. The changes of resistivity ρ (ohm cm) of polymers with temperature are described by the equation:

$$\rho = \rho_0 \exp \frac{E_t}{kT}$$

where ρ_0 is a constant, E_t is thermal activation energy, and k is Boltzmann's constant.

Investigations of the dependence of the resistivity ρ upon temperature, carried out over a wide range of temperatures, have shown that the plot of the relation of the logarithm of resistivity and the reciprocal of temperature, i.e. the plot of the function $\log \rho = f\left(\frac{1}{T}\right)$, consists of two segments: a linear one, corresponding to temperatures below the glass transition temperature, i.e. to the range $T < T_g$, and another, generally curved (often, however, approaching a straight line), corresponding to $T > T_g$, i.e. to the temperature range in which the polymer is in the viscoelastic state.

The exponential dependence of resistivity on temperature $\rho = \rho_0 \exp \left\{ \frac{E_t}{kT} \right\}$, found for all plastics, is also characteristic of semiconductors. Despite this, not all polymers should be considered as semiconducting substances. In semiconducting polymers, as in other semiconductors, there occurs a different mechanism of electrical conduction; the basic role is played here not by the ions, but by the electrons and holes which are charge carriers in the investigated material.

Substances usually qualified as semiconductors have the following properties:

- (i) Electrical conductivity ranging from 10^{-12} to 10^4 ohm $^{-1}$ cm $^{-1}$;
- (ii) Negative temperature coefficient of resistivity;
- (iii) Non-ohmic, and often rectifying contact with other substances (metals);
- (iv) High values of the thermoelectric power whose sign is independent of the kind of metal with which the given semiconductor comes into contact;
- (v) Photoconductivity;
- (vi) Dependence of resistivity on the impurities introduced.

In conventional inorganic semiconductors the majority of these properties occur very distinctly. When organic materials are characterized by at least a few of the properties mentioned above, they can be classed as organic semiconductors. Typical polymers do not satisfy these conditions — their electrical conductivity is generally lower, thermoelectric and photoelectric effects do not occur in them, and changes of conductivity caused by impurities are visible only if the impurities introduced are ionic in character.

As a result of investigations of the electrical conductance and photoconductance of low-molecular weight crystalline organic materials with molecules made up of many condensed aromatic rings, it has been found that the presence of conjugated systems of double bonds favours electronic or hole conductance. Moreover, it has been established beyond doubt that the relatively large values of conductivity observed cannot be related to the presence of ions derived from impurities. Owing to the very low mobility of ions in solids the impurities of ionic character would have to occur in large amounts, considerably exceeding their actual concentration determined by the use of very sensitive analytical methods.

Thus, features typical of organic semiconductors must also be expected to occur in high-molecular weight systems characterized by greater concentration of double bonds.

It seems advisable at the beginning to make a few basic remarks on the electrical properties of organic semiconductors, starting with low-molecular weight materials.

Although the widespread interest in the problems of electrical conductance in organic compounds is of fairly recent date the number of publications devoted to them is quite considerable. The earliest reference to interesting electrical properties of organic compounds, and especially to photoconductance, go back to the beginning of the twentieth century. Later studies dealing with the conductance of organic compounds concerned mainly polycrystalline materials partially hygroscopic, and not always completely purified and thus did not allow for data on the mechanism of electrical conductance to be obtained.

Considerable interest in the electrical conduction of organic compounds was aroused by the work of Szent-Györgyi [2190], who drew attention to the fundamental role of charge transfer phenomena in biological processes. This has led to the discovery of photoconduction in proteins [2191] and to interesting hypotheses concerning the mechanism of photoconduction of organic compounds and their semiconducting properties [1110].

Since several monographs [169, 378, 825, 1906, 2168, 2265] and valuable review papers [462, 599, 618, 721, 826, 999, 1801, 1181, 1182, 2223, 2225] have already been devoted to the electrical conductance and semiconducting properties of low-molecular weight organic compounds, we shall confine ourselves to general remarks on the subject.

There is no doubt that the compounds most closely resembling typical polymers with regard to chemical structure are low-molecular weight aliphatic hydrocarbons. In the solid and liquid state (after suitable purification) they are characterized by large resistivity and should be classed as good insulators. Aromatic hydrocarbons, on the other hand, especially the polycyclic ones, show semiconducting properties.

Comparatively much research has been done in the field of electrical conductance of anthracene, both polycrystalline and in the form of monocrystals [419, 998, 1539, 1688]. Anthracene is a classical model compound for which many electrical properties have been measured, e.g. the dependence of conductance on the temperature as well as the anisotropy of conduction [293, 1137] (the dependence of conductance on the orientation of electric field), and carrier mobility [906, 1802, 1803]. Of considerable significance are investigations of the electrical properties of monocrystals. By comparing the results obtained in the case of monocrystals with the results of studies of polycrystalline substances, the effect of intercrystalline contacts on the value of conduction can be determined. The role of intercrystalline contacts or of intergranular contacts will be discussed in some detail in Chapter 8. In the case of monocrystals it is also possible to perform measurements of the anisotropy of optical absorption and to compare them with the results of measurements of the anisotropy of electrical properties. Thus, many of the studies performed were also devoted to other low-molecular weight materials that undergo crystallization relatively easily.

It should be emphasized that the different values of electrical conductivity of anthracene in various directions are related to the anisotropy of carrier mobility, and not to a change in the value of the thermal activation energy, which is constant, even after the melting of the crystals.

Investigations of the electrical conduction of several polycyclic aromatic hydrocarbons [845] and polycyclic quinones [1984] have shown that with increasing pressure the conductivity increases, whereas the value of the activation energy diminishes. These few remarks concerning the results of investigations into the electrical properties of anthracene show that an