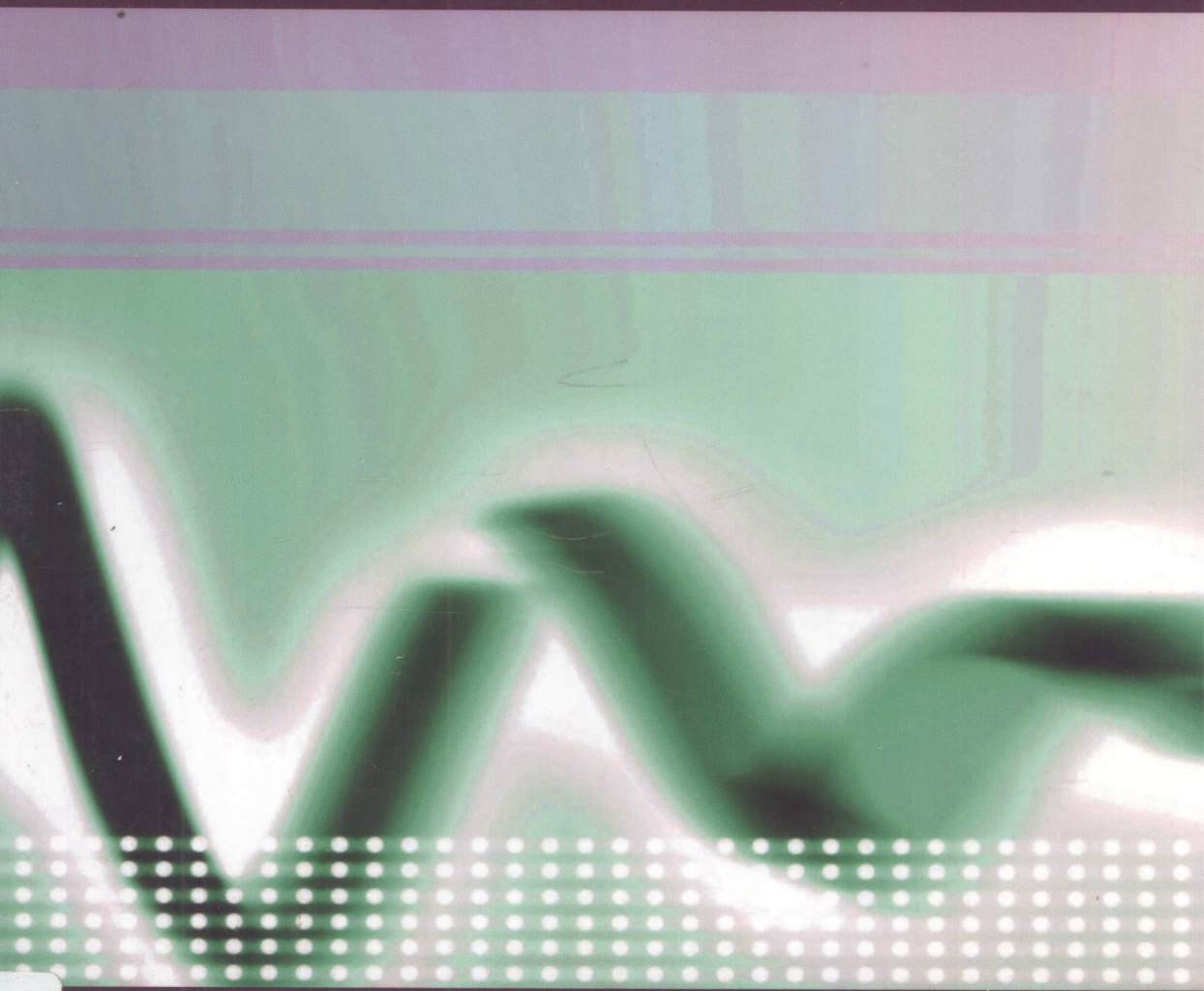


Electrical Properties of Polymers

SECOND EDITION

Tony Blythe and David Bloor



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ELECTRICAL PROPERTIES OF POLYMERS

Second edition

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ELECTRICAL PROPERTIES OF POLYMERS

Second edition

Fully revised and expanded, this new edition of Anthony Blythe's successful title on electrical properties of polymers covers both the fundamental and recent developments in this growing area. The book provides a broad and comprehensive account of the topic, describing underlying physical principles and synthesis through to emerging technologies. The second edition places particular emphasis on the new generation of conductive polymers, describing emerging uses of polymers in industrial applications and covering topics such as light emitting diodes, flexible polymers and soft electronics.

Written in an accessible style, without complicated theory, this book combines key concepts with applications. With the inclusion of further reading material at the end of each chapter for interested readers, this book is an authoritative guide to advanced-level undergraduates and graduates studying polymer materials and physical sciences. It will also be of significant interest to researchers working in this evolving field.

ANTHONY BLYTHE has been active in the area of polymer materials and processing for over 40 years. He has successfully initiated numerous ground-breaking projects in the polymer field, specifically for the wire and cable industry, and his achievements are recognised by the several patents he holds. He has also been an external lecturer to established universities in the UK and has authored more than 40 scientific papers.

DAVID BLOOR is Emeritus Professor of Physics at the University of Durham. Since his retirement in 2002 he has continued his research in

the area of optical materials and conductive materials, with particular interest in the developing areas of liquid crystalline materials and display devices. He holds a number of patents and has authored over 300 scientific papers.

Preface

The predecessor to this book was published in the Cambridge Solid State Sciences Series in 1979 following a series of lectures given to graduate students in the Polymer Physics Group at Leeds University. It was written as an introductory text on electrical aspects of polymeric materials, principally electrically insulating polymers, but with a description of work on electrically conductive organic materials up to the mid-1970s. Since that time intrinsically conductive polymers have progressed from laboratory curiosities with either poor chemical and physical stability frequently, indeterminate composition, to widely explored materials that have demonstrated new physics and use in diverse commercial applications. An account of these developments has displaced most of the content on organic conductors from the original volume.

Emphasis is mainly laid on the description and explanation, in molecular and electronic terms, of the observed phenomena, so as to give a basic understanding of the electrical behaviour of polymers. Principles of measurement methods are also stressed, since a sound framework of experimental techniques and data is so essential for proper scientific development of such a subject. The choice of subject matter was made with the aim of being educative and stimulating rather than exhaustive and exhausting. It is hoped that the book will be of most help to those venturing into research in polymer science, or to those joining the industrial sectors that utilise both insulating and conductive plastics, who want an insight into the somewhat specialised area of electrical properties. Only a general knowledge of physics and chemistry is assumed, and for this reason an introduction to polymer structure is included.

The electrical properties of polymers are a subject which is inherently interdisciplinary in nature. The development of intrinsically conductive polymers has benefited immensely from the contributions of synthetic chemists.

Electrical properties are closely allied with the mechanical properties of polymers studied by both physicists and engineers. Established models of the semiconductive properties of inorganic substances and metals provide a starting point for understanding similar properties of polymers, although subsequent critical input from across the disciplines eventually led to the view that the underlying physics is distinctly different. A primary objective, therefore, was to collate the relevant aspects of these contingent subjects to form a more unified treatment than is generally available.

Since the early days of plastics technology, when such materials were regarded electrically as simply good insulators, observations of subtleties in electrical response have shed a great deal of light on the underlying microscopic structure and molecular dynamics. This has contributed to polymer science in a general way, and has, at the same time, enabled the development of materials which meet exacting electrical engineering requirements. This process has continued in the development of intrinsically conductive polymers over the last 25 years of the twentieth century. The book encompasses both this well-established area of dielectric science and the modern frontiers concerned with non-linear optical and electrically conductive plastics. Research along these lines has demonstrated the feasibility of obtaining materials with entirely novel sets of properties, that have opened up new areas of application for polymers.

The bibliography has been considerably expanded, partly due to the inclusion of new topics, e.g. linear and non-linear optical properties, and partly reflecting the steady and sizeable flow of papers on intrinsically conductive polymers. The authors have made extensive use of the literature in the preparation of this book. The selection of papers included in the bibliography is meant to be indicative of this literature since it cannot possibly include more than a small fraction of the published output. The final choice is not intended as any indication of the quality of work that is not included.

SI units have been used throughout the book.

Special thanks are due to Professor I. M. Ward for encouraging us to update the earlier book and for reading and commenting on the whole of the draft manuscript. We should also like to thank Dr G. H. Cross and Dr G. R. Davies for constructive criticism on much of the manuscript, and Professors J. S. Dugdale and A. P. Monkman for suggestions on Chapters 4 and 9 respectively. ARB is grateful for the invaluable help and advice from colleagues at BICCGeneral, and DB for similar assistance from colleagues at the University of Durham. Valuable inputs were received from Professor D. Baeriswyl, Professor A. Kaiser, Professor W. R. Salaneck, Professor G. Weiser, Dr D. de Leeuw and Dr S. Roth. Dr Mile H. Bertein, Mr W. Reddish, Dr D. J. Groves and Mr J. Billing kindly supplied photographs.

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Finally, we are especially grateful to our wives for their constant moral support during this project.

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1

Introduction

1.1 Overview

Although unified by direct concern with the effects produced by electric fields, the subject of the electrical properties of polymers covers a diverse range of molecular phenomena. Until the latter part of the twentieth century, known polymers generally displayed a much less striking electrical response than inorganic materials. While inorganic solids behave as semiconductors and metals (where the electrical response is overwhelmingly one of electronic conduction), or as insulators, the common polymers were distinctly confined to the latter category. From 1950 onwards this situation changed with the emergence of polymers displaying semiconducting properties and the discovery in the 1970s of polymers that even had metallic levels of conductivity. Since then there has been an explosion in fundamental and applied research and numerous conductive polymers have been produced and studied. While the macroscopic properties of these materials resemble those of their inorganic counterparts, their microscopic behaviour is markedly different and reflects fundamental differences between the rigid crystal lattices of inorganic materials and the deformable, molecular structure of polymers.

The absence of conduction in insulating polymers allows a whole set of more subtle electrical effects to be readily observed. For instance, polarisation resulting from distortion and alignment of molecules under the influence of an applied field becomes apparent. Examination of such polarisation not only gives valuable insight into the nature of the electrical response itself, but it also provides a powerful means of probing molecular dynamics. In conductive polymers the presence of charge carriers produces pronounced local deformation of the molecular framework, significantly larger than that found in inorganic semiconductors. The Coulomb interaction of charge carriers is less effectively screened in conductive polymers. Hence electron-phonon and

electron–electron interactions have more profound effects in conductive polymers. It should also be noted that single crystal polymers are rare and the complex morphology of partially crystalline polymers has an impact on their electrical properties. For all these reasons electrical studies form a desirable supplement to studies of mechanical and thermal properties aimed at reaching an understanding of the behaviour of polymers on a molecular basis.

In the remainder of this chapter we outline the main features of polymer structure and its relation to electrical properties, as a basis for the subsequent more detailed explanation and discussion of electrical behaviour.

1.2 Structure of polymers

Most of the synthetic high polymers with which this book is concerned are organic compounds consisting of long, chain-like molecules where repeated molecular units are linked by covalent bonds. A single molecular chain can contain a thousand or more repeat units and reach a total length in excess of 1 μm . Such large molecules have complex shapes and form solids that may be either amorphous or crystalline, but are commonly partially crystalline. The atoms, which form the *backbone* of organic polymers, are predominantly carbon atoms, sometimes in combination with oxygen and/or nitrogen. The nature of the chemical bonding in the polymer directly influences the electrical properties.

1.2.1 Chemical structure – saturated polymers

The carbon atoms in a polymer are primarily bound together by *covalent bonds* formed by the interaction of two electrons, one from each of the atoms linked by the bond. We illustrate this process with the simpler example of bond formation between two hydrogen atoms. As the atoms are brought together their 1s-electron orbitals overlap forming two new σ -orbitals around the atoms, which are symmetric and have zero angular momentum with respect to the interatomic axis. One orbital, the bonding orbital, is formed by the linear superposition of the two s-orbitals, shown by the solid curves in Fig. 1.1(a). This gives a high electron density between the hydrogen nuclei, the dashed line in Fig. 1.1(a), which reduces their electrostatic repulsion. Thus the nuclei are drawn together and an electron in the bonding orbital has a lower energy than one in the isolated atom orbital. The other, the antibonding orbital, is formed by the superposition of s-orbitals with opposite sign, see solid curves in Fig. 1.1(b), giving a lower electron density between the nuclei, shown by the dashed curve in Fig. 1.1(b). The electrostatic repulsion between

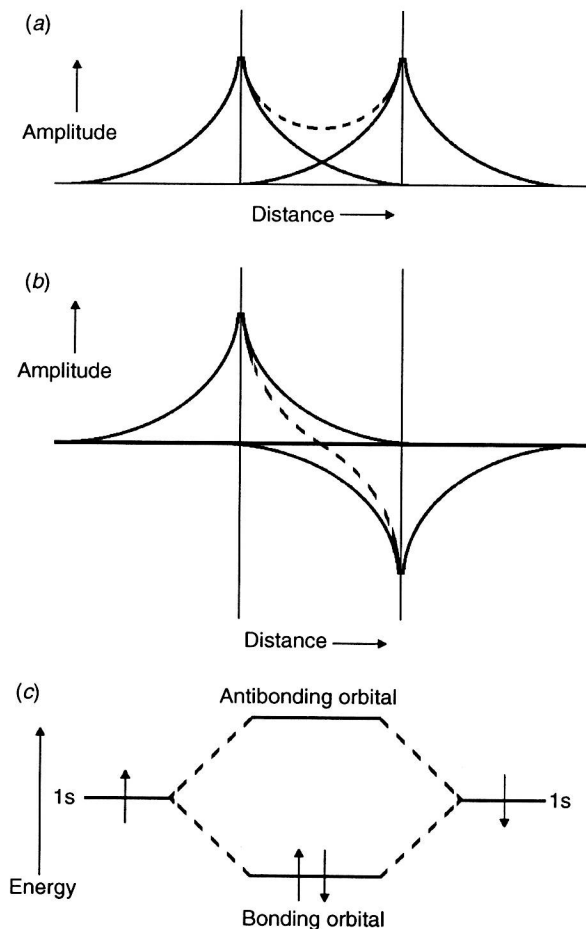


Fig. 1.1 Overlap of hydrogen atom orbitals to form (a) a bonding orbital, and (b) an antibonding orbital, with energies as shown in (c).

the nuclei is not screened and the energy of an electron in this orbital is increased, as indicated in Fig.1.1(c). The Pauli exclusion principle allows the two electrons from the hydrogen atoms to *pair* in the bonding orbital, if they are of opposite spin, to give a stable molecule with total energy less than that of the two isolated hydrogen atoms.

A neutral carbon atom has six electrons, which occupy the $1s$, $2s$ and $2p$ orbitals giving an electronic configuration of $1s^2 2s^2 2p^2$. When a carbon atom forms a bond with another atom, an s -electron is promoted to the vacant p -orbital to give an sp^3 configuration (s , p_x , p_y , p_z) in the outer valence shell. These electronic orbitals do not bond separately but hybridise, i.e. mix in linear combinations, to produce a set of orbitals oriented towards the corners of

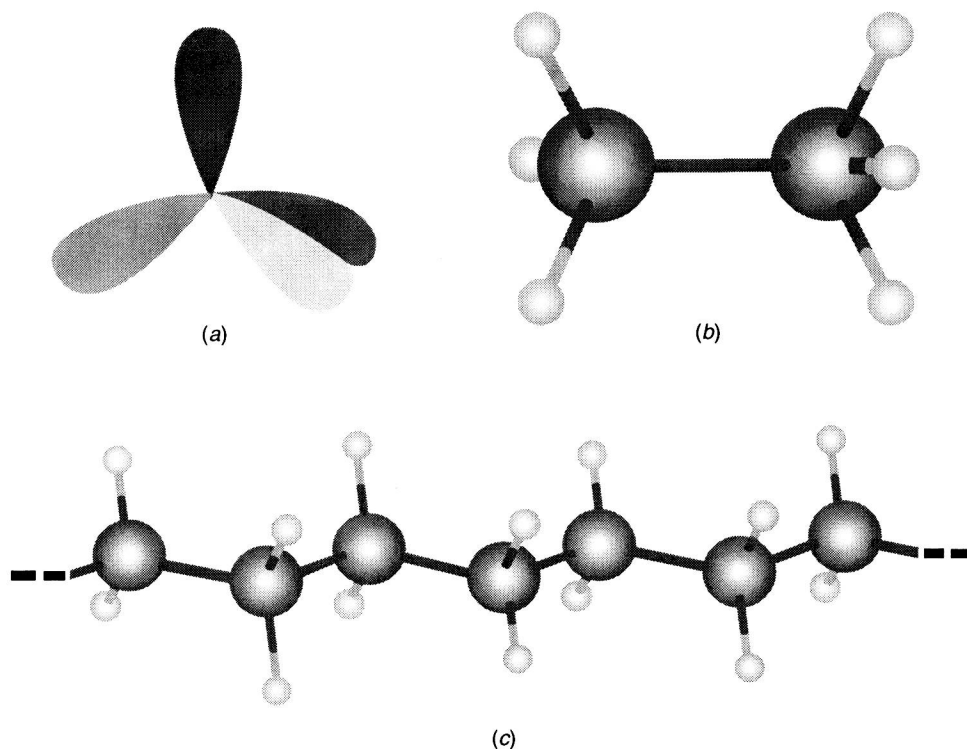


Fig. 1.2 (a) sp^3 hybrid orbitals, and the molecular structure of (b) ethane and (c) polyethylene. H atoms have light shading.

a regular tetrahedron. Figure 1.2(a) shows the form of the wavefunctions that describe the hybridised orbitals. The sp^3 hybrids allow a much greater degree of overlap in bond formation with another atom, and this, in turn, produces extra bond strength and stability in the molecules. The arrangement of bonds resulting from overlap with sp^3 hybrid orbitals on adjacent atoms gives rise to the tetrahedral structure that is found in the lattice of diamond and in molecules such as ethane, C_2H_6 , as depicted in Fig. 1.2(b). In these structures all the available electrons are tied up in strong covalent bonds, σ -bonds. Carbon compounds containing σ -bonds formed from sp^3 hybrid orbitals are termed *saturated* molecules. Polyethylene, $-(CH_2)_n-$, is a typical saturated polymer where the σ -bonds between adjacent carbon atoms form the zigzag of the polymer backbone and the two remaining bonds are to the pendent hydrogen atoms, as in Fig. 1.2(c). The strong σ -bonding gives rise to chemically stable compounds and localises the electrons in the molecular structure rendering saturated compounds electrically insulating.

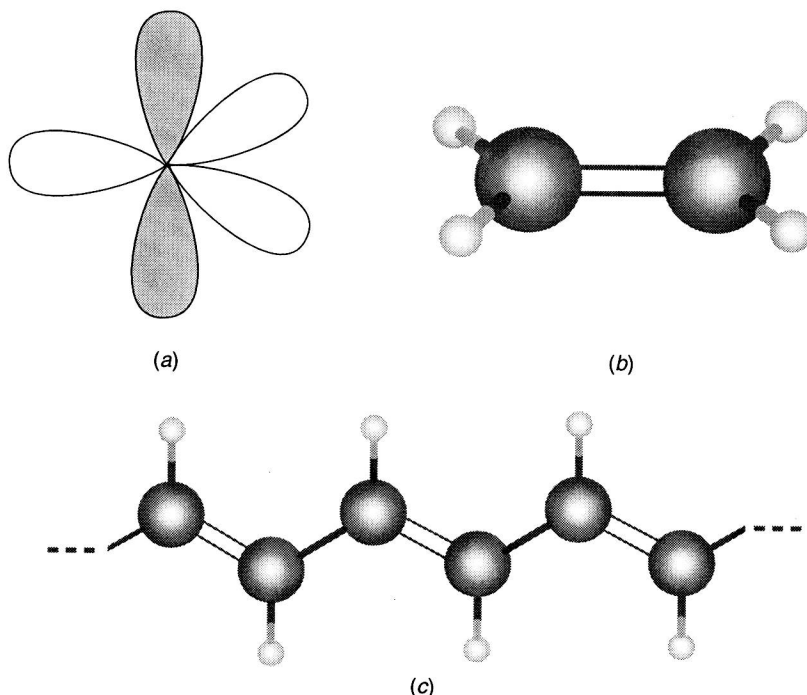


Fig. 1.3 (a) sp^2 hybrid orbitals, and the molecular structure of (b) ethylene and (c) polyacetylene.

1.2.2 Chemical structure – unsaturated polymers

While tetrahedral bonding is common in carbon compounds, it is not the only possibility. A planar σ -bond structure occurs if the hybrid orbitals are formed from one s - and two p -orbitals. sp^2 hybrid orbitals, which lie in a plane with angles of 120° between them, are shown by the unshaded lobes in Fig. 1.3(a), whilst the remaining p -orbital (p_z), which lies orthogonal to the plane of the σ -bonds, is shown by the shaded lobes. This p_z electron is then available to form additional π -orbitals, with unit angular momentum about the bond axis, with p_z electrons in adjacent atoms. The resulting π -bond will form parallel to the underlying σ -bond, resulting in a multiple (double) bond, as in ethylene, C_2H_4 , as shown in Fig. 1.3(b). Compounds where orbitals are used in this way to form double bonds between carbon atoms, rather than to form single bonds with other atoms, e.g. hydrogen, are said to be *unsaturated*. Where successive carbon atoms in a chain engage in π -bonding, the structure is said to be *conjugated*, and may be represented as a sequence of alternating single and double bonds, as shown in Fig. 1.3(c), which illustrates the bonding in polyacetylene, $\{CH=CH\}_n$.